

**APOPHYLLITE WEATHERING AND THE
AQUEOUS GEOCHEMISTRY OF A
KAROO BRECCIA PIPE**

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Abstract

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Apophyllite is a phyllosilicate mineral commonly associated with hydrothermal environments. It is a major secondary phase occupying fractures in a dolerite breccia pipe on the farm Kopoasfontein, outside Calvinia in the western Karoo, South Africa. Groundwater abstracted from this breccia is uncharacteristically alkaline (pH 10) and high in fluoride (11 mg/L) for a natural water and the link between the groundwater chemistry and breccia pipe minerals has been investigated.

The paucity of existing dissolution data for apophyllite provided an opportunity to make a meaningful contribution to low-temperature silicate weathering research. Laboratory batch tests were conducted to measure the rate of apophyllite dissolution under various reaction conditions. Dissolution is slow and strongly pH-dependent, as is typical of silicate minerals. Dissolution rate ranged from a long-term steady state rate of 1×10^{-12} moles of apophyllite per square metre per second at pH 9 to the relatively rapid release of interstitial calcium, potassium and fluoride at normalised stoichiometric rates of 1.5×10^{-9} moles per square metre per second in 0.01 molar hydrochloric acid. In all, fifteen apophyllites were characterised by X-ray diffraction, X-ray fluorescence, thermal analysis and wet chemical techniques. Fluorapophyllite from Kopoasfontein was found to have the highest ammonium content, sufficient to qualify it as the first reported ammonian end-member of the mineral series. Substitution of ammonium for potassium in the lattice has less effect on the stability of apophyllite than the substitution of hydroxyl for fluoride, which was found to increase dissolution rate and decrease thermal stability.

A study of the groundwater geochemistry around Calvinia has allowed improved understanding of the geohydrology of breccia pipes. Chemical and isotope analyses of groundwater samples from six breccia pipes permitted tracing of their inflow from the local alluvial and fractured-rock aquifer systems and showed that local water-rock interactions in the Kopoasfontein pipe imprint a distinctive chemical signature on this groundwater. Forward modelling of apophyllite

dissolution and mass balance modelling of groundwater evolution using PHREEQC software indicated that while fluorapophyllite dissolution under closed system conditions may be partly responsible for the high pH, it cannot be the only source of fluoride in Kopoasfontein groundwater.

The slow dissolution rate of apophyllite and existence of additional fluoride sources have important implications for the management of the Kopoasfontein breccia pipe, which is currently being tested for the underground storage of emergency water supplies for Calvinia. The findings of this study are expected to have wider application in the western Karoo, where several breccia pipes are known to occur, and to facilitate the selection of suitable sites for water storage, should the Calvinia recharge experiments prove successful.

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ABBREVIATIONS ¹

b.d.l.	below detection limit
CSIR	Council for Scientific and Industrial Research
DO	dissolved oxygen
DOC	dissolved organic carbon
DTA	differential thermal analysis
DWAF	Department of Water Affairs and Forestry
EC	electrical conductivity
EDX	energy dispersive X-ray (fluorescence spectrometry)
EGA	evolved gas analysis
FAAS	flame atomic absorption spectrophotometry
IAP	ion activity product
IC	ion chromatography
ICP-AES	inductively coupled plasma - atomic emission spectroscopy
ICP-MS	inductively coupled plasma - mass spectrometry
i.d.	insufficient data (for calculated parameters)
JCPDS	Joint Committee for Powder Diffraction Standards
LOI	loss on ignition
Ma	1 000 000 years
mbgl	metres below ground level
m/e	mass to charge ratio
n.d.	not determined
NGDB	National Groundwater Database
n.r.	not reported
NWQDB	National Water Quality Database
pCO ₂	partial pressure of carbon dioxide gas
PDB	Pee Dee belemnite
pmC	percent modern carbon
R ²	linear correlation coefficient
RI	relative intensity
RSD	relative standard deviation
SAR	sodium adsorption ratio
SEM	scanning electron microscope
SI	saturation index
SMOW	standard mean ocean water
Std. dev. (or s.d.)	standard deviation of the mean
TGA	thermogravimetric analysis
TIC	total inorganic carbon
UCT	University of Cape Town
USGS	United States Geological Survey
(WD)XRFS	(wavelength dispersive) X-ray fluorescence spectrometry
XRD	X-ray diffraction

¹ List excludes chemical symbols and common units of measurement

THERMODYNAMIC NOTATION

ΔG°_f	standard Gibbs free energy of formation from the elements at 298 K and 0.101 MPa (kJ/mol)
ΔG°_r	standard Gibbs free energy of reaction at 298 K and 0.101 MPa (kJ/mol)
ΔH°_f	standard enthalpy of formation from the elements at 298 K and 0.101 MPa (kJ/mol)
ΔH°_r	standard enthalpy of reaction at 298 K and 0.101 MPa (kJ/mol)
K	thermodynamic equilibrium constant (no units)
K_{sp}	equilibrium solubility product constant (no units)
R	gas constant = 8.314 J/mol.K

CHAPTER 1
INTRODUCTION :
THE KOPOASFONTEIN BRECCIA PIPE

1.1 Problem description

Natural groundwaters acquire their chemical composition from the chemistry of their recharge sources, modified by interactions with minerals and organic matter in the soil zone and the rocks through which the water passes. This thesis examines the relationship between groundwater geochemistry and the composition and reactivity of mineral solids in a breccia pipe near Calvinia in the western Karoo region of South Africa. The work addresses the factors controlling the evolution of the current groundwater composition and the direction and kinetics of chemical reactions that may arise from anticipated anthropogenic perturbation of the system.

The geohydrological research site at the breccia pipe on Kopoasfontein farm affords an excellent opportunity for the investigation of natural alkaline groundwater interactions with a hydrothermally-altered shale mineral assemblage. The pipe is convenient for study in that it provides a subsurface environment with poor hydraulic connection to the surrounding groundwater systems. The chemistry of groundwater from boreholes in the breccia pipe is uncharacteristic of Karoo groundwaters and apparently unrelated to that of groundwater in the surrounding shallow aquifers. Geochemical evidence from earlier research (Cavé, 1999) suggests a strong control of local water-rock interactions on the groundwater chemistry may be active. Because the Calvinia breccia pipes extend to the base of the Karoo Supergroup, they may also afford an opportunity to investigate the chemistry of deep groundwater in the Karoo basin (Woodford *et al.*, in prep.).

The uncommon phyllosilicate mineral, apophyllite, is a major phase in the subsurface cavities of the Kopoasfontein breccia pipe, but little is known about its reactions in low temperature aqueous environments. No published thermodynamic or kinetic data for the mineral could be found. Detailed laboratory experimentation investigating the dissolution behaviour of apophyllites has been conducted as part of this work. This has been motivated by the need to improve the understanding of the role of fluorapophyllite in the aqueous geochemistry of the

Kopoasfontein breccia pipe, and particularly its relation to high fluoride concentrations in the groundwater. The experimental results contribute to the body of knowledge on silicate mineral dissolution rates and the factors controlling dissolution kinetics at near surface temperatures (Cavé *et al.*, 2001).

Apart from satisfying scientific curiosity, investigation of aqueous geochemical reactions at the Kopoasfontein research site is also of practical benefit in terms of water supply opportunities in the semi-arid western Karoo. Boreholes drilled into breccia pipes are often high yielding in comparison to those in the surrounding shales, because of their high porosity and permeability (Woodford *et al.*, in prep.). Although of limited sustainability for long-term abstraction, breccia pipes make promising targets for emergency groundwater reservoirs, particularly in the light of recent developments in underground water storage by artificial recharge (Murray and Tredoux, 1998a). Pilot borehole injection experiments are underway at Kopoasfontein with the aim of storing surplus winter runoff in the breccia pipe for use as a backup drinking water reservoir for Calvinia (Cavé *et al.*, 2002).

Geochemical factors could be the major limitation in the potential use of breccia pipes for water supply if fast reacting minerals in the pipe release solutes that impair groundwater quality. The natural Kopoasfontein groundwater contains elevated concentrations of fluoride and arsenic species, while the rocks are unusually high in nitrogen (Cavé, 1999). The health-related aspects of these elements in drinking water merit the study of the geochemical reactions controlling their mobility in this system.

1.2 Research hypothesis

The Kopoasfontein breccia pipe imprints a chemical signature on the groundwater which distinguishes it from other groundwater sources in the area. The key hypothesis examined in this thesis is:

- ▶ Local water-rock interactions in the Kopoasfontein breccia pipe are responsible for the unusually alkaline, high-fluoride groundwater in contact with the breccia.

Some of the key questions arising from this hypothesis are:

- ▶ Is fluorapophyllite the mineral phase controlling dissolved fluoride concentrations?
- ▶ Can nitrogen in the groundwater be mineralogically derived?
- ▶ What geochemical reactions are responsible for the high pH?
- ▶ Do all breccia pipes yield groundwaters that are distinct from the local aquifer systems?
- ▶ Do breccia pipes of similar mineralogy produce similar groundwater compositions?

The approach used to test the hypothesis involves the collection of geochemical data from natural systems combined with laboratory experimentation. Rocks and mineral samples have been reacted with solutions of varying composition under controlled conditions, measurements taken of groundwater chemistry and isotopic composition and its variations with depth and time, detailed investigations conducted of rock mineralogy and use made of geochemical modelling techniques.

1.3 Research site description

1.3.1 Location, physiography and drainage

The farm Kopoasfontein 698 lies 12 km east of Calvinia in the Northern Cape province of South Africa (Figure 1.1). The region is sparsely populated, rural in character and primarily devoted to agriculture, of which sheep farming is the major activity. Calvinia, a town of about 10 000 inhabitants, is the principal settlement in the Hantam District and provides a service centre for the surrounding farming community.

The Calvinia district is situated on a broad, flat plateau which ranges from approximately 1000 to 1500 m above sea level. A large dolerite sheet capped with sandstone forms the flat-topped Hantamsberg mountain range which overshadows the town to the north. Mesas, inselbergs and koppies are scattered across a typical Karoo landscape. Calvinia is located on the Oorlogskloof River which drains westwards across a broad plain before joining the Doring River. Numerous tributary channels lead into the Oorlogskloof valley from the Hantamsberg mountains, but these are episodic streams and are for the most part dry.

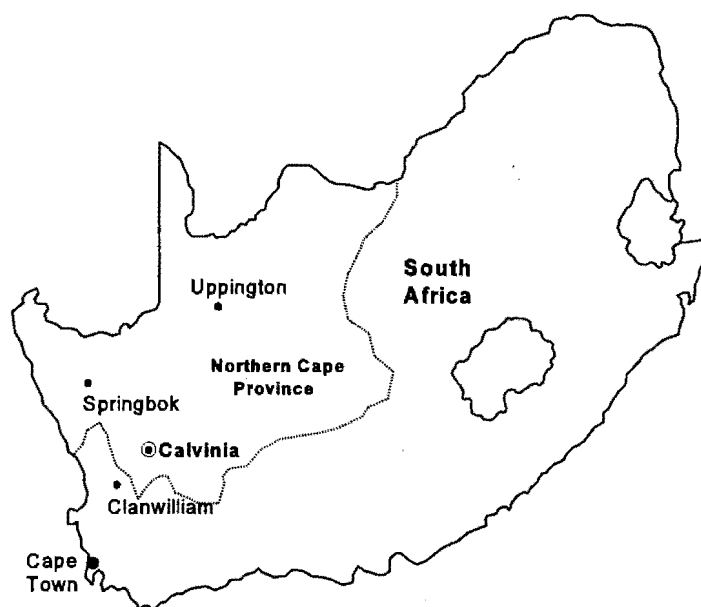


Figure 1.1. Locality map showing the position of Calvinia in the Northern Cape Province, South Africa.

A geohydrological research site is located at the foot of the Hamtamsberg mountain around the outcrop of a breccia pipe on the south western portion of Kopoasfontein farm, between the railway line and the main road from Calvinia to Williston (Figure 1.2). Original exploration drilling at the site was conducted by the Department of Water Affairs and Forestry (DWAF) as part of an investigation into the groundwater potential of breccia pipes and other geological structures in the Karoo, in conjunction with the Council for Geoscience (Woodford *et al.*, in prep.). The site was later selected by the Council for Scientific and Industrial Research (CSIR), in partnership with the Municipality of Calvinia, as a pilot site for testing the application of artificial groundwater recharge in hard rock aquifers (Murray and Tredoux, 1998a, b).

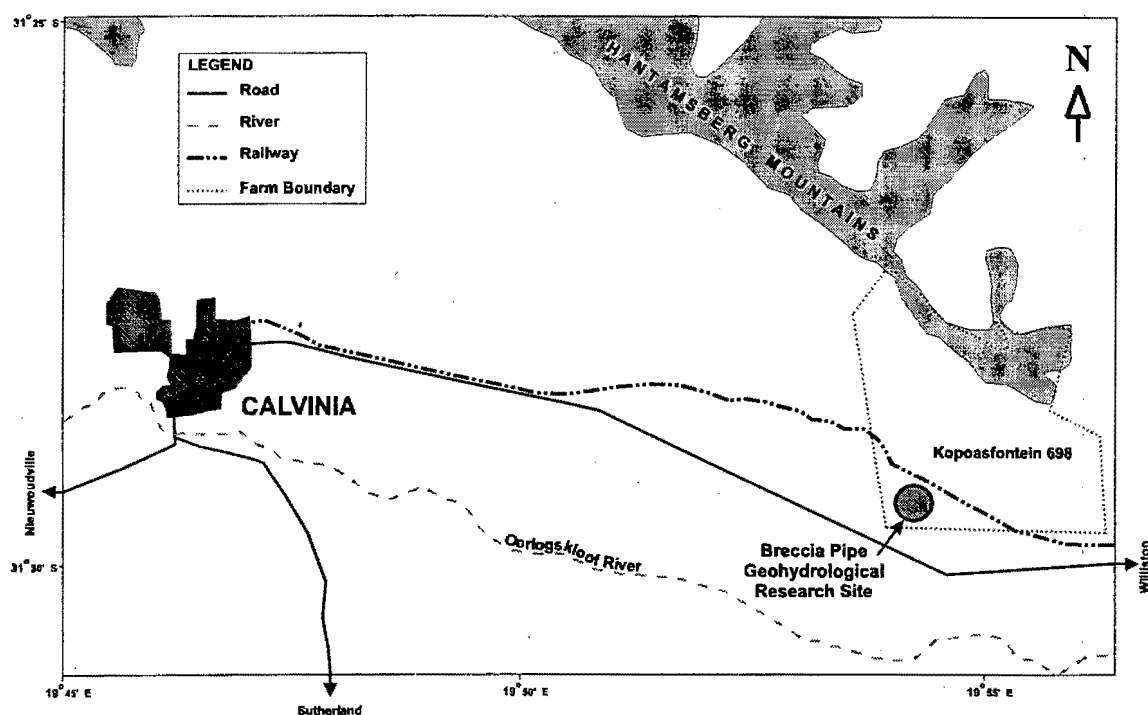


Figure 1.2. Location of the Kopoasfontein geohydrological research site near Calvinia.

1.3.2 Climate

Climate data for the weather station at Calvinia (station 0134479A3) was obtained from the South African Weather Service. Calvinia falls within the arid western region of Southern Africa, west of the 250 mm rainfall isohyet. The mean annual rainfall for the 30 year period from 1971 to 2000 is 230 mm per annum. The winter wet season usually lasts from April to September with occasional thunderstorms in the summer months, but rainfall patterns are often unreliable. Potential evaporation exceeds precipitation by far and the 30 year (1958 to 1987) annual average evaporation (Symons tank) recorded at Calvinia is 2213 mm. Evaporation is greatest during the hot, dry summer months leading to further depletion of available moisture in the western Karoo.

Temperature extremes are common at Calvinia. Summer maximum air temperatures average 31°C in January and February while midday temperatures in June and July average 17°C. Winter temperatures average 3.6°C at night and Calvinia records some of the coldest night-time lows in South Africa with the temperature dropping to as low as -8°C. Severe frost occurs overnight in winter. Snowfalls have been reported on the Hantamsberg mountains.

1.3.3 Geology

Calvinia is located on the western margin of the Karoo sedimentary basin. The region is mainly covered by rocks of Permian age belonging to the Eccca Group of the Karoo Supergroup (Figure 1.3). Surface outcrops around Calvinia are predominantly shales and mudstones of the Tierberg Formation, with Waterford Formation sandstones capping areas of high relief such as the Hantamsberg mountains. Thin deposits of recent alluvium occur along the floors of the Oorlogskloof River valley.

Drilling core samples from around Calvinia reveal that the Tierberg Formation is underlain by the thin, pyritic, carbonaceous shale band of the Whitehill Formation and then the shales and mudstones of the Prince Albert Formation. Glacial tillite of the Dwyka Group forms the base of the Karoo Supergroup and outcrops at surface near the town of Nieuwoudville, approximately 40 km west of Calvinia (Figure 1.4).

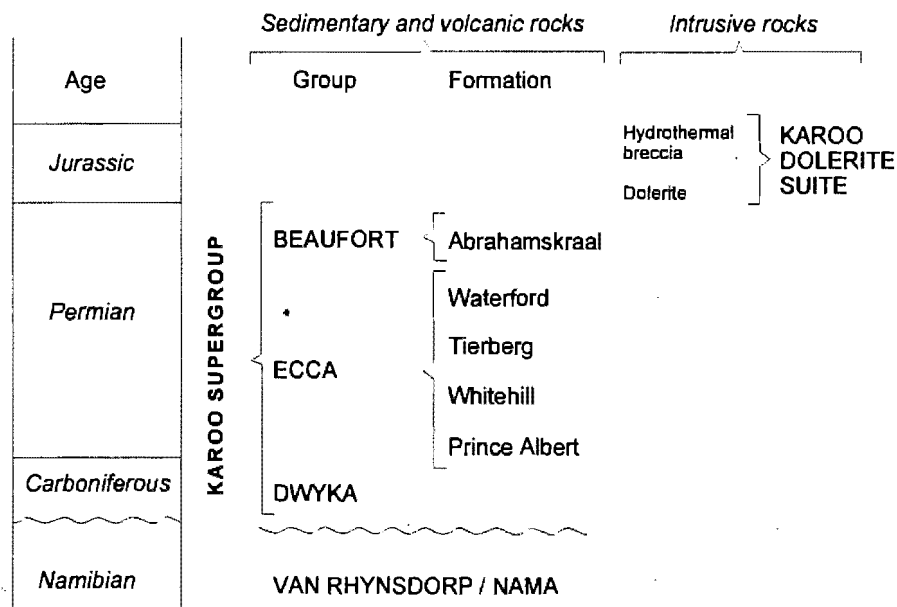
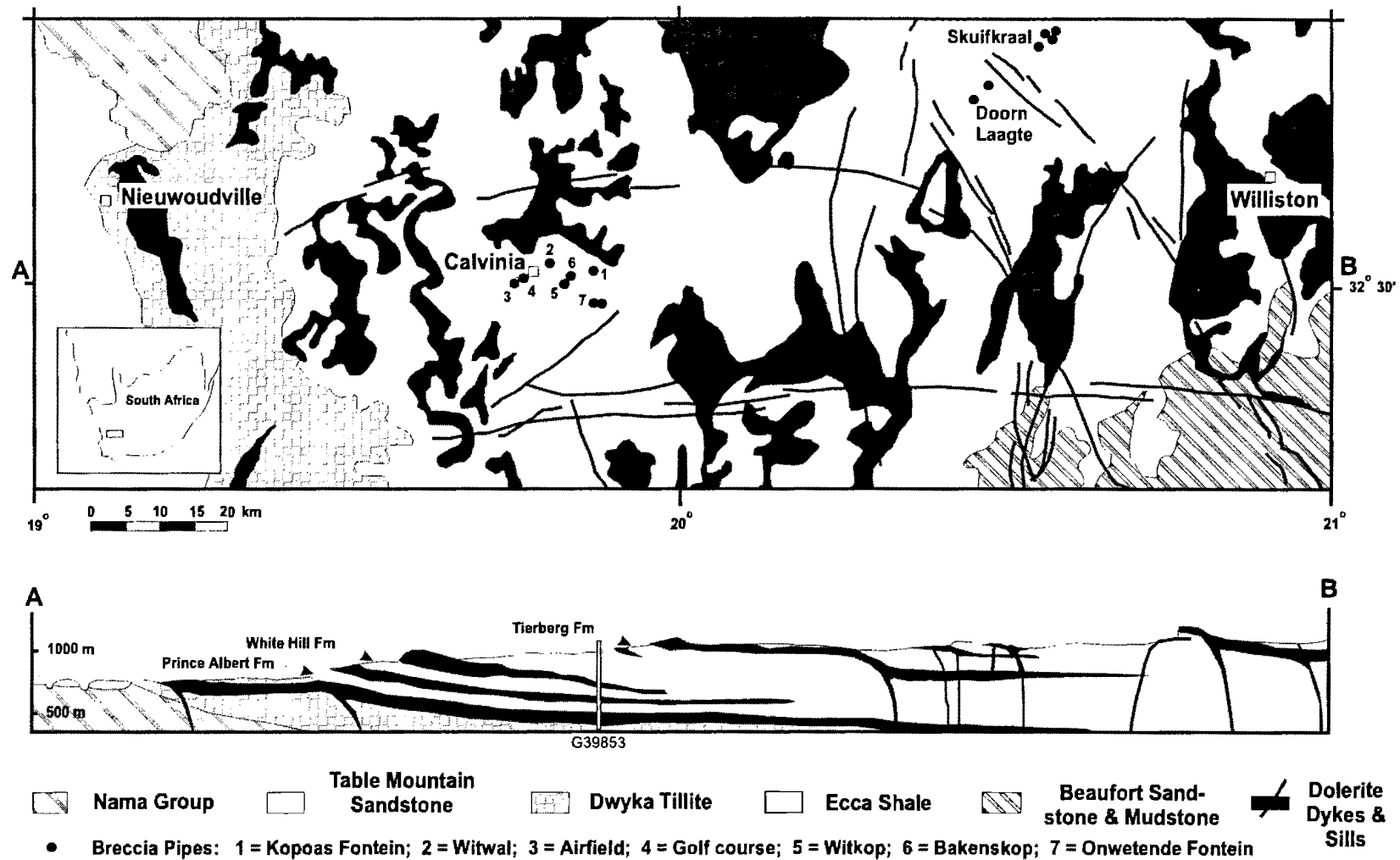


Figure 1.3. Stratigraphic sequence in the Calvinia area.



1.7 Figure 1.4. Geological map of the Calvinia area, showing the dominant stratigraphic formations and the position of breccia pipes (After Hallbauer *et al.*, 1995).

The Eccra Group sedimentary rocks were intruded by a network of dolerite dykes and sills during the Jurassic breakup of the Gondwana supercontinent. Several clusters of breccia pipes occur in the Eccra Group rocks around the Western margin of the Karoo, associated with the magmatic activity at this time.

The geology and structural evolution of the Calvinia area are described in further detail in Chapter 4.

1.3.4 Geohydrology

Because of the arid climate and unreliable rainfall patterns, most of the towns and villages in the Karoo rely, to some extent, on groundwater schemes for their water supply (Kirchner *et al.*, 1991). Calvinia uses groundwater from a small wellfield to supplement the town water supply from the Karee dam, while many of the farmers in the region are dependent on groundwater for stock watering and domestic supply.

Three main types of aquifer are present in the Karoo basin (Chevallier *et al.*, 2001):

- ▶ *Recent alluvial deposits:* Primary integranular aquifers occur where deep deposits of alluvium have accumulated along large drainage systems.
- ▶ *Karoo Supergroup sediments:* These are generally poor aquifers with complex geometry. Weathering of near-surface strata extends to depths of 20 to 30 m and forms laterally extensive shallow aquifers with more or less constant fracturing in the weathered zone.
- ▶ *Dolerite dykes, sills and ring complexes:* Localised two-dimensional secondary aquifers are associated with fault zones or contact zones between sedimentary rock and dolerite dykes or sills. Fracturing associated with the intrusive body improves the water yielding capacity of the nearby sedimentary rocks.

The various breccia pipes around Calvinia are also important water-bearing features, although they are highly localised and have limited storage in comparison to the other aquifer types. These highly fractured, permeable structures provide initially high yields and may act as conduits for access to deep groundwater.

Groundwater potential in the Karoo is, on the whole, poor. Ecca and Beaufort Group rocks are characterised by a virtual absence of primary porosity and permeability. In addition, low rainfall over most of the Karoo area, especially towards the western side, causes low groundwater recharge. Groundwater mining may occur where aquifers are not recharged regularly, leading to limited borehole lifetimes.

Most of the potable groundwater abstracted in the Calvinia area is derived from rocks that transmit groundwater along secondary structures. The permeability of the Karoo sedimentary rocks can be improved by the presence of fracturing in the weathered zone, but even then borehole yields in Ecca Group shales seldom amount to more than 2 L/s (Meyer, 2000). Higher yields (typically 2 to 3 L/s) are associated with the contact zones along dolerite dykes or sills, where well-developed fracture systems often exist. Dolerite contact zones are a favoured target for drilling in the Karoo away from the major alluvial valleys and most of the successful deeper boreholes around Calvinia intercept dolerite contact zones. Several shallow boreholes have been constructed in the extensive alluvial deposits along the drainage systems and valley floors. Although initially high borehole yields may be obtained, the alluvial aquifers around Calvinia are thin, have limited storage and often contain saline groundwater.

Groundwater in the western Karoo is generally of inferior quality in comparison to surface water supplies. The slow movement of groundwater in the low permeability formations often leads to a stagnant water composition with elevated salinity. There is also a risk that nitrate or fluoride may be present at unacceptable levels in old Karoo groundwaters. Van Wyk (1981) noted that fresh, low salinity groundwater was found near the base of the Hantamsberg mountains, which he concluded to be the recharge zone. Poor quality, brackish water was attributed to the stagnant conditions which develop in the discharge zone along the Oorlogskloof river. Seward (1983) and Woodford (1994) also noted that groundwater in shallow alluvial aquifers in the Calvinia area was generally, brackish, but that lower salinity water was intercepted in boreholes tapping deeper water-bearing structures, where faster flow was assumed to occur through fractures.

The aquifers in the Calvinia area and their geochemistry are discussed in Chapter 3.

1.4 Previous geological and geochemical work

In response to a severe water shortage in the late 1970's, DWAF investigated the groundwater potential in the Calvinia municipal area with the aim of finding additional water resources for town supply (Van Wyk, 1981). When this attempt failed to locate any promising aquifers, the study was extended by Seward (1983), who conducted a detailed hydrocensus in the Calvinia area as part of the "Hantam Survey". This work was followed up by Woodford, who also evaluated a number of high yielding boreholes for water supply potential (Woodford, 1994). Some of the boreholes drilled at this time are located at the Kopoasfontein research site, and details of their construction, pumping test results and preliminary water chemistry analyses can be found in Woodford's report.

The geology, mineralogy and hydrogeology of several breccia pipes in the western Karoo, with particular emphasis on the Kopoasfontein breccia pipe, were investigated by DWAF and the Council for Geoscience between 1992 and 1996 (Chevallier *et al.*, 2001; Woodford *et al.*, in prep.) with additional funding by the Water Research Commission. The focus of these studies was to assess the groundwater and economic mineral potential of the breccia pipes. Water samples were collected and sections of rock core containing visible sulphide mineralisation were examined in detail. Iron, copper, lead and zinc sulphides were discovered, but at grades too low to consider mining them profitably. Groundwater in breccia pipes was found to vary in quality.

Hallbauer *et al.* (1995) advocated the use of borehole water composition as a low cost prospecting method for identifying mineralised breccia pipes for mining purposes. The authors documented a strong relationship between geological and/or geochemical facies and groundwater composition in the western Karoo. Using capillary ion analysis, they studied the interaction of host rocks and water from a number of geological environments in the Calvinia area, including the breccia pipe at Kopoasfontein.

This work represents an initial attempt to link groundwater geochemistry with host rock composition by distinguishing the major and trace ion composition of mineralised and non-mineralised breccia pipes. Mineralised lithologies yielded Na-HCO₃ dominant waters with elevated Zn²⁺, Fe²⁺ and F⁻. Groundwaters from non-mineralised breccia pipes were Ca/Mg-Cl

dominant. Hallbauer *et al.* (1995) concluded that hydrothermal brines or their associated minerals and not sedimentary basin brines, dominate the groundwater components from mineralised breccias in the western Karoo.

Murray and Tredoux (1998a) initially proposed the use of the Kopoasfontein breccia pipe for water storage and designed the artificial recharge scheme. The report produced for the Calvinia Municipality (Murray and Tredoux, 1998a) is primarily concerned with the design and geohydrological aspects of the scheme. A comprehensive water quality assessment was also undertaken for the artificial recharge feasibility study and formed the subject of an MSc research project (Cavé, 1999) and a related conference paper (Cavé, 2000).

The MSc research investigated the geochemistry of the Karee dam and four municipal boreholes in the Calvinia area to select the most appropriate source of recharge water. The rock and water chemistry of the Kopoasfontein breccia pipe were also examined to predict possible reactions that might occur in the pipe after injection.

Natural groundwater in the Kopoasfontein breccia pipe was found to be unusually alkaline (pH = 9.8) and to have low salinity (EC $\approx$ 70 mS/m). The presence of species such as NH_4^+ , H_2S and CH_4 , indicate a reducing environment. The water is of Na-Cl type, but HCO_3^- and CO_3^{2-} are also important anions in solution. High concentrations of F^- (12 mg/L) and As (0.33 mg/L) present a health risk for potential users of the groundwater and could become problematic if similar concentrations develop in the stored water. Average concentrations of F (360 mg/kg) and As (11 mg/kg) in the Kopoasfontein rocks are not abnormally high for shales, but the alkaline geochemical environment is suspected to favour mobilisation of F^- and H_2AsO_3^- in the groundwater.

The water from the surrounding shallow alluvial and weathered shale aquifers has vastly different chemical characteristics, being hard (hardness = 1400 to 3090 mg/L as CaCO_3), brackish (EC $\approx$ 400 to 770 mS/m) and near neutral pH (7.4 to 7.7). The dominant ions are Na^+ , Mg^{2+} and Cl^- . These waters were rejected as recharge sources because of their potential to produce large quantities of calcium carbonate precipitate if brought into contact with the high pH breccia water. Instead the neutral pH (7.1), low salinity (EC = 20 mS/m) surface water is the chosen source for

injection into the Kopoasfontein breccia reservoir.

Water-leachable components in the Kopoasfontein rocks are dominated by Na^+ , K^+ and alkalinity. Batch-type leaching tests (Cavé, 1999), which reacted powdered rock samples with deionised water, produced solutions with a strong $\text{Na/K-HCO}_3/\text{CO}_3$ signature and an average pH close to 9. Reaction of surface water with the Kopoasfontein rock led to similar solution composition to those of the leaching tests ($\text{Na/K-HCO}_3/\text{CO}_3$). Karoo groundwater composition, however, was little changed by reaction with the rock, because of the high solute concentrations in the original waters.

Rock samples from the Kopoasfontein breccia pipe contain appreciable amounts of a well-crystallised hydrothermal mineral, identified by X-ray diffraction as apophyllite (Cavé, 1999). The high fluoride content of the groundwater suggests that this may be a fluoride-rich member of the fluorapophyllite-hydroxyapophyllite solid solution series. Apophyllite coats the surfaces of fractures and vugs in the breccia and will therefore have extensive surface contact with the groundwater, since these structures contribute most of the permeability of the rock body. Part of the research reported in this thesis builds on the findings of the MSc study, by examining in detail the mineral composition and low-temperature reactions of apophyllite in aqueous solution.

1.5 Outline and scope of the thesis

The research in this thesis covers three main focus areas, which form the basis of Chapters 3, 4 and 5. These are:

- ▶ the natural hydrochemistry of the Kopoasfontein breccia pipe in the context of other breccia pipes and the surrounding aquifers in the Calvinia area (Chapter 3);
- ▶ the composition of the rocks and minerals in the Kopoasfontein breccia pipe, including preliminary conclusions regarding the causes of brecciation, the origin of minerals in the pipe and their influence on water chemistry (Chapter 4); and
- ▶ experimental investigations of the thermal properties, compositional ranges, and low temperature dissolution kinetics of apophyllite (Chapter 5).

The experimental studies in Chapter 5 are supported by a literature review (Chapter 2) presenting the current state of knowledge of the dissolution kinetics of silicate minerals in near-surface environments. This chapter includes reaction rates and mechanisms for common rock-forming silicates, the various factors that may enhance or inhibit dissolution and laboratory-based experimental techniques.

Chapter 6 discusses the water-rock interactions in the Kopoasfontein breccia pipe, using data from the previous chapters, geochemical equilibrium modelling simulations and mass balance calculations to test the research hypothesis. The practical implications of the study for the water storage project at Calvinia are also addressed in this final chapter.

CHAPTER 2

THE KINETICS OF SILICATE MINERAL WEATHERING IN LOW TEMPERATURE ENVIRONMENTS: A LITERATURE REVIEW

2.1 Introduction

Silicates comprise by far the largest group of rock-forming minerals on earth. Although the changes in water chemistry resulting from silicate weathering are less apparent than those of carbonate or evaporite dissolution, weathering of silicate minerals is, nevertheless, estimated to contribute almost half of the total dissolved solid load of the world's rivers (Stumm and Wollast, 1990). Silicate weathering is also expected to constitute a more important long-term control on atmospheric CO₂ levels and the associated impact on global climate change, than carbonate weathering (Berner, 1995).

Silicate mineral weathering has been an active field of geochemical research over the last three decades. This work has been motivated by such diverse aims as assessing the risks of radioactive waste disposal, understanding the effects of acid precipitation and estimating the contribution of mineral dissolution reactions in the consumption of atmospheric CO₂ (White and Brantley, 1995). Despite the large scale of such processes, many of the changes in the earth's chemical systems are controlled on a molecular level by reactions which occur at the mineral-water interface (Hochella and White, 1990; Vaughan and Pattrick, 1995). These are based on the two rudimentary mechanisms of chemical species attachment to and detachment from mineral surfaces. A fundamental goal of studying silicate dissolution kinetics is to understand the factors which control mineral surface reactions and the rates at which these occur.

The study of silicate dissolution kinetics considers the rate at which silicate weathering reactions occur and, by investigating the factors controlling this rate, allows some elucidation of the pathways or mechanisms by which dissolution proceeds. This review discusses experimental techniques and data collected on the dissolution rates of ortho-, tecto-, ino- and phyllosilicates and the reaction mechanisms by which these dissolve at or near room temperature. Systematic variations in environment and solution composition have been used to determine the effects of

temperature, pH, dissolved inorganic and organic species, ionic strength and saturation state on dissolution rates. This information provides valuable clues as to the nature of the species involved in rate-determining elementary reactions at the mineral surface.

Models of varying complexity have been developed to assist in explaining and predicting mineral dissolution rates, based on a growing understanding of the nature of chemical processes occurring at the mineral-water interface. Despite careful experimentation, however, dissolution rates obtained in the laboratory continue to overestimate dissolution rates observed for the same minerals in field studies of soils or catchments. One of the many possible reasons for this discrepancy is the role played by microorganisms in natural environments. Biogeochemical processes, which will be discussed at the end of this chapter, add an interesting and challenging dimension to problems of natural silicate weathering.

Much of the recent work in the field of silicate mineral dissolution kinetics has been summarised in *Reviews in Mineralogy, Volume 31, Chemical Weathering Rates of Silicate Minerals*, edited by White and Brantley (1995), which has provided an important source of information for this review. Comprehensive discussions of surface coordination chemistry (ligand exchange theory) and its application to the mechanisms of mineral dissolution can be found in the review paper by Stumm and Wollast (1990) and in a chapter by Casey (1995) in the book on *Mineral Surfaces* (Vaughan and Pattrick, 1995). These and other reactions at the mineral-water interface are also reviewed in detail in *Reviews in Mineralogy, Volume 23, Mineral-Water Interface Geochemistry* (Hochella and White, 1990). Stumm (1992) also provides a good general introduction to the kinetics of surface-controlled dissolution in Chapter 5 (p. 157 - 209) of his book, *Chemistry of the Solid-Water Interface*.

2.2 Weathering reactants and products

Mineral weathering generally occurs whenever water comes into contact with primary minerals, which are thermodynamically unstable under the physical and chemical conditions of the earth's surface (Furrer and Stumm, 1986). Silicate weathering involves hydrolysis reactions, where H_2O acts as both a reactant (as a source of H^+) and as an agent for the transport of solutes to and from the site of reaction at the mineral surface. Other reactants that may enhance chemical weathering

are derived from the atmosphere, which provides a reservoir of CO₂ and oxidant gases. These dissolve in water to provide an additional source of electron-acceptors or hydrolyse to produce protons by reactions such as:

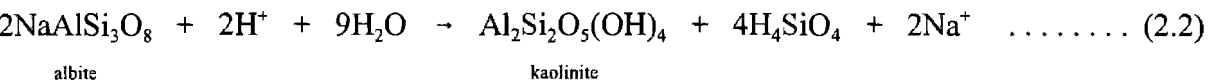


Weathering reactions can also be assisted by biota (as will be discussed in Section 2.9.2). Microorganisms provide organic ligands and acids, which become involved in mineral surface reactions and locally increase CO₂ partial pressure by their respiration (Stumm and Wollast, 1990). Organic matter may also serve as a reducing agent or produce organic solutes which act as complex-forming ligands and enhance dissolution by interacting with the solid mineral surface (Furrer and Stumm, 1986).

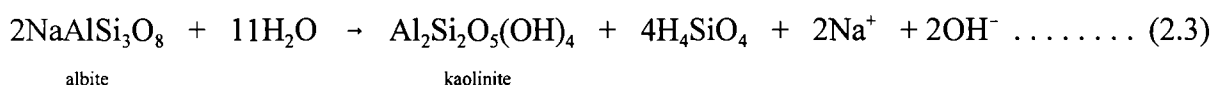
The products of mineral weathering include solutes and particulate components which may be transported from the reaction site. Evaporite and carbonate dissolution lead to significant increases in dissolved concentrations of their constituent ions, while silicate weathering primarily contributes cations, silica and alkalinity to the solution. Total dissolved concentrations of ions in waters from silicate rock catchments are usually low, because of the slow dissolution rates of most silicate minerals and limited contact of water with mineral surfaces in impermeable hard rock environments (Appelo and Postma, 1996; p. 205).

Silicate mineral dissolution is often incongruent, i.e. the dissolution of one phase may be accompanied by the formation of a new solid such as gibbsite, kaolinite, smectite, illite or iron oxides. Aluminium and ferric iron, in particular, are often conserved in insoluble solid phases.

Dissolution reactions may increase or decrease the solution pH, depending on the reaction mechanism and the speciation reactions that occur in solution following mineral dissolution. Many silicate dissolution reactions consume H⁺, as shown in the example of the incongruent dissolution of albite to kaolinite in equation 2.2.

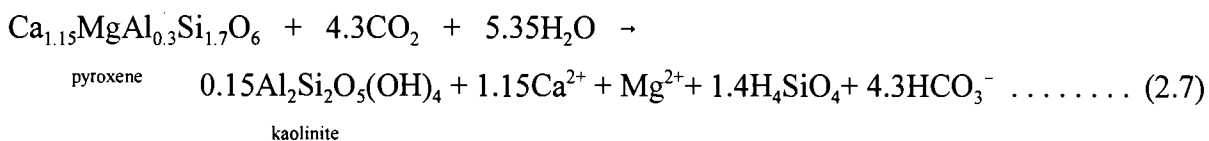
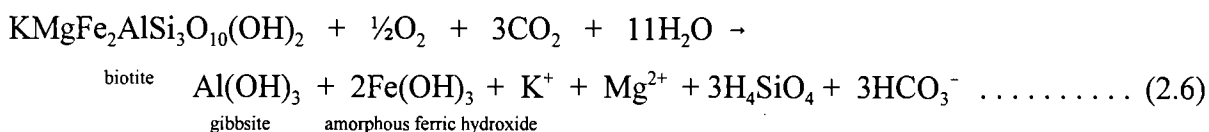
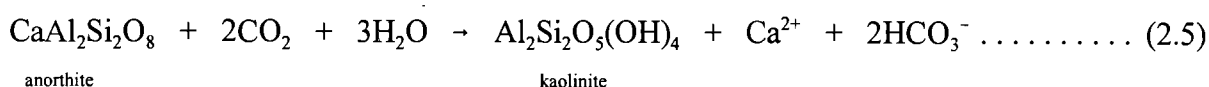
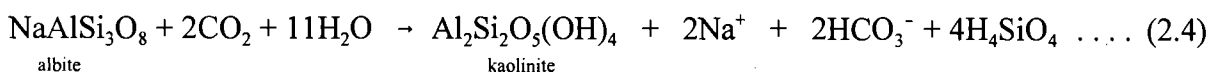


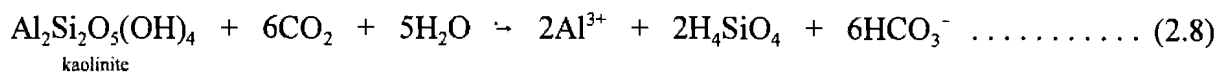
In the absence of other proton sources, the protons necessary for dissolution reactions may be provided by the dissociation of water itself, sometimes generating OH^- alkalinity (McBride, 1994; p. 275; Drever, 1997; p. 204). e.g.



Carbon dioxide is ubiquitous in near-surface environments and intensifies most weathering reactions by producing a greater degree of proton availability than would be available from the simple dissociation of H_2O ($K = 10^{-6.35}$ for reaction 2.1 compared with $K_w = 10^{-14.00}$ for dissociation of water).

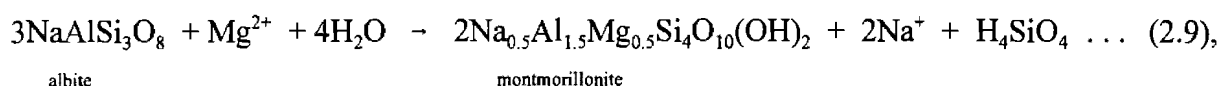
Some examples of incongruent silicate weathering reactions in the presence of CO_2 are given in the equations which follow. There are no unequivocal weathering reactions for silicate minerals and the products, especially secondary mineral precipitates, depend on the nature of the parent rock, flow conditions and whether closed or open system conditions prevail.





In all the above cases, water, which acts as a proton source, and carbon dioxide are the primary reactants. The net result of weathering is the release of base cations (e.g. Na^+ , Ca^{2+} , K^+ , Mg^{2+}) and the production of HCO_3^- alkalinity. Groundwater in silicate rocks is generally characterised by significant Na^+ which is not balanced by Cl^- ions and is derived from the weathering of albite and other plagioclase minerals. Calcium is often the major cationic component, released from weathering of plagioclase, amphiboles, calcic pyroxenes and other calcic silicates. Dissolution of mafic minerals, such as forsterite, can also lead to high concentrations of dissolved Mg^{2+} . Where Fe(II) is present in the mineral (e.g. biotite, reaction 2.6), dissolution may take place via an oxidative process, where O_2 availability is an important factor in the weathering reaction. The above reactions also show that hydrolysis of silicate minerals often releases silicic acid to the solution. Dietzel (2000) has found that polymeric species are initially released and decompose as a function of time to stable monomeric H_4SiO_4 .

The nature of secondary mineral products is controlled by thermodynamic stability relationships between the secondary minerals (Garrels and Christ, 1965) and the relative rates of dissolution and precipitation reactions (Lasaga *et al.*, 1994). The phase which is most likely to form depends on the availability of protons, activity of dissolved silica and cation concentrations, related to the intensity of leaching, which is a function of the climate under which weathering takes place. In dry climates or areas of rapidly dissolving volcanic material, where there is little flushing of solutes, preferential formation of montmorillonite has been observed (Kittrick, 1971a; 1971b). Reactions such as



where Mg^{2+} is available from weathering of pyroxene or biotite, for example, preserve a high proportion of the silica in the solid phase and do not require the consumption of acid. Increased leaching of Si is favoured under high rainfall and well-drained acidic conditions to form kaolinite, and eventually gibbsite, as secondary weathering products (Kittrick, 1966).

Increased Ca^{2+} , Mg^{2+} and HCO_3^- concentrations, accompanied by an increase in solution pH, can also, in some cases, lead to supersaturation and the precipitation of secondary carbonate minerals such as calcite and dolomite as a result of silicate weathering. Both carbonate and silicate dissolution reactions are acid-consuming and provide a pH buffering mechanism in natural waters. Silicate weathering can generate higher pH solutions in systems where CO_2 is depleted, for example deep groundwater environments where closed system behaviour occurs.

2.3 Reactivity of silicate minerals

Evaporite mineral salts and calcareous minerals are soluble and dissolve rapidly and, in general, congruently. Their weathering reactions can often be described by solubility equilibria. By contrast silicate minerals are generally slow to degrade and often dissolve incongruently. Dissolution kinetics must, therefore, be considered when describing the weathering of silicate minerals. The variation in rates of silicate mineral dissolution depends on the arrangement of the silica tetrahedra in the mineral framework and the nature of the cations, which determines the relative strengths of the metal-oxygen bonds (Stumm and Wollast, 1990).

Studies of soils exposed to weathering for thousands of years show variations in mineralogical composition with depth which are related to the relative dissolution rates of the slowly-reacting silicate minerals. This kinetic control on the distribution of primary silicate minerals is recognised in the empirical weathering sequence derived by Goldich (1938) (Figure 2.1).

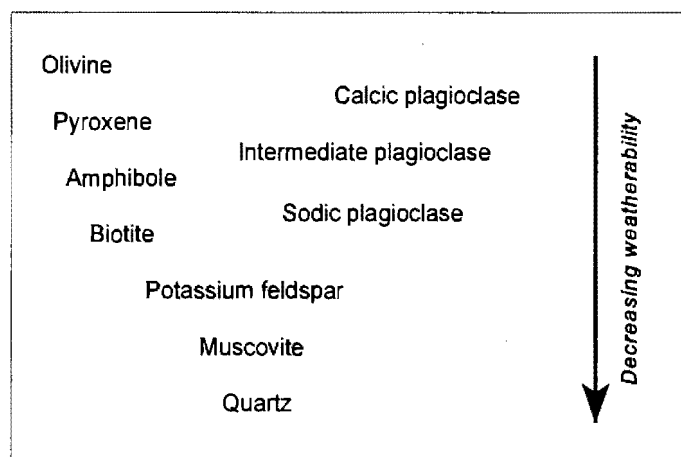


Figure 2.1. The Goldich weathering sequence for primary silicate minerals, based on observations of mineral weathering profiles in soils (After Goldich, 1938).

The same sequence may be found when comparing experimentally derived dissolution rates, such as those compiled by Lasaga *et al.* (1994) (Table 2.1).

Table 2.1. Approximate time for a hypothetical 1 mm sphere of mineral to dissolve in dilute solution at pH 5 far from equilibrium (Lasaga *et al.*, 1994 as cited in Drever, 1997; p. 233).

Mineral	Lifetime (years)
Calcite	0.1
Dolomite	1.6
Olivine (forsterite)	2 300
Calcic clinopyroxene (diopside)	6 800
Orthopyroxene (enstatite)	10 100
Calcium-rich plagioclase (bytownite)	40 000
Intermediate plagioclase (andesine)	80 000
Sodium plagioclase (albite)	575 000
Biotite	900 000
Potassium feldspar (microcline)	921 000
Epidote	923 000
Muscovite	2 600 000
Kaolinite	6 000 000
Quartz	34 000 000

2.3.1 Silica

Several polymorphs of silica are found as common minerals in most natural systems. Silica is the end-member oxide for the other classes of silicate minerals considered in this review. The fundamental control on the reactivity of the silica compounds, therefore, provides an important baseline for the study of the behaviour of Si-O bonds in multi-oxide crystalline silicate minerals. The chemistry of silica itself, however, is complex and the kinetic and thermodynamic controls on silica reactivity could easily form the subject of a separate review. Recent research on this topic has been summarised by Dove (1995).

The solubility of silica polymorphs increases with increasing disorder and decreasing density in the crystal structure. Quartz is the silica polymorph which is most resistant to chemical and physical weathering at the temperatures and pressures of the earth's surface. Thermodynamic

data for the solubility of silica polymorphs at 25°C are presented in Table 2.2. The solubility of crystalline and amorphous phases are essentially constant as a function of pH up to about pH 8.5. Above this pH, the silicic acid molecule dissociates, increasing silica solubility.

Table 2.2. Relative solubility of silica phases at 25°C. (Data from Dove, 1995, after Robie *et al.*, 1978).

Polymorph	ΔG_f° (kJ/mol)	$K = \alpha(\text{H}_4\text{SiO}_4)$ *	$\alpha(\text{SiO}_2) = K / K_{\text{quartz}}$ **
quartz	-856.288	1.11×10^{-4}	1.00
cristobalite	-854.512	2.28×10^{-4}	2.05
tridymite	-853.812	3.02×10^{-4}	2.71
coesite	-850.850	9.98×10^{-4}	8.97
glass	-850.559	1.12×10^{-3}	10.08

* $\alpha(\text{H}_4\text{SiO}_4)$ = activity of H_4SiO_4 at equilibrium.

** $\alpha(\text{SiO}_2)$ expresses the relative solubility of the mineral forms with respect to quartz.

The rate of quartz dissolution follows a rate law which is zero-order in silicic acid (see Section 2.4.2), while precipitation follows a first order rate dependence on silicic acid in solution (White and Brantley, 1995). The quartz dissolution rate in pure water at 25°C has a minimum of about 2×10^{-14} mol/m²/s in the acid range near pH 3, increases to 8×10^{-14} mol/m²/s at pH 1 and pH 7 and reaches approximately 10^{-12} mol/m²/s near pH 12 (Wollast and Chou, 1986).

2.3.2 Feldspars

Feldspars are the most common minerals in the earth's crust and have been the most intensely studied silicate mineral group in terms of dissolution kinetics. The reader is referred to Blum and Stillings (1995) and Blum (1994) for a detailed discussion of feldspar dissolution. Feldspar weathering in natural environments is generally incongruent with primary feldspar minerals dissolving irreversibly to form secondary clay minerals and solutes (see, for example, reactions 2.4, 2.5 and 2.9, Section 2.2).

Feldspar weathering reactions occur via two separate processes: 1) dissolution of feldspar into solution and 2) precipitation of a secondary phase from solution, with the relative rates of reaction controlled by solution composition. In near-surface, open systems, the dissolution reaction is slow and rate-limiting in the overall weathering of feldspar to clay (Blum and

Stillings, 1995). Table 2.3 compares dissolution rates for various feldspar minerals at 25°C, calculated from the rate constants compiled by Blum and Stillings (1995).

Table 2.3. Far-from-equilibrium dissolution rates of feldspar minerals in water at 25°C (Data from Blum and Stillings, 1995). All rate data reported as mol feldspar/m²/s, calculated from reported rate laws as a function of pH.

Mineral	Dissolution rate at pH 2	Dissolution rate at pH 5	Dissolution rate at pH 12
Albite	2×10^{-11}	7×10^{-13}	3×10^{-11}
K-feldspar	1 to 5×10^{-11}	4 to 8×10^{-11}	2×10^{-10}
Labradorite	1×10^{-10}	4×10^{-12}	no data
Anorthite	5×10^{-6} to 8×10^{-9}	4×10^{-12} to 6×10^{-11}	no data

In natural systems, potassium feldspars have been observed to weather more slowly than sodic plagioclase (e.g. in the Goldich weathering sequence, Figure 2.1). This is probably related to thermodynamic, rather than kinetic constraints. Pore waters are often closer to saturation with respect to K-feldspar than with respect to albite, which suggests that the dissolution rate of K-feldspar in such environments would be slower than the “far-from-equilibrium” rates measured in the laboratory.

Calcic plagioclase is more reactive than sodic plagioclase in soils and an exponential increase in dissolution rate with increasing anorthite content (from An₀ to ~An₈₀) is observed in acid solutions. Above An₈₀ the increase in reaction rate is even faster, with anorthite reaching a dissolution rate near 5×10^{-6} mol/m²/s at pH 2.2 (data from Sverdrup, 1990, reported by Blum and Stillings, 1995).

2.3.3 Olivines, pyroxenes and amphiboles

Studies of the dissolution of olivines, pyroxenes, amphiboles and other framework silicate minerals are not as common as for feldspars and their dissolution kinetics have not been as well defined. The rate of weathering of these minerals is, however, expected to play an important role in the global regulation of atmospheric CO₂ concentration (Berner, 1995) and to provide the principal input of Fe and Mg to natural waters (Brantley and Chen, 1995). Research on chemical

weathering rates of pyroxene and amphibole minerals has been compiled by Brantley and Chen (1995), while the dissolution kinetics of forsterite olivine at 25°C has recently been described in detail by Pokrovsky and Schott (2000a, b).

Brantley and Chen (1995) summarise published dissolution rates calculated from Si release for a range of inosilicate minerals at ambient temperatures. Rates vary considerably due to differences in sample preparation and experimental conditions as well as differences in mineral chemistry or structure. Table 2.4 presents a compilation of data calculated from what Brantley and Chen (1995) consider to be best estimates of inosilicate dissolution rate laws as a function of pH, as well as forsterite dissolution rates at pH 2 and pH 5 from Pokrovsky and Schott (2000b).

Table 2.4. Far-from-equilibrium dissolution rates of olivine, pyroxene, pyroxenoid and amphibole minerals in relation to pH in water at 25°C (Data from Brantley and Chen, 1995 and Pokrovsky and Schott, 2000b). All rate data reported as mol silicate/m²/s normalised by initial surface area.

Mineral	Dissolution rate at pH 2	Dissolution rate at pH 5
Forsterite	2×10^{-8} Si	7×10^{-10} Si
Enstatite	2×10^{-10}	3×10^{-11}
Bronzite*	2×10^{-11}	6×10^{-13}
Diopside	3×10^{-11}	2×10^{-11}
Augite*	5×10^{-10}	6×10^{-13}
Wollastonite*	3×10^{-9}	6×10^{-10}
Anthophyllite	1×10^{-13}	1×10^{-14}
Tremolite*	5×10^{-12}	1×10^{-11}
Hornblende	n.d.	1×10^{-12} **
Glaucophane*	n.d.	1×10^{-10}

^{Si} rate of Si release at pH 2.13 and 4.95; * indicates dissolution measured for less than 1000 hours; n.d.= not determined, since reported rate law was not valid for this pH; **hornblende dissolution rate at pH 4.

Under acid conditions, in the absence of oxygen, dissolution rate trends among the orthosilicate minerals have been found to be predictable from the reactivity trends for ligand-exchange reaction rates of analogous hydrated metal complexes (Casey and Westrich, 1992). Just as the rates of solvent exchange increase with increasing cation size for the hydrated alkaline earth metals, $\text{Be}(\text{H}_2\text{O})_4^{2+} < \text{Mg}(\text{H}_2\text{O})_6^{2+} < \text{Ca}(\text{H}_2\text{O})_6^{2+}$, so Ca-olivine ($\gamma\text{Ca}_2\text{SiO}_4$) dissolves at a much

faster rate than forsterite (Mg_2SiO_4), which in turn dissolves faster than phenakite (Be_2SiO_4) at pH 2. Ion size is important because larger ions can more easily accommodate extra ligands around the metal cation in an associative ligand exchange mechanism. Smaller ions form more stable complexes which have a slower rate of dissociative ligand exchange.

For orthosilicates containing first-row transition metal cations, the trends for solvent exchange and mineral dissolution are also similar. In this case, it is the d-orbital occupancy rather than the ion size which controls the relative rate of reaction. Dissolution rates, like ligand exchange rates, correspond with ligand field stabilisation energies so that the order of reactivity is Zn_2SiO_4 (willemite) $\approx$ Mn_2SiO_4 (tephroite) $>$ Fe_2SiO_4 (fayalite) $>$ Co_2SiO_4 $>$ Ni_2SiO_4 (liebenbergite).

These observations suggest a link between the mechanism of solvent exchange and that of surface reactions during mineral dissolution, which Casey and Westrich (1992) proposed could be extended to predict relative reactivities of other silicate minerals such as pyroxenes.

The correlation between overall dissolution rate and the strength of divalent metal-oxygen bonds, however, largely disappears with increasing polymerisation of the silicate framework in chain, sheet and tectosilicate minerals. Banfield *et al.* (1995) found that correlations between composition and rate of dissolution were less predictable for the ino- than orthosilicates and suggested that dissolution may be controlled by the polymerised silicate chains rather than the interstitial cations. As would be expected, there is a decrease in dissolution rate with increasing polymerisation of the silicate structure so that at similar pH values, orthosilicates dissolve faster than pyroxenes, which in turn dissolve faster than amphiboles of comparable cation composition, in agreement with the Goldich weathering sequence.

2.3.4 Phyllosilicates

Many layer silicate minerals differ from the other silicate minerals in that they both dissolve and precipitate from aqueous solutions under ambient conditions during chemical weathering. Chemical equilibrium concepts and the role of solution saturation state, therefore, need to be considered in conjunction with kinetics when describing the weathering reactions of these minerals. Examples of weathering reactions involving sheet silicates are the incongruent

dissolution of feldspars to kaolinite (e.g. reactions 2.4 and 2.5) and the dissolution of kaolinite in reaction 2.8. The speciation of Al^{3+} in solution is a function of pH and in the pH range of natural waters, kaolinite dissolution is also likely to be incongruent, with precipitation of secondary aluminium hydroxides.

Knowledge of sheet silicate dissolution rates is more comprehensive than for precipitation rates, because of greater experimental difficulties in studies of mineral growth and nucleation. This review will only consider sheet silicate dissolution, but the reader is referred to Nagy (1995) for more information on both the dissolution and precipitation kinetics of sheet silicates. Kaolinite, the most simple of the layered aluminosilicates, is the most commonly studied mineral in this group. The surface chemistry and dissolution kinetics of kaolinite are reviewed by Stumm (1992; pp. 63 - 65 and 179 - 182).

Overall sheet silicate dissolution rates near neutral pH (e.g. pH = 5) are all in the region of $\sim 10^{-13 \pm 0.5}$ mol/m²/s at 25°C (Table 2.5), when the mineral formula is reduced such that one mol represents a single layer of the mineral¹ (Nagy, 1995).

Table 2.5. Selected dissolution rates of sheet silicates and related minerals at 25°C and pH 5 (Nagy, 1995).

Mineral	Rate (mol/m ² /s)	Mineral	Rate (mol/m ² /s)
Brucite	6×10^{-6}	Gibbsite	3×10^{-13}
Chrysotile	1×10^{-12}	Kaolinite	1 to 4×10^{-13}
Talc	1×10^{-12}	Muscovite	1×10^{-13}
Chlorite	3×10^{-13}	Biotite	6×10^{-13}
Phlogopite	4×10^{-13}	Montmorillonite	4×10^{-14}

Minerals such as talc and chrysotile (Bales and Morgan, 1985), which do not contain aluminium, dissolve slightly faster than the aluminosilicates in this group. Gibbsite, which approximates the alumina octahedral sheet, dissolves at a similar rate to that of aluminosilicates in the phyllosilicate group, while brucite, an analogue for the magnesium octahedral sheet in talc has

¹ i.e. when the formula of a 2:1 interlayer phase is normalised to the $\text{O}_{10}(\text{OH})_2$ formula unit. For example one layer of muscovite would include the 2 tetrahedral silicate layers, the octahedral layer and one interlayer of potassium.

a dissolution rate seven orders of magnitude faster than the other phases in Table 2.5 (Nagy, 1995).

2.4 Reaction mechanisms

2.4.1 Reaction sequence and rate-limiting steps

The elementary reaction steps involved in mineral dissolution are (Stumm and Wollast, 1990):

1. Mass transport of dissolved reactants (H^+ , OH^- , ligands, oxidants, reductants) from the bulk solution to the mineral surface.
2. Adsorption of solutes at the mineral surface.
3. Interlattice transfer of reacting species.
4. Surface chemical reactions.
5. Detachment of species or atoms from the mineral surface.
6. Mass transport into the bulk solution.

Usually one step in the reaction is slower than the others and this rate-limiting step determines the overall rate of the dissolution reaction. Steps 1 and 6 in the reaction sequence involve mass transport in solution, which proceeds at a much faster rate than the overall dissolution rate under laboratory conditions and is generally not rate-limiting. For weathering reactions the rate is usually controlled by mass transfer of reactants and products in the solid phase (step 3) or a surface chemical reaction (step 4) and detachment of reactants from the surface (step 5) (Stumm and Wollast, 1990).

2.4.2 Diffusion-controlled versus surface-controlled mechanisms

Reaction steps may be divided into diffusion-controlled (transport-controlled) processes and surface-controlled (reaction-controlled) processes. Diffusion-controlled processes involve the physical movement of chemical species to and from the site of reaction. In the case of mineral dissolution, the aqueous diffusion of reactants and products in the bulk solution and the diffusion of species through the mineral lattice are both diffusion-controlled processes. Surface-controlled

processes involve the formation or destruction of chemical bonds at the site of reaction. Reactions which are controlled by diffusion in the aqueous phase, i.e. transport to and from the mineral surface, may be recognised by low activation energies (see section 2.6.7), the formation of rounded mineral grains instead of etch pits on the mineral surfaces and a marked increase in the reaction rate with increased agitation or stirring of the solution (Drever, 1997; p. 221).

Two primary mechanisms have been proposed for silicate dissolution:

1. the rate-limiting step is a diffusion-controlled step involving transport of a reactant or a weathering product through a mineral surface layer, or
2. the rate-limiting step is controlled by a surface reaction (Stumm and Wollast, 1990).

Figure 2.2 compares some of the features of diffusion- and surface-controlled processes and illustrates the observed effects on solute concentration with time.

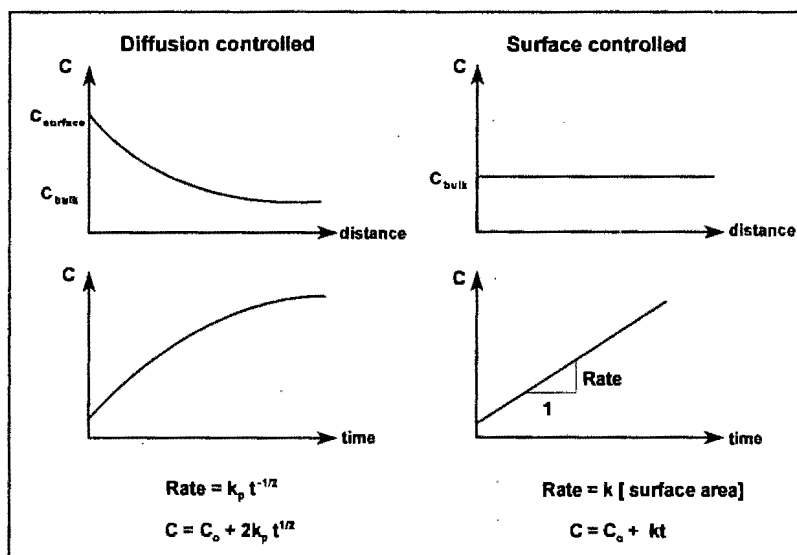


Figure 2.2. Diffusion- vs. surface-controlled dissolution. Schematic diagram of the concentration in solution, C , as a function of distance from the dissolving mineral surface. Also shown is the change in concentration as a function of time, t , as in a batch dissolution experiment. Equations describe the parabolic rate law for diffusion controlled reactions and the linear rate law for the surface controlled mechanism, along with the corresponding expressions for concentration change. k_p is the parabolic rate constant, k the linear rate constant and C_0 the initial solute concentration (After Stumm, 1992; p. 160).

Diffusion-controlled mechanisms follow a parabolic rate law and the concentration of solutes increases with the square root of time. Surface-controlled processes display linear dissolution kinetics and follow a zero-order rate law under steady state conditions. The rate of dissolution is proportional to the surface area of the mineral and solute concentrations increase linearly with time under surface control.

2.4.3 Surface reactions during silicate dissolution

Silica surfaces in water are readily hydroxylated and become dominated by ionisable $>\text{SiOH}$ (silanol) groups² which participate in protonation/deprotonation reactions. The dissociation of mobile protons imparts an electrical charge to the silica surface. Using a double layer model, protons coordinate with the silica surface as inner-sphere complexes, while sodium and other weakly hydrated cations are modelled as outer-sphere complexes. Surface acid and base reactions lead to the formation of the surface complexes $>\text{SiOH}$ and $>\text{SiO}^-$ in pure water and complexes such as $>\text{SiO}^-\text{Na}^+$ and $>\text{SiOH}_2\text{Cl}$ in electrolyte solutions. The relative proportions of these complexes is largely controlled by the association constants for the surface reactions (Table 2.6). Surface equilibria lead to the pH dependence of the distribution of surface complexes and, since dissolution is controlled by surface reactions, to the pH dependence of dissolution rates (Wieland *et al.*, 1988).

Table 2.6. Association constants for acid-base complexation reactions at the quartz surface at 25°C (Dove, 1995 and references therein).

Surface reaction	K_a
$>\text{SiOH} = >\text{SiO}^- + \text{H}^+$	$10^{-6.8}$
$>\text{SiOH} + \text{Na}^+ = >\text{SiO}^-\text{Na}^+ + \text{H}^+$	$10^{-7.1}$
$>\text{SiOH}_2^+ = >\text{SiOH} + \text{H}^+$	$10^{-2.3}$
$>\text{SiOH} + \text{H}^+ + \text{Cl}^- = >\text{SiOH}_2\text{Cl}$	$10^{-6.4}$

Lasaga (1995) describes a step-wise reaction mechanism for the hydrolysis of quartz by water molecules which is supported by quantum mechanical calculations of the energies involved in atomic bond-forming and -breaking. Adsorbed water molecules react with $>\text{Si-O-Si}<$ bonds near

² $>\text{Si}$ is used to denote a tetrahedral silicon atom at the mineral surface.

the surface, hydrolysing in turn each of the four links holding a SiO_4 tetrahedral unit in the quartz structure and effectively loosening the tetrahedron from the surface. After all four anchoring $>\text{Si-O-Si}<$ bonds are broken, the tetrahedron is protonated to H_4SiO_4 which desorbs into solution.

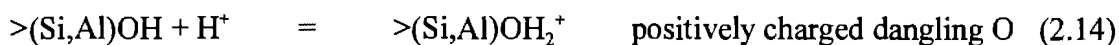
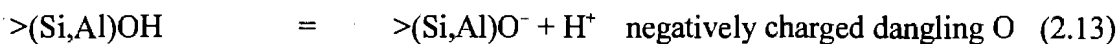
Feldspar surfaces are more complex than silica minerals and three fundamental types of surface reactions may be involved in feldspar surface chemistry during dissolution (Blum and Lasaga, 1991):

1. Exchange and/or sorption reactions involving the interstitial cation sites (Na^+ in albite, K^+ in K-feldspar, Ca^{2+} in anorthite).

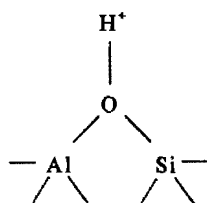


where X is a cation site accessible for exchange with solution and X^- is an unfilled cation site. The depth of the exchange layer is several unit cells in albite and slightly deeper in the K-feldspars and anorthite.

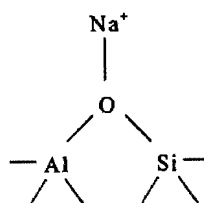
2. Adsorption/desorption of H^+ on dangling oxygens at the surface. These are rapidly hydrated to silanol ($>\text{SiOH}$) or aluminol ($>\text{AlOH}$) groups.



3. Adsorption reactions at bridging oxygens at the surface, e.g.



(A)



(B)

Blum and Lasaga (1991) suggested that only a small proportion of bridging oxygens are protonated at any specific time, but that this may be an important step in the feldspar dissolution mechanism.

Various researchers have proposed that one or more of these surface reactions controls the overall rate of feldspar dissolution. Blum and Lasaga (1991) suggested that protonation of Al sites controls H^+ adsorption on albite surfaces as a function of pH. Their proposed dissolution mechanism involves protonation and deprotonation of dangling $>AlOH$ sites (reaction 2.14), which control surface charge, while the hydrolysis of bridging Al-O-Si bonds adjacent to protonated aluminium hydroxide groups ($>AlOH_2^+$) is the rate-limiting step. Observed dissolution rates are proportional to H^+ adsorption below pH 6.8 and OH^- adsorption in the basic region.

This is in contrast to Brady and Walther's (1989) proposal that $>SiOH$ and not $>AlOH$ groups are deprotonated under alkaline conditions and that Si detachment controls feldspar dissolution at high pH. Amhrein and Suarez (1988) argued that proton-promoted dissolution occurs at Si centred sites and ligand-promoted dissolution at Al centred sites, with the hydrolysis of uncharged Si sites also contributing to dissolution, especially in the pH-independent region.

Oxburgh *et al.* (1994) developed a surface speciation model where proton adsorption at the $>Al-O-Si<$ bridging oxygen sites (species A, above), rather than at adjacent $>AlOH$ groups, is the dominant dissolution mechanism. The reaction order is related to the average number of these sites coordinated around each Si centre.

Oelkers and Schott (1998) observed that the rate of feldspar dissolution is proportional to $[(a_H^+)^3/a_{Al}^{3+}]^n$, where a_i is the activity of species i in solution and n is a stoichiometric coefficient. Their model for alkali feldspars involves the formation of an Al-deficient precursor complex, which is a network of partially detached silica tetrahedra remaining on the mineral surface after rapid destruction of tetrahedrally coordinated Al-O bonds relative to that of Si-O bonds. The mechanism proceeds via three steps consisting of 1) rapid exchange of H^+ and alkali ions near the mineral surface (reaction 2.10), 2) an exchange reaction involving 3 H^+ in solution and one Al atom in the mineral structure, causing breaking of Al-O bonds and formation of the Si-rich precursor complexes, and 3) the hydrolysis of Si-O bonds, releasing the precursor complex into solution.

The mechanism advocated by Pokrovsky and Schott (2000a, b) for the dissolution of forsterite

olivine in acid solution follows a sequence involving: 1) rapid exchange of 2H^+ for Mg^{2+} near the mineral surface, 2) polymerisation of two silica surface sites to form a surface silica dimer and 3) adsorption of H^+ on the $>\text{Si-O-Si}<$ bridging oxygen. The overall dissolution rate is controlled by decomposition of this protonated $>\text{Si-OH}^+-\text{Si}<$ surface complex. In alkaline solutions the rate is controlled by hydrolysis of Mg-O-Mg surface bonds after preferential release of H_4SiO_4 from the orthosilicate.

Sheet silicate dissolution is also largely controlled by surface reactions in aqueous solutions (Nagy, 1995). Surfaces become hydrated in contact with water, forming active surface silanol ($>\text{SiOH}$) and aluminol ($>\text{AlOH}$) groups at the edges, where sheet silicates have broken bonds with unsatisfied charge. Aluminol groups also occur on the basal surfaces of aluminium-bearing phases and on the gibbsitic sheet of kaolinite, which are active planes of dissolution. The reactivity of the sheet silicate edge sites means that these minerals typically dissolve inward from edge to core (White and Brantley, 1995).

For kaolinite dissolution, Wieland and Stumm (1992) proposed that Al-O-Si and Al-OH-Al bonds on the gibbsitic basal surface are broken simultaneously, while Ganor *et al.* (1995) argued that disruption of the Al-O-Si bond only is the rate-limiting step and proposed a reaction mechanism consisting of a sequence of slow hydrogen ion mediated hydrolysis steps. In basic solutions, Si detachment is likely to be rate-limiting (Carroll and Walther, 1990). Oelkers *et al.* (1994) proposed that an Al-deficient precursor complex on the kaolinite surface controls the dissolution rate and is responsible for the dependence of the dissolution rate on dissolved Al^{3+} concentrations.

2.5 Experimental determination of silicate dissolution kinetics

2.5.1 Experimental techniques

Two types of experiments have been used to generate the majority of available data on the dissolution rate of silicate minerals in the laboratory: batch and flow-through experiments.

Batch experiments

Earlier experiments were usually conducted as batch tests, because of their simplicity. A batch reactor consists of a vessel containing a fixed volume of solution and a fixed mass of solid which is set up either closed or open to the atmosphere, held at constant temperature and agitated or stirred to minimise the effects of mass transport in solution. Buffers may be used to reduce pH and/or ionic strength fluctuations (e.g. Carroll and Walther, 1990; Rose, 1991) and solutions may be changed periodically to provide some restriction on the drift in solution composition during the experiment (e.g. Amrhein and Suarez, 1988). Buffer solutions containing organic molecules have been largely avoided since it became known that organic ligands can enhance or inhibit dissolution. Resins or chelating materials have also been used to remove accumulated solute ions (e.g. Amrhein and Suarez, 1988). Semi-batch reactors such as pH-stat experiments are also considered in this class.

Batch reactor systems are closed to mass flow but not necessarily to energy flow (Rimstidt and Dove, 1986). The batch vessels are loaded with reactants and allowed to react towards equilibrium, while measuring the change in composition of the solution over time. Reaction rates are then calculated from the rate of change of solute concentration with time, correcting for any removal of the solution during monitoring (Brantley and Chen, 1995).

Batch tests have been criticised for having several limitations which affect the interpretation of dissolution rate data. Among these are the fact that the solution changes composition as the mineral dissolves. The measured rate may, therefore, change as a function of time as the solution chemistry changes. Accumulation of solutes in the reaction vessel can also lead to supersaturation with respect to secondary mineral products, causing a change in the solute concentration-time pattern each time a new phase forms. Rimstidt and Dove (1986) are of the opinion that a major failing of batch experiments is the fact that the reaction rates are not measured directly, but the concentration versus time data are fitted to the integrated form of a presumed rate law, and the reaction mechanism interpreted from the form of the differential rate law.

Flow-through experiments

Most of these limitations are overcome by the use of flow-through reactors, which have become a more popular choice for kinetic experiments involving silicates. Stirred flow-through reactors

allow easier interpretation of reaction rate data and maintain constant solution chemistry during the experiment (Brantley and Chen, 1995). Examples of flow-through reactors include the fluidised bed reactor used by Chou and Wollast (1985) to study albite dissolution and the mixed flow reactor (or continuously stirred tank reactor) used by Rimstidt and Dove (1986) in their investigation of wollastonite dissolution.

In a mixed flow reactor, a peristaltic pump is used to pump reagent solution continuously from a reagent tank into a closed reaction chamber at a constant flow rate, Q (L/s). The mineral sample is placed in the bottom, or may be suspended between nylon mesh inside the chamber. The reaction chamber is held in a water bath to maintain constant temperature and the solution inside stirred by a propeller or by agitation. A fluidised bed reactor is an externally recycled mixed flow reactor, which combines the slow single pass flow system of the mixed flow reactor with a second, much faster, recirculating flow that is used to suspend and stir the mineral particles in the reaction chamber. An outlet port allows the flowing solution to be collected for analysis after reaction with the mineral. The chamber, therefore, maintains a constant volume of solution in contact with the solid sample. The difference in the concentration of a solute component at the inlet, c_i (mol/L), and for the same component derived from dissolution of the mineral at the outlet of the reaction chamber, c_o (mol/L), is used to determine the reaction rate, R (mol/m²/s), by the relation (Brantley and Chen, 1995):

$$R = \frac{Q(c_o - c_i)}{A_s m} \dots\dots\dots (2.15)$$

where A_s is the specific surface area of the mineral (m²/g) and m is the initial mass of mineral in the reaction chamber (g). Steady state conditions are assumed when the outlet solution concentrations become constant.

The advantage of using flow reactors is that the fluid composition can be regulated by changing the flow rate or the input solution without dismantling the reactor and/or changing the amount of mineral present during the experiment (Oelkers and Schott, 1999). Once steady state has been reached, the solution composition is constant and precipitation of dissolved products is usually

avoided because they are removed from the system via the outlet flow before the solution becomes saturated (Rimstidt and Dove, 1986).

Column experiments

A third type of experimental set-up is the use of plug-flow reactors which involve packing the mineral sample into a small column, to simulate natural systems more closely. The flow and dispersion patterns and changing solution composition as a function of distance in the column, make modelling of dissolution data from plug-flow experiments a difficult task (Brantley and Chen, 1995).

Surface area measurements

Dissolution rates are reported with respect to the solution chemistry as measured at the end of the batch test or at the outlet port of the flow reactor once steady state conditions are reached. Whether using batch or flow type experiments, the mineral dissolution reaction rates are usually normalised to the mineral surface area. Geometric surface area can be calculated from the particle size distribution of the sample, based on an assumed particle geometry, which is usually taken to be spherical. Surface areas are now more commonly measured by the Brunauer, Emmett and Teller (BET) adsorption method using N₂ or Kr gas (Brunauer *et al.*, 1938) at the start or end of the experiment.

Surface titrations

Since it has been recognised that protonation and deprotonation reactions at the mineral surface play an important role in mineral dissolution, acid-base titrations of the mineral surface have sometimes been performed to complement the data from batch or flow-through dissolution tests. Such titrations generate information on the amount of H⁺ or OH⁻ adsorbed at the surface as a function of pH. Adsorption experiments can also be conducted by adding known quantities of some other solute (e.g. metal cation or organic ligand) to the reaction vessel and indirectly measuring the amount adsorbed by analysing the solution composition after equilibration with the solid. Blum and Lasaga (1991), Xie and Walther (1994), Walther (1996) and others have shown that adsorption isotherms obtained from such titrations can be correlated with the pH dependence of dissolution rates. Adsorption isotherms model surface exchange reactions and can be used to identify the surface charged species involved in the rate-limiting dissolution step under

far-from-equilibrium conditions. Surface exchange reactions are, however, sometimes not the only proton-consuming or -producing reactions in the titration and care has to be taken when interpreting the results (e.g. Pokrovsky and Schott, 2000a).

Direct observation of mineral surfaces

Various spectroscopic, microscopic and diffraction techniques are now available that enable direct study of the mineral surfaces before, after and, in some cases, even during dissolution. These tools enable researchers to probe the composition, microtopography and atomic structure of the mineral surface, often on a very fine scale.

Surface composition may be determined by X-ray photoelectron spectroscopy (XPS), auger electron spectroscopy (AES), Rutherford backscattering spectroscopy (RBS), resonant nuclear reaction (RNR) and scanning tunnelling spectroscopy (STS) among others. Casey *et al.* (1988) gives an example of the use of RBS, elastic recoil detection (ERD) and infra red spectroscopy to examine the surface chemistry of labradorite, while XPS and infra red methods were used on forsterite surfaces by Pokrovsky and Schott (2000a).

Microtopographic investigations have employed several forms of light- and electron microscopy including phase shift interferometry, scanning electron microscopy (SEM), (high resolution) transmission electron microscopy ((HR)TEM), scanning tunnelling microscopy (STM) and atomic force microscopy (AFM), the last two of which can also be used to examine the atomic structure of the surface. The reader is referred to Hochella (1990) for a discussion of these techniques as applied to mineral surface investigations.

2.5.2 Surface preparation effects

Early laboratory batch experiments investigating silicate dissolution kinetics often led to observations of decreasing solute concentrations with time. Since mass transport in the aqueous solution was expected to be relatively rapid, the parabolic rate laws derived from these observations resulted in several workers concluding that diffusion-controlled phenomena in the outer layer of the solid were limiting the rate of dissolution reactions (e.g. Wollast, 1967; Busenberg and Clemency, 1976; Chou and Wollast, 1984).

In most cases these observations have now been ascribed to experimental artifacts (Petrovic, 1981a, b). Preferential dissolution occurs during the initial stages of the experiments at sites of excess free energy, which are created by the adherence of highly reactive ultrafine particles to mineral surfaces and exposure of a high proportion of reactive surface sites after crushing of minerals. Later the rates decrease as active sites and fine particles are consumed, causing apparent parabolic dissolution kinetics. Secondary mineral precipitation, induced by high solute concentrations in the batch reactions, may also lead to an apparent decrease in the dissolution rate. Ultrafine particles can be removed by suitable pre-treatment such as ultrasonication, sieving and washing in organic solvents.

2.5.3 Initial versus steady state rates: The effect of experiment duration

For reaction kinetics studies in soils, Sparks (1995; p. 163) advocates measuring the initial dissolution rate (i.e. the limit of the rate of reaction as time tends to zero) as a method of ensuring that back reactions are not effective i.e. that true “far-from-equilibrium” conditions exist and that the rate dependence on reaction affinity or Gibbs free energy of reaction (section 2.6.6) is negligible. Most current work on silicate dissolution, however, reports what are considered to be steady state rates, obtained after some period of time, once initial transient effects have passed. Such long-term, steady-state dissolution rates are considered to be of the greatest relevance in most geological environments.

Initial rates measured in batch reactors are usually large and are generally disregarded as they do not reflect the dissolution rate of the bulk mineral (Rimstidt and Dove, 1986). In most cases, where a sufficiently long reaction time has been allowed, initial parabolic increases in concentration in batch reactors have apparently become linear, or output concentrations from flow-through reactors become essentially constant, and this has been assumed to represent steady state conditions.

For slowly dissolving silicate minerals, however, there is some dispute over whether true steady-state conditions can ever be achieved within a reasonable time frame in the laboratory (White and Brantley, 1995). Experimental results often reveal that dissolution rates, which started out high, have progressively slowed throughout the experiment. Long-term dissolution rates of anorthite

at 25°C have been found to be up to 200 times slower than previously reported rates for feldspar dissolution after 4.5 years of reaction (Amrhein and Suarez, 1992). Evidence has even suggested that weathering of some silicate minerals under field conditions may not reach a steady state (Brantley and Chen, 1995; White, 1995). If steady-state is not achieved, then the observed trends indicate that the longer the time of measurement, the slower the rate of weathering will be for any given mineral surface.

2.5.4 Sample agitation effects

Sample agitation was initially thought to have no effect on the rate of surface-controlled reactions. Several studies have shown, however, that silicate dissolution rates are affected by shaking or stirring because of the impact on the reactive mineral surface area, rather than due to improved solute transport.

Agitation of the reaction vessel was found to have a marked effect on anorthite dissolution rate, the rate derived from reciprocating shaker experiments being approximately double that for quiescent systems (Amrhein and Suarez, 1992). Particle abrasion was expected to be responsible. Ganor and Metz (2001) studied the effect on kaolinite dissolution rate of different sample stirring speeds and showed that faster stirring increased the rate. They also interpreted this as a result of the faster dissolution of ultrafine particles of kaolinite, formed by spalling off or abrasion of the mineral. The effect of particle abrasion is well-known in soil adsorption experiments, where agitation can have a significant influence on the experimental results.

Ganor and Metz (2001) have recommended the standard use of non-stirred reaction vessels for kinetic experiments of silicate mineral dissolution that is slow enough to be surface controlled. Their calculations show that diffusion-controlled reactions should not be affected significantly by surface abrasion and should be studied with stirred experiments.

2.5.5 Other experimental effects

Sample composition, sample preparation and the conditions under which dissolution experiments are performed may all affect the measured dissolution rate for a particular mineral and lead to

discrepancies in rate data that are unrelated to the solution composition.

Normalising dissolution rate data to surface area provides a means of comparing dissolution rates from different samples and for extrapolating from laboratory to field conditions, but there are several uncertainties introduced by this practice. Estimates of geometric surface area, based on particle size distribution, are generally different from those of surface area made using adsorption techniques and do not take into account surface roughness or pore spaces. Reactive sites on the mineral surface also occupy only a fraction of the total surface area, and the density of reactive sites is affected by crushing and other means of mineral preparation. The surface area might also change significantly during the dissolution experiment, either by removal of solid material into solution or by mechanical abrasion during stirring or shaking. Brantley and Chen (1995) report different rates for pyroxene dissolution depending on whether rates are normalised by initial or final surface area.

Amrhein and Suarez (1992) investigated the effects of various experimental practices on anorthite dissolution rates. No simple correlation could be found between particle size and surface area and reaction rates, leading the authors to conclude that reactive site density was not directly proportional to surface area. A decrease in reaction rate was noted with increasing suspension density (mineral:water ratio). Wetting and drying cycles during the experiment with drying of the feldspar at different temperatures up to 150°C had no effect on the rate of reaction, suggesting that migration of water into the crystal or sloughing of a surface leached layer, as a result of drying and cracking, are not important rate-controlling factors.

Topotactic alteration and/or incongruent dissolution during the experiment can lead to poisoning of the mineral surface. Surface poisoning changes the structure and composition of the surface over time and can contribute to the apparent slowing of the dissolution rate. Partial surface coatings of polymeric or crystalline secondary weathering products, such as amorphous SiO_2 or $\text{Al}(\text{OH})_3$, can alter the reactive surface area and hence the measured dissolution rate (which is a function of surface area). In such cases the rate measured using solute concentrations near the end of the experiment is no longer the dissolution rate of the original mineral sample.

2.6. Factors controlling the rate of silicate mineral dissolution

2.6.1 The general rate law

There are many factors that govern the rate of mineral dissolution and growth in contact with aqueous solutions. A general form of the overall rate law for heterogeneous mineral surface reactions is given by Lasaga (1995):

$$\text{Rate} = k_0 A_{\min} e^{-E_a/RT} a_{H^+}^{n_H} g(I) \prod_i a_i^{n_i} f(\Delta G_r) \quad \dots\dots\dots (2.16)$$

where:

- ▶ k_0 is an intensive rate constant with units mol/m²/s and incorporates all the pre-exponential factors involving the mineral surface dynamics;
- ▶ $A_{\min}$ is the reactive surface area of the mineral;
- ▶ E_a is the apparent activation energy of the overall reaction, R, the gas constant and T the absolute temperature (The Arrhenius expression is incorporated into the rate law to account for the temperature dependence of the rate of reaction);
- ▶ a_{H^+} is the activity of the hydrogen ion in solution and n_H is an empirical parameter, obtained from the pH dependence of the rate of reaction;
- ▶ $g(I)$ is a term to account for the possible dependence of the rate on the ionic strength of the solution other than the specific effects of individual ions or saturation state;
- ▶ a_i is the activity of other ions of species i in solution and n_i is an empirical parameter, used to account for the possible catalytic or inhibitory effect of each species where $\prod$ indicates that the product of all such terms is taken; and
- ▶ $f(\Delta G_r)$ accounts for the variation of the rate with deviation from equilibrium.

Equation 2.16 is written as a series of products, allowing for an effective separation of the variables controlling the kinetic rate law. The individual terms in the rate law expression account for the various factors which influence the rates of mineral dissolution reactions and will be discussed in the following pages.

An alternative form of equation 2.16 recognises the role of surface reactions in controlling

mineral dissolution and replaces the solute activities (a_{H^+} , a_i) with the mole fractions of adsorbed reactants on the mineral surface, $X_{i,ads}$:

$$Rate = k_0 A_{min} e^{-E_a/RT} X_{H^+,ads}^{n_{H^+,ads}} g(I) \prod_i X_{i,ads}^{n_i} f(\Delta G_r) \dots\dots\dots (2.17)$$

2.6.2 pH

Most silicate mineral dissolution studies have examined the dependence of the dissolution rate on solution pH. Under acid conditions, silicate dissolution rates for most minerals are proportional to a fractional power of the hydrogen ion activity and most researchers fit their dissolution data to an empirical rate law:

$$Rate = k_H (a_{H^+})^n \dots\dots\dots (2.18)$$

where k_H is an empirical constant, a_{H^+} is the hydrogen ion activity in solution and n (or n_{H^+} from equation 2.16), the reaction order with respect to hydrogen ion activity, is derived from the slope of a linear plot of log (rate) versus pH. The value of n is generally, but not always, between 0 and 1 (Lasaga, 1995). Considering the rate as a function of the proportion of H^+ adsorbed at the surface, $X_{H^+,ads}$, rather than a_{H^+} in the bulk solution, should produce an integer value for the exponent if dissolution occurs by only one mechanism (Furrer and Stumm, 1986).

Dissolution rates of the silica polymorphs appear to have a dissolution rate minimum near the zero point of net proton charge for silica of pH 2 (Walther, 1996). Dissolution rates increase in solutions which are more acidic and less acidic than this pH, both at low temperature and at hydrothermal temperatures.

Solution pH also exerts a strong control on feldspar dissolution rates. Albite dissolution rates reach a minimum at pH 6 to 8 with increasing rates in the acid and alkaline regions. This dissolution behaviour is explained by a proton-promoted dissolution mechanism under acid conditions and hydroxyl-promoted mechanism in the alkaline region (Blum and Lasaga, 1991). Some workers have also suggested a third pH-independent mechanism in the neutral pH region

from ~5 to 8 (e.g. Chou and Wollast, 1985; Drever, 1994), although the determination of slow dissolution rates in the neutral pH region is difficult, being complicated by measuring of solute concentrations near analytical limits and very long reaction times to reach steady-state.

Using an extension of the previous law (equation 2.18), the rate dependence on pH over the whole pH range may be expressed as (Stumm and Wollast, 1990):

$$\text{Rate}_{\text{total}} = k_{\text{H}} (a_{\text{H}^+})^n + k_{\text{N}} + k_{\text{OH}} (a_{\text{OH}^-})^m \dots\dots\dots (2.19)$$

where first, second and third terms on the right hand side of equation 2.19 account for the behaviour of the dissolution rate in the acid, neutral and basic pH ranges, respectively. The typical pH-dependence curve for feldspars and phyllosilicates is shown in Figure 2.3, which illustrates the exponential increase in dissolution rate in the low pH and high pH domains.

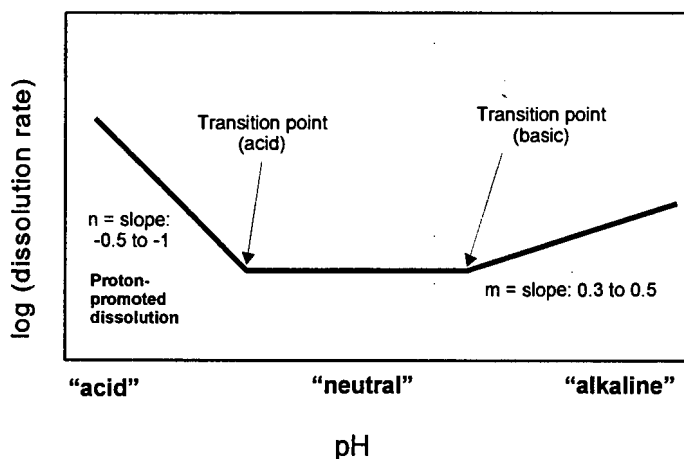


Figure 2.3. Schematic representation of pH control on silicate mineral dissolution rates in systems far from equilibrium (After Drever, 1997; p. 229).

At 25°C, the value of n is ~0.5 for albite, K-feldspar and labradorite, while the pH dependence of the rates is less strong in the alkaline range and $m \approx -0.3$ for albite. Values for n of 1 to 1.5 have been reported for anorthite dissolution in acid (Blum and Stillings, 1995). The dependence of the rate on pH for plagioclase minerals increases with decreasing Al content, corresponding to an increasing Ca content towards the anorthite end-member. The reaction order, n , increases from 0.5 for albite to 0.75 for bytownite (An_{76}) (Oxburgh *et al.*, 1994) and 1.0 for anorthite

(Sverdrup, 1990).

K-feldspar dissolution rate below pH 6 is the same as that of albite and displays the same pH-dependence, but data for the alkaline region are sparse. It appears that K-feldspar dissolution in basic solution may have a stronger dependence on pH and could be slower than albite dissolution in this range by a factor of up to 10 (Blum and Stillings, 1995). The base cations may have a more important influence on dissolution rates at high pH and readsorption of K^+ may stabilise the K-feldspar structure to a greater degree than Na^+ readsorption on albite. In acid solutions, rapid exchange of H_3O^+ for Na^+ or K^+ forms a hydrogen feldspar surface layer which is essentially identical for albite and K-feldspar, hence the similarities in dissolution kinetics. Alkali feldspars, therefore, dissolve via an Al-deficient precursor surface complex (Oelkers *et al.*, 1994).

Dissolution rates of pyroxenes and amphiboles in dilute solutions decrease with increasing pH, but plots of $\log(\text{rate})$ versus pH do not show the “u-shaped” pH dependency curve of the silica minerals and feldspars (Figure 2.3), since dissolution rates continue to decrease above neutral pH. The slope of the curve appears to flatten at higher pH in some cases, indicating a weaker dependence on pH under alkaline conditions. Values of n for the inosilicates generally range from 0.2 to 0.8 with long-term experiments yielding $n = 0.2$ to 0.3 for Fe- and Al-free inosilicates (Brantley and Chen, 1995). Values of n for Fe-free orthosilicates range from 0.3 to 0.54 (Casey and Westrich, 1992). Forsterite dissolution rate has a pH dependence of $n = 0.5$ for $1 < \text{pH} < 9$, but becomes almost pH independent ($n \approx 0.1$) above pH 9.5 (Pokrovsky and Schott, 2000b).

The pH-dependence of sheet silicate dissolution generally shows decreasing dissolution rates with increasing pH in the acidic range, near-constant rates in the neutral range and increasing rates with increasing pH in the alkaline range, similar to feldspars and other aluminosilicates. In the acid region, n varies from near 0 (i.e. almost independent of pH) for some experimental conditions to around 0.5 for kaolinite and chlorite in pure acid solutions at 25°C. Trotignon and Turpault (1992) report a value of 0.9 for the pH dependence of Mg release from biotite. The values of reaction order reported for gibbsite are generally greater, with n reported as 1 or even as high as 1.6 (Nagy, 1995). Values for m in the alkaline region at 25°C range from -0.1 for muscovite, illite and montmorillonite (Nagy, 1995) to -0.2 for chrysotile (Bales and Morgan, 1986) and -0.25 for kaolinite (Carroll and Walther, 1990).

The pH dependence of dissolution rates varies with temperature. Shifts in position of the dissolution minimum (e.g. Hellman, 1994) and steepening of slopes (i.e. increased n and m values e.g. Brady and Walther, 1992) have been noted on the log (rate) versus pH plot at temperatures above 25°C. Brantley and Chen (1995) report a change in n from 0.23 at 25°C to 0.77 at 90°C for diopside and from 0.37 at 25°C to 0.64 at 90°C for anthophyllite.

2.6.3 Ionic strength

Solution ionic strength may affect dissolution rates through charge interactions with the mineral surface. Dove (1994) has shown that increasing ionic strength may accelerate dissolution and precipitation rates for quartz. A measurable effect of ionic strength on forsterite dissolution rate was also noted by Pokrovsky and Schott (2000b), with doubling of the forsterite dissolution rate between pH 3 and 5 when ionic strength was increased from 10^{-3} to 0.1 M.

Some workers have noted very little effect of changing solution ionic strength in dissolution experiments. Bales and Morgan (1985) found no increase in dissolution rate of chrysotile when increasing SO_4^{2-} or NO_3^- in solution from 0.01 to 0.1M at pH 8 to 8.5 and Carroll-Webb and Walther (1988) observed no systematic change in kaolinite dissolution rates when increasing buffer salt concentrations from 0.005M to 0.05M.

Increasing KCl concentrations from 0.1 to 1M doubled montmorillonite dissolution rates at pH 2.5 (Furrer *et al.*, 1993), possibly by modifying the electrical properties of the surface and allowing greater mobility of H^+ ions into the surface. Potassium saturation of the montmorillonite surface could inhibit the adsorption of dissolving Mg^{2+} onto the negatively charged mineral surface. This would then promote a greater Mg^{2+} concentration gradient from the solid into the adjacent solution and enhance Mg^{2+} movement out of the solid.

Based on transition state theory, if the ions in solution are involved in the formation of an activated complex at the mineral surface, the rate of reaction should vary as a function of (ionic strength)^{1/2} (Lasaga, 1995). The effect of ionic strength on dissolution is, however, difficult to separate out experimentally from the catalytic or inhibitory effects of the specific ions in solution and the effect of the solution saturation state. As a consequence, ionic strength effects are poorly

understood in silicate mineral dissolution kinetics.

2.6.4 Inorganic ions

Several di- and trivalent metal cations, including Al^{3+} , Fe^{3+} , Zn^{2+} , Cu^{2+} , Be^{2+} and Ga^{3+} have been observed to inhibit the dissolution kinetics of silica polymorphs (Dove, 1995). Dissolved Al at low concentrations ($<10^{-5}$ M) has been observed to inhibit albite (Chou and Wollast, 1985) and K-feldspar (Gautier *et al.*, 1994) dissolution rates at low pH. Inhibition occurs by specific adsorption to the feldspar surface in dilute solutions far from equilibrium, but there is no evidence for inhibition of anorthite dissolution by this mechanism. Increasing concentrations of Al in solution have also been observed to inhibit phyllosilicate dissolution rates for kaolinite at pH 2 and 7.8 (Oelkers *et al.*, 1994) and montmorillonite at pH 4 (Furrer *et al.*, 1993). For Al, it is often difficult to distinguish direct catalytic or inhibitory effects from the contribution of Al to the solution saturation state, because of the low solubility of many Al-bearing phases (Lasaga, 1995). Evidence for inhibition of feldspar or phyllosilicate dissolution by Si is lacking at this stage.

Alkali cations interact with the surface of silica minerals causing significantly increased dissolution rates of quartz and amorphous silica under ambient conditions. In basic solutions containing alkali cations, rate increases in the order $\text{Li} \approx \text{Cs} < \text{Rb} \approx \text{Na} < \text{K}$ (Dove, 1995). Increasing pH decreases the magnitude of the catalytic effect of alkali cations on silica dissolution, while increased temperature enhances catalysis. At low pH (< 3) in HF solutions at 25°C, kaolinite dissolution is catalysed by the presence of monovalent cations Na^+ , Li^+ and NH_4^+ (Kline and Fogler, 1981a,b).

Sodium in solution has a weak specific inhibitory effect on albite dissolution, except above pH 9, where exchange of Na^+ for H^+ in the surface layer may have some retarding effect. Unlike for silica minerals, alkali and alkaline earth cations have also been observed to inhibit the dissolution kinetics of microcline and sanidine in 10^{-2} M chloride solutions at pH 3 and 25°C. Relative degrees of inhibition increase in the order $\text{NH}_4^+ > \text{Sr}^{2+} > \text{Na}^+ > \text{Li}^+$ (Schweda, 1990, cited in Blum and Stillings, 1995). In basic solutions, the opposite effect is observed and K-feldspar dissolution rates are enhanced by cations in solution.

Solution chemistry, other than pH, appears to have a negligible effect on pyroxene and amphibole dissolution rates (Brantley and Chen, 1995). Magnesium concentration does not appear to affect forsterite dissolution rate, but addition of Si causes a significant decrease in the rate above pH 9 (Pokrovsky and Schott, 2000b).

Carbonate ions in solution inhibit the dissolution of forsterite at high pH, with a linear decrease in log (dissolution rate) with increasing $a_{\text{CO}_3^{2-}}$ at $a_{\text{CO}_3^{2-}} > 10^{-4}$ M (Pokrovsky and Schott, 2000b). Significant inhibition of wollastonite dissolution rates has also been noted by Xie and Walther (1994) at high pH in the presence of CO_2 . The formation of Mg- or Ca carbonate surface complexes has been proposed to explain this effect (Knauss *et al.*, 1993; Xie and Walther, 1994; Pokrovsky and Schott, 2000b). Brantley and Chen (1995) have also suggested that this may affect the pH dependence of inosilicate dissolution rates in the alkaline region, and that an alkaline enhancement of the dissolution rate may be observable in CO_2 -free systems, but experimental evidence for this is still lacking.

2.6.5 Organic ligands

The effects of naturally-occurring organic compounds on silicate dissolution, and particularly the dissolution of feldspars, has been widely studied in the context of soil formation and fertility and the formation of secondary porosity in petroleum oil reservoirs. Organic acids are believed to increase silicate mineral reactivity and dissolution rates through the formation of surface chelates *via* ligand exchange reactions with surface hydroxyls (Furrer and Stumm, 1986). Such chelates weaken the metal-oxygen bonds in the mineral and result in release of the metal to solution. Ligand-promoted surface reactions of this type take place in parallel with proton-promoted dissolution. The attachment of organic ligands to surface metal atoms may also enhance dissolution by blocking reverse reactions (precipitation) at the mineral surface.

Recently, calculations by Oelkers and Schott (1998) have suggested that it is the formation of aqueous Al-organic acid complexes, and the resulting decrease in Al^{3+} activities in solution which increases the dissolution rate, rather than the formation of bidentate organic ligand-Al surface complexes weakening adjoining Al-O bonds as proposed by Furrer and Stumm (1986).

Multifunctional organic ligands, such as citrate and oxalate, are most effective in promoting feldspar dissolution, because of their ability to form strong complexes with polyvalent cations, eg. Al^{3+} and Ca^{2+} (Drever, 1994). The effectiveness of rate enhancement increases following the order acetate < aspartate acid < salicylate < citrate $\approx$ oxalate (Huang and Kiang, 1972; Manley and Evans, 1986).

Organic acid anions such as oxalate, have been found to accelerate feldspar weathering rates by 2 to 10 times over those observed for inorganic solutions at the same pH for a range of feldspar compositions (albite, labradorite, bytownite) (Welch and Ullman, 1992). The relative increase in reaction rate is higher in the neutral pH range than under acid conditions and also higher with increasing Al content in the calcic feldspars. A kinetic description of plagioclase dissolution in organic acids must consider the synergistic effects of proton-promoted reactions at Si sites and ligand-promoted reactions at the Al sites on the mineral surface (Amrhein and Suarez, 1988).

Oxalate anions also increase kaolinite dissolution rates at pH 2 to 6, with rate enhancement increasing with increasing oxalate concentration. Salicylate enhances kaolinite dissolution from pH 4 to 6, but not at pH 2 where protonation of the anion restricts its ability to bind to Al surfaces (Wieland and Stumm, 1992).

Where the dissolving mineral does not contain Al, organic acids may not cause obvious catalytic or inhibitory effects. The rate of Mg release from chrysotile showed no significant increase in the presence of catechol or oxalate (up to 10 mM) after the initial 24 hours of Bales and Morgan's (1985) experiments. Catechol caused a slight increase and oxalate a slight decrease in Si release rate at pH 8.

Blum and Stillings (1995) have compiled an extensive table of feldspar dissolution rates in the presence of a range of organic acid solutions. Bennett and Casey (1994) may also be referred to for detailed discussion of the mechanisms of silicate dissolution in the presence of organic acids.

2.6.6. Saturation state

Most early kinetic experiments were carried out far from equilibrium where the greater speed of the reaction facilitates measurement of the rate. Little or no attempt was made to determine the effects of the solution saturation state on dissolution. This has recently been recognised as a major flaw in the interpretation of mineral dissolution kinetic data (Lasaga, 1995).

Efforts have now been made by various workers to investigate what happens to silicate mineral dissolution rates as the solution approaches chemical equilibrium, particularly for phyllosilicate minerals, where there is a greater possibility of achieving equilibrium than for other silicates. This is generally expressed as the rate dependence on chemical affinity (reaction affinity) or Gibbs free energy of reaction, ΔG_r , both of which are means of expressing the solution saturation state with respect to the dissolving mineral. Cama *et al.* (1999) explore the theory of the “deviation from equilibrium effect” on dissolution rate and activation energies using kaolinite as an example.

The solution saturation state is a function of the concentration of all mineral components in solution. Simultaneously increasing Si and Al concentrations in solution causes decreased kaolinite dissolution rates, for example. This occurs because the rate of the reverse reaction, i.e. reprecipitation of kaolinite, becomes finite with increased saturation state near equilibrium. In general, dissolution rates slow down as equilibrium is approached, although the rate change with chemical affinity varies between different mineral phases and is a function of solute composition.

By definition, $\Delta G_r = 0$ at equilibrium. Consistent with the laws of thermodynamics, the rates of the forward (dissolution) and reverse (precipitation) reactions at equilibrium are equal, giving an overall reaction rate, $\text{rate}_{\text{overall}} = \text{rate}_{\text{fwd}} - \text{rate}_{\text{rev}}$, which approaches zero as the solution saturation state approaches $\Delta G_r = 0$. In equation 2.16 at equilibrium $f(\Delta G_r) = 0$ and, if the principle of detailed balancing applies to the overall reaction, then the derivative of f at equilibrium $f'(0)$ has the same value as equilibrium is approached from undersaturation ($\Delta G_r \leq 0$) or supersaturation ($\Delta G_r \geq 0$) (Lasaga, 1995).

In some cases, $f(\Delta G_r)$, obtained from models involving elementary reactions at specific surface sites, takes the form:

$$f(\Delta G_r) = 1 - e^{-\Delta G_r/RT} \dots\dots\dots (2.20)$$

Cama *et al.* (1994), however, found smectite dissolution to be a linear function of ΔG_r to undersaturations of ~ 92 kJ/mol at 80°C and pH 8.8. Nagy *et al.* (1991) investigated kaolinite dissolution as a function of solution saturation state (Figure 2.4) at pH 3 and 80°C and found that the dissolution rate dependence on ΔG_r could be expressed as:

$$\text{Rate}_{\text{diss}} = k_1 (1 - \exp (\Delta G_r/RT))^n \dots\dots\dots (2.21)$$

with $k_1 = -1.24 \pm 0.120$ and $n = 0.850 \pm 0.217$.

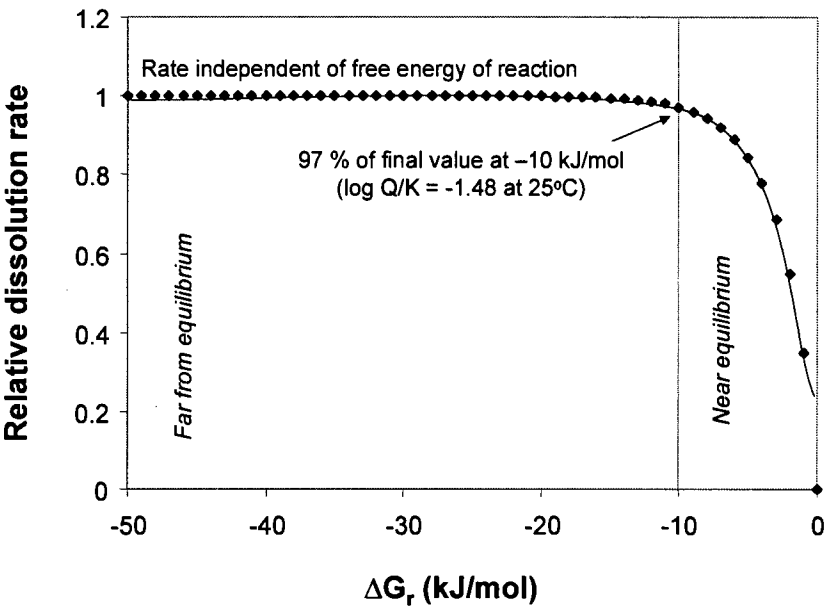


Figure 2.4. Relative dissolution rate of kaolinite as a function of saturation state at pH 3 and 80°C from the model of Nagy *et al.* (1991). The rate is essentially independent of ΔG_r when the departure from equilibrium is greater than about -10 kJ/mol.

The deviation between near-equilibrium and far-from-equilibrium dissolution rates for kaolinite increases as temperature increases, suspension density increases and pH tends to neutral (Cama *et al.*, 1999).

2.6.7 Temperature and apparent activation energies

Data compiled by Tester *et al.* (1994) show that quartz dissolution rate constants in pure water increase linearly with respect to reciprocal temperature from 25 to 300°C, following Arrhenius' law:

$$k_+ = A e^{-E_{app}/RT} \dots\dots\dots (2.22)$$

which is consistent with the laws of statistical mechanics and quantum theory, where k_+ is the forward rate constant, A is the pre-exponential frequency factor, a proportionality constant related to the frequency of effective collisions between reacting species, R is the gas constant, T the absolute temperature and E_{app} the apparent activation energy³ of the overall dissolution reaction. The same rate law (equation 2.22) can be used to describe dissolution rate data for all the silicate minerals described in this review. The exponential nature of equation 2.22 implies a strong dependence of the dissolution rate on temperature. Apparent activation energies are calculated from the slope of a linear plot of data for $\ln(k_+)$ versus $1/T$.

Calculated apparent activation energies for the dissolution of quartz and amorphous silica range from 36 to 96 kJ/mol and increase with increasing pH (Dove, 1995). Typical values for quartz of 60 - 80 kJ/mol are consistent with a reaction mechanism which is limited by rates of bond breaking at the mineral surface rather than diffusion of reactants. Diffusion controlled reactions have $E_{app} < 20$ kJ/mol, while surface controlled reactions are characterised by E_{app} values of around 40 to 80 kJ/mol (Lasaga, 1984).

Apparent activation energies for feldspar dissolution are similar to those for silica, although E_{app} values at neutral pH appear to be lower than those in acid or basic solution. Values for albite range from 59 to 117 kJ/mol in acid solutions, 51 to 69 kJ/mol in neutral solutions and 32 to 85 kJ/mol in basic solutions (Blum and Stillings, 1995). K-feldspar activation energies are similar, being 52 to 78 kJ/mol in acid, 35 to 38 kJ/mol in neutral and 58 to 70 kJ/mol in basic solutions.

³ The activation energy is labelled "apparent" since it describes the overall reaction and not the classical activation energy of an elementary reaction as required by transition state theory (Lasaga, 1995).

Data for the other feldspars in basic solutions are lacking, but apparent activation energies of 80 kJ/mol for oligoclase, 65 kJ/mol for labradorite and 33 to 35 kJ/mol for anorthite in acid solutions have been reported (Blum and Stillings, 1995 and references therein). These values suggest a decrease in activation energy with increasing Al and Ca content in the plagioclase minerals at low pH.

Apparent activation energy data for olivines, pyroxenes and amphiboles have been tabled by Brantley and Chen (1995). Apparent activation energy for forsterite is reported as 80 kJ/mol and for anthophyllite as 77 kJ/mol. The pyroxenes range in apparent activation energy from 44 kJ/mol for bronzite, 42 to 49 kJ/mol for enstatite, 50 to 150 kJ/mol for diopside and 78 to 115 kJ/mol for augite under acid conditions. Examples of data available for other silicates include wollastonite, 79.2 kJ/mol at pH 7 (Rimstidt and Dove, 1986); kyanite, 75 kJ/mol at pH 1.6 to 2.2 (Oelkers and Schott, 1999) and epidote 83 kJ/mol at pH 1.4 (Rose, 1991). These are all consistent with a surface-controlled dissolution mechanism.

Kaolinite activation energies as a function of pH have been calculated by Carroll and Walther (1990). Apparent activation energies decrease from 67 kJ/mol at pH 1 to a minimum of 7 kJ/mol at pH 7 and then increase once more to 41 kJ/mol at pH 12. This behaviour produces a “U-shaped” curve for E_{app} as a function of pH, similar to the Al solubility curve (Figure 2.5b) and aluminosilicate dissolution kinetic curve (Figure 2.3). The pH dependence of the apparent activation energy may arise from an enthalpy contribution of the H^+ ion adsorption reaction to the overall dissolution reaction (Lasaga, 1995). However, Lasaga (1995) and Cama *et al.* (1999) also point out that E_{app} varies as a function of solution saturation state. In the neutral pH range, solution saturation state for minerals such as kaolinite is likely to be closer to equilibrium than in the acid or basic regions, and it could be the saturation state effect, rather than a pH-dependent temperature effect which lowers the apparent activation energy. Far-from-equilibrium experiments on kaolinite did not show significant variations of activation energy with pH (Ganor *et al.*, 1995).

2.7 Dissolution stoichiometry and leached surface layers

Several studies have noted that the initial dissolution of pyroxenes and amphiboles (Brantley and Chen, 1995), sheet silicate minerals (Nagy, 1995) and feldspars (Blum and Stillings, 1995) is non-stoichiometric in acidic to neutral solutions. Where longer term experiments have been conducted, the release of solutes approaches the stoichiometry of the mineral with time in many cases. This implies that the near-surface region of the mineral initially develops a different composition from the bulk mineral during dissolution, which eventually reaches a constant steady-state thickness. The effect is strongly pH-dependent, with high ratios of Ca/Si or Mg/Si release occurring in the initial dissolution stages at low pH.

The development of a “leached-layer”, or build-up of a precipitated layer of secondary minerals (surface poisoning), was originally used to hypothesize that subsequent dissolution must take place by the diffusion of reactants or products through this solid surface layer, and this diffusion-controlled process was the rate-limiting step causing parabolic dissolution kinetics. It is now generally accepted that surface reactions control the overall rate of dissolution of most oxides and silicates (Stumm and Wollast, 1990) and that any leached layers that form during dissolution experiments are usually not thick enough to inhibit dissolution.

Non-stoichiometric release of solutes is a feature of feldspar dissolution in the acid region ($\text{pH} < 5$) and there is considerable evidence for the formation of Al and base cation depleted, Si-rich layers on the feldspar surface, although mineral impurities could also lead to apparent non-stoichiometric dissolution. These leached layers, which can extend up to several thousands of Ångströms thick, have both been postulated from solution chemistry during the initial phases of dissolution and measured directly using surface analytical techniques (e.g. Casey *et al.*, 1988).

The thickness of the leached layer on alkali feldspars increases with decreasing pH, decreasing ionic strength, increasing temperature and increasing anorthite mole fraction (Blum and Stillings, 1995). The Si-rich layer is highly porous and has a structure similar to hydrated silica gel, which allows relatively rapid diffusion of atoms or ions through the layer. The dissolution rate of feldspars in acid solutions is, therefore, not limited by diffusion through the leached layer and the development of such a layer does not indicate a change in kinetics from a surface-controlled to

a diffusion-controlled mechanism of dissolution (Casey *et al.*, 1988; Rose, 1991; Amrhein and Suarez, 1992).

Leached layers in the neutral pH range ($5 < \text{pH} < 8$) are generally less than 20 Å thick for all feldspars, since Si and Al dissolve stoichiometrically in this range. Hellmann (1994) observed a ~500Å thick Si-rich layer on albite at pH 10.8 and 200°C, but no reports of Al-leached layers at ambient temperatures were found for basic pH conditions. Brady and Walther (1989) explain that Si-rich layers should not occur in the alkaline range, since Si detachment controls the overall dissolution rate at high pH.

The pH-dependence of leached layers has been explained by the reactions at the Si and Al sites on the feldspar surface, which are analogous to the reactions of silica and alumina species in solution (Figure 2.5).

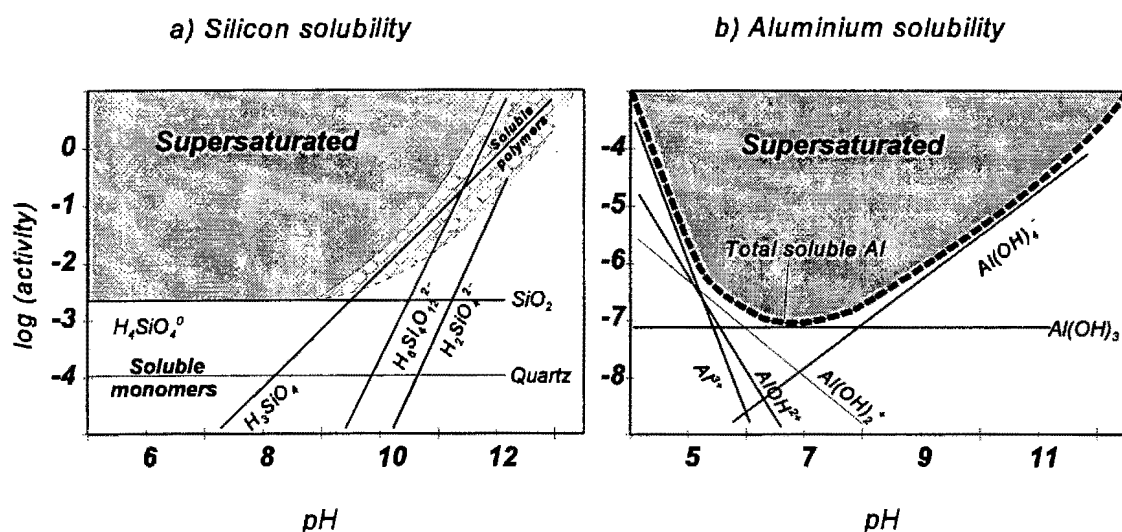


Figure 2.5. a) Solubility of Si as a function of pH, assuming equilibrium with amorphous SiO_2 . The hatched region indicates conditions promoting polymerisation of soluble silica species, while the shaded region denotes supersaturated conditions favourable to precipitation (After Stumm and Morgan, 1996). b) Solubility of Al as a function of pH, assuming equilibrium with gibbsite. The heavy dashed line depicts total soluble aluminium, being the sum of the activities of all dissolved Al species (After McBride, 1994).

At low pH, Al sites are more readily protonated than Si sites, leading to destabilisation of the Al-O bonds and the release of Al from tetrahedral sites in the mineral structure while silica tetrahedra

are left behind. Above pH ~3 to 5, the rate of silica dissolution is faster than the rate of feldspar dissolution and the remaining silica tetrahedra detach into solution so no leached layer can form. Below pH 3 silica dissolution rates are still decreasing, while feldspar dissolution rates increase and the silica fragments which accumulate at the mineral surface polymerise to form a continuous, porous, amorphous silica layer (Blum and Stillings, 1995).

Anorthite and bytownite plagioclase compositions are an exception in that dissolution is close to mineral stoichiometry even at pH < 3 and elevated temperatures. There is also a marked increase in dissolution rate for feldspar compositions near the anorthite end-member in comparison with alkali feldspars and sodic plagioclase. Anorthite has no continuously linked silicate fabric once the Al groups have been removed, since >Si-O-Si< groups are not present in the mineral structure, and isolated Si tetrahedra are released into solution along with Al during dissolution (Casey, 1995).

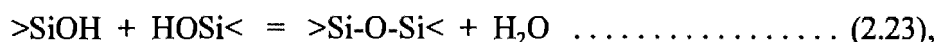
Similar to the feldspars, the initial stages of dissolution of olivines, pyroxenes and amphiboles are non-stoichiometric, with preferential release of the divalent cations, Ca²⁺ and Mg²⁺ or Fe²⁺ (under anoxic conditions) over Si under neutral to acidic pH conditions. Non-stoichiometric dissolution of the pyroxenoid mineral wollastonite was observed in some experiments (eg. Xie and Walther, 1994), but not in others (e.g. Rimstidt and Dove, 1986). Some of the cation sites in pyroxenes (labelled M1 or M2, depending on their position and coordination) and amphiboles (sites M1 to M4) are expected to be more reactive than others, so that Ca in the M2 site is released more rapidly from diopside than Mg in the M1 site. Calcium in the M4 site of tremolite and hornblende is also released preferentially to the cations in the M1, M2 and M3 sites. The initial stage of forsterite dissolution is also non-stoichiometric, with preferential release of Mg below pH 8, but preferential release of Si above pH 10 (Pokrovsky and Schott, 2000b).

Several workers have reported that dissolution eventually becomes stoichiometric as steady state is reached eg. enstatite after 500 hours at pH 7; tremolite, diopside and bronzite (under anoxic conditions) after 100 to 300 hours (Brantley and Chen, 1995); forsterite after about 1 week at pH 3 or pH 11 (Pokrovsky and Schott, 2000b).

Non-stoichiometric dissolution implies that the surfaces of ortho- and inosilicate minerals could

also develop a base cation-deficient leached layer. Mass balance calculations and direct observation of the surface by X-ray photoelectron spectroscopy have generally shown such layers on pyroxenes to be thin (e.g. $< 30\text{\AA}$; Schott and Berner, 1983) and unlikely to inhibit dissolution. Leaching is proposed to occur by exchange of the cations with H^+ , without rearrangement of the silica framework (Schott *et al.*, 1981) such that the surface layers become H enriched. The depth of H-enrichment is greater at low pH. At pH 2, wollastonite becomes enriched in H to several thousand Ångstrom units (Casey *et al.*, 1993).

The olivine structure consists of isolated silica tetrahedra bonded to divalent cations and so, like anorthite, olivine should not be expected to develop leached layers, since there is no bonded silicate network to maintain the integrity of the outer layer once the cations are removed. Pokrovsky and Schott (2000a), however, showed that a silica-rich layer several unit cells thick forms on the surface of forsterite in acidic to weakly alkaline solutions by the exchange of two hydrogen ions for a Mg atom. They proposed that condensation of the isolated silanol groups (after removal of Mg) occurs by reactions such as:



where $>\text{SiOH}$ is a hydroxylated tetrahedral silica group on the mineral surface, followed by protonation of the $>\text{Si-O-Si}<$ bridging oxygen. This allows the protons to penetrate deeper into the surface than would be possible by simple cation exchange.

The stoichiometry of sheet silicate dissolution has been summarised by Nagy (1995) as follows:

- ▶ Non-stoichiometric dissolution inevitably occurs under initial conditions, but dissolution approaches stoichiometry with increasing duration of the experiment. Dissolution approaches congruency more rapidly at higher temperatures or if samples are suitably pretreated, provided undersaturation with respect to Al and Mg phases is maintained.
- ▶ For 2:1 minerals in acid to neutral solutions, the rate of release follows the order:
Mg octahedral sheet (or Fe octahedral sheet, in O_2 -free environments) $>$ Al octahedral sheet $>$ Si tetrahedral sheet.
- ▶ For the 1:1 mineral, kaolinite in acid solution, Si release is faster than Al release.

The precipitation of insoluble secondary minerals such as gibbsite, brucite and iron (hydr)oxides and the nature and functioning of leached surface layers complicates the interpretation of dissolution stoichiometry in some experiments.

2.8 Models of dissolution kinetics

Several approaches have been developed for describing the dissolution kinetics of silicate minerals. These range from fitting observed experimental data to simple empirical rate law expressions, such as the pH dependency in equation 2.19, to complex theoretical atomistic models which require considerable computational power. Current theoretical approaches include *ab initio* methods, which solve quantum mechanical equations for clusters of atoms to study the energetics of reactions and reaction pathways during dissolution, molecular dynamics and Monte Carlo methods, which link atomic dynamics to macroscopic features such as overall rates and mineral surface structures. These computational methods are discussed by Lasaga (1995) with examples of their application to silicate dissolution, but will not be considered further in this review.

A comprehensive model of silicate mineral dissolution needs to be consistent with the observations of all the various factors affecting dissolution rates in section 2.6. Some theoretical approaches are more appropriate than others in accounting for various experimental observations, but there is, as yet, no consensus on the overall mechanism of silicate dissolution and no conceptual or mathematical model which can fully describe the dissolution kinetics.

2.8.1 Leached-layer/diffusion models

Early observations of non-stoichiometric dissolution and decreasing reaction rates with time (parabolic reaction kinetics) led to the proposal of a “leached layer” model where mixed-oxide silicate dissolution kinetics were controlled by solid state diffusion through a protective surface layer. This model is described in several textbooks and early papers on silicate dissolution kinetics but has largely been abandoned in favour of surface-reaction controlled models where the overall dissolution rate is controlled by hydrolysis of framework metal-oxygen bonds at the mineral surface.

2.8.2 Surface complexation models

Surface complexation models (surface speciation models) have been widely popularised in studies of dissolution kinetics and are favoured for their ability to describe the pH dependence of dissolution rates, the pH dependent retarding/catalysing effects of specific ions in solution, and non-stoichiometric dissolution effects. Surface complexation models are based on a molecular scale conceptual framework which attempts to relate observed dissolution rates to the equilibrium concentrations of specific chemical complexes on the mineral surface.

Surface controlled reactions occur in two sequences, each of which may consist of several smaller elementary reactions (Stumm and Wollast, 1990):



where 2.24 is a fast, reversible equilibrium and 2.25 is the slower, irreversible rate-determining step. The overall rate law is dependent on the concentration of the surface species, the reactant in sequence 2.25. If reaction 2.25 is equally probable each time a surface complex is formed, and only at sites where this specific complex occurs, then the rate law is (Wieland *et al.*, 1988):

$$\text{Rate} = k_r [\text{surface complex}] \quad \dots\dots\dots (2.26)$$

where the dissolution rate ($\text{mol/m}^2/\text{s}$) is directly proportional to the number of surface complexes (mol/m^2) and k_r is the rate constant (s^{-1}).

Surface complexation models provide a useful tool for interpreting the reaction controlling steps of mineral dissolution. Solutes in the water (e.g. H^+ , OH^- , ligands or metal ions) interact with the solid surface to form surface species, which influence the tendency of the mineral to dissolve. Surface coordination of OH^- , H^+ and ligands polarise and weaken the metal-oxygen bonds at the surface of the mineral lattice. This can be used to explain why dissolution rates depend on pH (proton-promoted mechanism) and dissolved ligand concentrations (ligand-promoted mechanism) (Stumm and Wollast, 1990). The activity of both catalysts and inhibitors may result from competition for the adsorption sites, which are blocked or enhanced by the adsorbed species.

Surface complexation models have been used successfully to describe the dissolution behaviour of quartz and amorphous silica (e.g. Dove, 1994); feldspars (e.g. Amrhein and Suarez, 1988) and orthosilicates (e.g. Pokrovsky and Schott, 2000a, b) and the dependence of dissolution rates on pH and alkali cation or anionic ligand concentrations. Surface complexation approaches have also been used to model protonation and deprotonation of the hydroxylated groups which control the pH-dependent dissolution of phyllosilicates (Bales and Morgan, 1985; Furrer and Stumm, 1986; Brady and Walther, 1989; Walther, 1996).

2.8.3 Transition state theory

Transition state theory is the most widely applied atomistic approach in dissolution kinetics. Transition state theory models apply a more rigorous and detailed handling of the energetics of the interactions between atoms on the mineral surface and molecules in solution than surface complexation models. One of the difficulties of applying transition state theory to mineral dissolution, is that the theory applies only to elementary reactions involving the exact molecular species participating in the reaction at the atomic level. Experimental work on mineral dissolution generally deals with overall reactions comprising several elementary reactions and the exact nature of the very short-lived reactive intermediate, or activated complex, is usually unknown. The surface complex in surface complexation theory is considered to be a precursor species to the activated complex (Wieland *et al.*, 1988). Transition state theory has been used to postulate the reactants in rate-limiting steps of silicate dissolution reactions using *ab initio* quantum mechanical calculations, but has not yet been used to calculate reaction rates, since the detailed knowledge of the chemical properties of the activated complex has been lacking.

2.8.4 Surface microtopography

A different approach to modelling silicate dissolution is based on larger-scale features such as solution saturation status and surface topography of the mineral, including dislocations, etch pits, impurities and other surface heterogeneities. Such models balance the energy changes in chemical potential during dissolution against the surface free energy of the system arising from changes in mineral surface area (Casey, 1995).

2.9 Natural weathering

2.9.1 *Field observations of weathering rates*

Field methods of measuring dissolution rates involve the definition of a natural drainage system, for example a closed catchment basin or a soil profile, and the estimation or quantification of mineral properties and solute fluxes within the system. Field weathering rates require, among other parameters, estimated values for the relative amounts of weatherable minerals, reactive surface area of the minerals, the stoichiometry of weathering reactions, the volume of rock or soil material that the weathering solutions have been in contact with and the effects of biological influences (e.g. anthropogenic effects, fauna and flora) on the system (Swoboda-Colberg and Drever, 1992; Hochella and Banfield, 1995). The difficulty in quantifying these parameters introduces a large degree of uncertainty in many field predictions of weathering rates. In laboratory studies, such variables can be tightly controlled, but laboratory experimental studies can never be totally relevant to the natural environment.

The aim of measuring mineral dissolution rates in the laboratory is generally to be able to predict reaction kinetics in field situations, for example the effects of weathering rates on neutralisation of acid inputs in a catchment. Predicted weathering rates from laboratory experiments have, however, been found to vary widely from those which have been derived in field studies of soil formation (White, 1995) or catchment solute budgets (Drever and Clow, 1995). The field-measured rates may be up to four orders of magnitude lower than the experimental values (Brantley, 1992). Some of the discrepancy can be attributed to uncertainties in measurements, but there are other factors which cause more systematic variations between field and laboratory methods of measuring mineral dissolution rates. Investigation of these factors is needed, to allow more accurate application of experimental data to real environmental problems.

Often the consideration of isolated chemical parameters in the laboratory provides inaccurate estimates of their relative impact on weathering because it fails to recognise synergistic and antagonistic effects between the various rate-controlling factors. For example, acidification would be expected to accelerate feldspar dissolution rate, but this would also mobilise dissolved Al, which is known to inhibit the dissolution of feldspars and sheet silicates, thereby providing a

buffering mechanism for the reaction rate (White and Brantley, 1995).

Extrapolation of laboratory data to the field relies on the assumption that the rate-limiting step is the same in both environments (Brantley, 1992). This may not always be the case. For most rock forming silicates, reactions at the mineral surface are sufficiently slow that reactant or product transport in the bulk solution does not control the overall dissolution rate in stirred or agitated laboratory reactors. In natural environments, however, overall reaction rates may be controlled by solute transport, particularly in subsurface environments where solute transport distances can be quite large and low permeability may restrict mass transport (Casey, 1995). "Internal weathering surfaces" are defined by Hochella and Banfield (1995) as the very small pore spaces where diffusional processes control the flux of material to and from the mineral interface. In these very small pores the chemical properties and viscosity of water differ from those of the bulk solution, restricting solute transport. Solute concentrations near internal weathering surfaces may accumulate so that primary mineral dissolution or secondary mineral precipitation takes place at near-saturated conditions. The rate-controlling processes at internal weathering surfaces may, therefore, not be the same processes as those which control the rate for laboratory samples.

Brantley (1992) discusses possible causes of the discrepancy between laboratory and field dissolution rates, including experimental error in the laboratory, differences in solution compositions, including background electrolytes and organic acids, the effects of chemical affinity, variations in temperature and difficulties in estimating surface area and total reactive surface or mineral-water contact area in the field. Early experimental data often reported initial rates before solutions reached steady state composition in the experiments, which are much faster than long-term weathering rates. Changing mineral surface areas during dissolution, or by armouring with secondary precipitates and preferential flow paths or stagnant zones in soils and aquifers are common field conditions which are particularly difficult to account for using laboratory data. Even if solution chemistry and temperature effects can be quantified, difficulties in estimating mineral surface areas and time of contact in the field continue to cause errors in field-measured rates.

2.9.2 Biogeochemical weathering of silicate minerals

Biogeochemical weathering of silicate minerals is the topic of a comprehensive review paper by Barker *et al.* (1997).

Bacteria have been found to enhance or inhibit the weathering of silicate minerals by a variety of direct and indirect mechanisms. Microorganisms are ubiquitous in soils and microbial ecosystems, which rely on chemical weathering reactions as their energy source, have even been found in the deep terrestrial subsurface up to several thousand metres below surface (Stevens and McKinley, 1995; Onstott *et al.*, 2000).

Biological processes which affect the chemical weathering of silicate minerals include (Barker *et al.*, 1997):

- ▶ acid production, primarily carbonic acid from CO₂ produced during respiration, but also other inorganic and organic acids, which accelerate weathering rates.
- ▶ organic ligand production, which induce ligand-promoted dissolution at mineral surfaces or a change in the solution saturation state by forming complexes with dissolved ions.
- ▶ complex extracellular polymers, which moderate water potential, act as ligands or chelators, maintain diffusion channels and serve as nucleation sites for secondary mineral precipitation.
- ▶ nutrient (K, Fe and P) absorption, which decreases solution saturation state and enhances weathering.
- ▶ oxidation, especially of Fe and S species, which generate acid and destabilise the structure of minerals containing reduced species.

The most basic mechanism whereby bacteria may affect dissolution is by the production of carbonic acid from respired CO₂, which lowers the solution pH, encouraging proton-promoted dissolution reactions (Barker *et al.*, 1997). At very high total CO₂ concentrations and high ionic strengths, however, silicate dissolution can be inhibited by the formation of carbonate complexes, or precipitates on the mineral surface (Pokrovsky and Schott, 2000b).

Ullman *et al.* (1996) have investigated other mechanisms whereby bacteria and their metabolites enhance or inhibit mineral dissolution with respect to abiotic control samples. One process involves the production of soluble dissolution-enhancing organic ligands such as oxalate, gluconate, lactate and formate. A ligand-promoted dissolution mechanism, active at Al-sites on the mineral surface, can enhance feldspar dissolution to up to 10 times the proton-promoted rate. The degree of enhancement depends on the ligand type, ligand concentration, pH and mineral composition. Soluble organic acids may be produced by the processes of fermentation, catabolism and excretion and are favoured by environments which are rich in metabolizable carbon, but poor in nutrients and depleted in oxygen.

Bacterial metabolism can also produce insoluble polymers that can inhibit dissolution, particularly when they contain acidic side-chain functional groups such as alginate and 26 KD polyaspartate (Ullman *et al.*, 1996). Such ligands adsorb strongly and irreversibly to mineral surfaces, limiting the interaction of the mineral with other reagents in the fluid. Bacteria may also metabolise dissolution-enhancing organic compounds, leading to a net decrease in mineral dissolution rates with changing conditions of decreasing carbon availability.

Another mechanism whereby bacteria may affect dissolution rates is through the interaction of their metabolites with other ions in solution. Dissolution rates may be indirectly enhanced or retarded by changing the activities of species in solution, for example by complexation of dissolved metal cations by organic metabolite ligands (Oelkers and Schott, 1998).

While some bacteria are free-living in natural solutions, most occur attached to mineral surfaces, where they directly affect mineral surface chemistry and mineral-water interactions. *In situ* microcosm experiments in a shallow, oil-contaminated aquifer showed that quartz- and particularly feldspar weathering increased over that of sterile control samples when surface-adhering bacteria colonised the mineral surfaces (Hiebert and Bennett, 1992). This enhancement of dissolution took place even though the groundwater solutions were supersaturated with respect to quartz and close to equilibrium with respect to amorphous silica. The presence of etch-pits on reacted mineral surfaces, especially in the vicinity of attached bacterial cells, led Hiebert and Bennett (1992) to propose that bacteria create a micro-reaction zone at the bacteria-mineral interface. High concentrations of organic acids are generated in this zone during metabolism of

hydrocarbons, causing local enhancement of mineral dissolution rates.

Bennett and Rogers (2000) have noted that silicate weathering can be driven by the nutrient requirements of microbial communities, which can alter accepted weathering patterns in nutrient-limited environments. Biologically-mediated destruction of microcline, in preference to the chemically more unstable olivine, was observed in their experiments on an anaerobic aquifer, lasting 3 to 14 months. The authors' explanation for this was that the microcline contained inclusions of phosphorus-containing apatite, which is of nutrient value to the microbial population and encouraged attack of microcline feldspars in preference to the other silicate minerals.

CHAPTER 3
HYDROCHEMISTRY OF THE KOPOASFONTEIN BRECCIA PIPE,
WITH REFERENCE TO OTHER GROUNDWATERS FROM THE CALVINIA AREA

3.1 Introduction

Understanding water rock interactions in the Kopoasfontein breccia pipe system requires comprehensive characterisation of the aqueous species in the groundwater. This chapter describes the collection and interpretation of water chemistry data from the research site. Water samples were also collected and historical data accumulated for other breccia pipes near Calvinia, as well as alluvial and fractured rock aquifer systems in the area, to place the Kopoasfontein breccia in the context of the overall groundwater environment.

3.2 Groundwater occurrence in the Calvinia area

In the western Karoo, groundwater is primarily exploited from fractured rock aquifers and is commonly abstracted from boreholes that target fractured zones along the contact between sedimentary rocks and sheet-like dolerite intrusions. During a survey of over 300 boreholes around Calvinia, Seward (1983) noted that groundwater was invariably struck in alluvium, weathered shale or shale and that these water strikes were almost always of poor quality and/or low yielding.

The lithological units making up the major aquifer systems in the Calvinia area are illustrated on the geological map in Figure 3.1. The map also shows the location of known breccia pipes and the position of boreholes for which chemical data is available, either from this study or from previous investigations in the area.

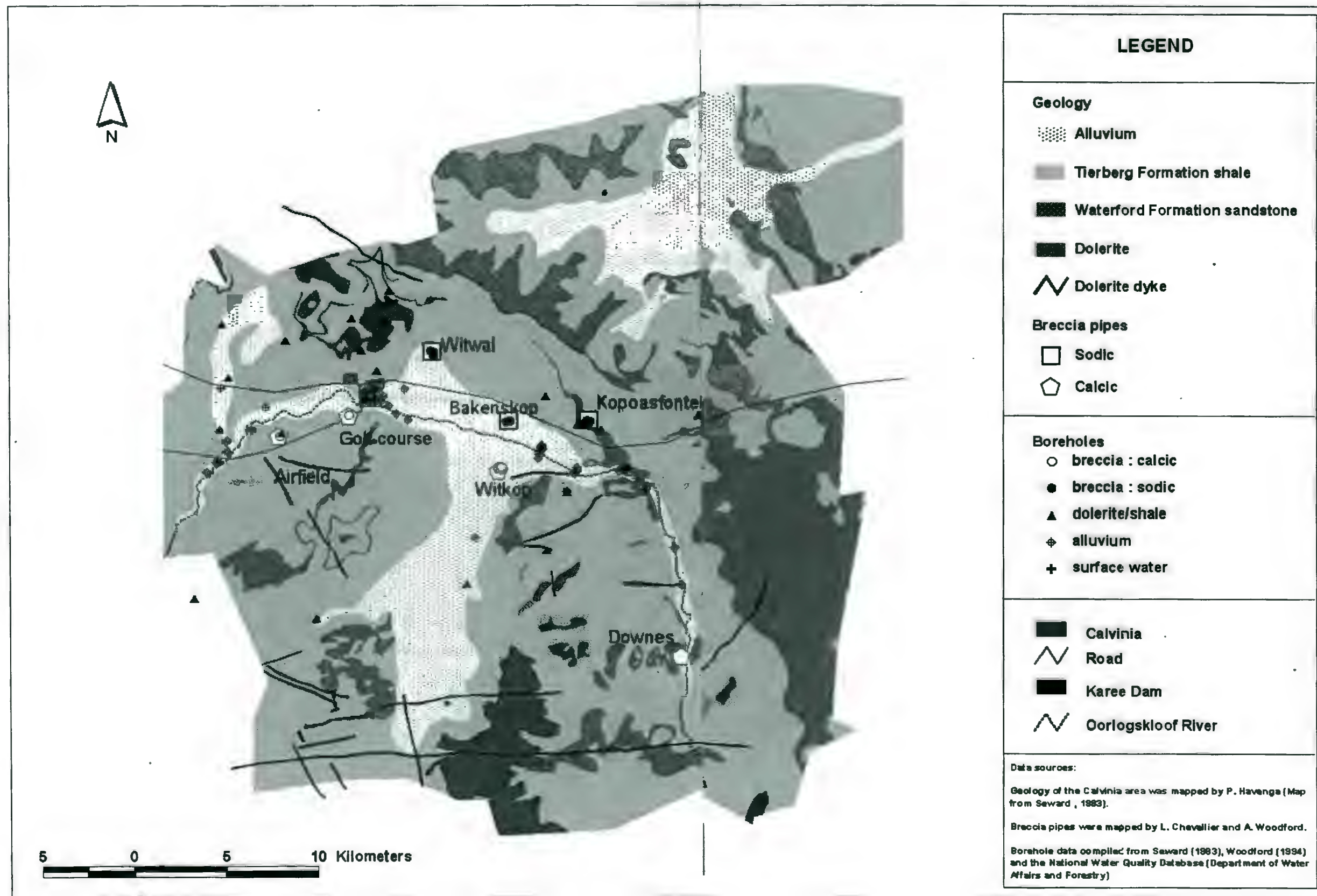


Figure 3.1. Detailed geological map of the Calvinia area showing location of breccia pipes and the position of boreholes used in geochemical characterisation of groundwater.

3.2.1 Primary aquifers

Recent alluvial deposits can sometimes form an important part of the groundwater supply for towns in the main Karoo basin, especially along large drainage systems e.g. the Klein Brak river catchment area near Middelburg. The most productive local aquifers are often found where water-bearing alluvial deposits of appreciable storage overly the fractured and weathered Karoo strata (Kirchner *et al.*, 1991).

Alluvial deposits are widespread along the Oorlogskloof river floodplain around Calvinia, but these are, for the most part, thin and offer limited storage for bulk supply. Several shallow, private boreholes, typically less than 10 m deep, have successfully exploited this primary aquifer for agricultural use and short term yields of up to 50 L/s have been reported (Seward, 1983).

3.2.2 Secondary aquifers

Ecca Group shales

The permeability of unweathered, non-fractured, joint-free Karoo sedimentary rocks is in the order of 10^{-8} m/s or less (Kirchner *et al.*, 1991). With the exception of a few sandstone units, this applies to the whole range of rock types making up the Karoo Supergroup, including tillites, shales, mudstones, siltstones, greywackes, arkoses and sandstones. Fracturing and weathering, which increase porosity and open joints and fractures, are usually responsible for the water-bearing properties of Karoo rocks. Weathering is generally limited to the upper 30 m below surface. Joints, faults or fractures in the hard rock are formed by compressional, tensional or shearing forces during tectonic or magmatic activity, unloading by denudation or weathering.

The slowly permeable, argillaceous shales of the Ecca Group generally offer poor groundwater potential away from dolerite contact zones. In the weathered zone, yields of 0.5 to 1 L/s may be struck and are considered sufficient for windpump supply (Chevallier *et al.*, 2001). Kirchner *et al.* (1991) report a median yield of 0.34 L/s for 40 boreholes drilled in the Tierberg Formation at De Aar, of which 80% yielded less than 1 L/s. The sandstones of the Beaufort Group and the dense, impervious Dwyka tillites are also poor aquifers.

Dolerite dykes and sills

The complex network of dolerite sills and dykes that intruded the Karoo strata are hydrogeologically very important, since the more prolific water-yielding structures are associated with the dolerites. The most favoured groundwater exploration targets in the Karoo are weathered and jointed sedimentary rock alongside dykes, weathered and fractured dolerite dykes and weathered and fractured upper and lower contact zones of dolerite sills (Kirchner, *et al.*, 1991). Recently, the water-bearing potential of dolerite ring structures has also been investigated (Chevallier *et al.*, 2001).

In the Karoo basin, transgressive oblique fractures may extend for up to tens of metres away from dykes into the country rock. Chevallier *et al.* (2001) propose that these are related either to the intrusion of nearby dolerite sheets or to late tectonic stresses during cooling and hydrothermal activity following the magmatic event.

Dolerite dykes represent thin, linear zones of relatively higher permeability than the sedimentary rocks. Together with the associated fracturing in the surrounding country rock, this makes them good conduits for groundwater flow within Karoo aquifers. Dyke contact aquifers are confined and commonly give yields of 2 to 3 L/s. Structural complexity in the dyke sheet, for example offshoots, en-echelon segmentation or changes in dip, may substantially improve groundwater yields (Chevallier *et al.*, 2001).

3.2.3 Groundwater occurrence in breccia pipes

The Karoo breccia pipes constitute highly permeable bodies of uniformly-fractured material of high porosity, extending to a considerable depth. This makes them desirable targets for groundwater exploration. Twenty-six boreholes were drilled into breccia pipes during an exploration programme between 1992 and 1996, of which 70% yielded in excess of 3 L/s and four boreholes produced a final blow yield of more than 10 L/s (Woodford *et al.*, in prep.). The pipes can act as rapid conduits for the extraction of subsurface water, but the sustainable yield of boreholes in breccia pipes is restricted because of their limited size. Water levels drop rapidly during abstraction and recovery is slow, being reliant on the local recharge conditions and the permeability of the host rocks. The potential of breccia pipes as emergency underground storage

reservoirs is an exciting new development, currently under investigation (Murray and Tredoux, 1998a, b; Cavé *et al.*, 2001).

3.3 Groundwater chemistry data collection

3.3.1 Water sample collection and field measurements

The author made three field trips to Calvinia in 1999 and collected groundwater samples from boreholes at the Kopoasfontein research site and surroundings, following the recommended practices of Weaver (1992). During one of the trips, a submersible multiprobe was used to measure vertical profiles of pH, temperature, EC, dissolved oxygen and redox potential down three of the boreholes at the research site. No new boreholes were drilled for this project and all measurements and groundwater samples were collected from pre-existing boreholes. Boreholes sampled near Calvinia during the field work phase of this project, as well as the boreholes sampled by the author for a previous investigation (Cavé, 1999) are shown on Figure 3.2. A more detailed map of the borehole positions at the Kopoasfontein site is shown as Figure 3.3.

In this thesis, borehole names are indicated by the last two digits of the G-number identifiers assigned by DWAF, unless these are the same for two different boreholes, in which case the last three digits are used for older boreholes. Some private boreholes were also sampled and these are either referred to by the identifier used in DWAF reports (e.g. Seward, 1983) or assigned a name using the initials of the farm name.

Construction details and drilling logs that were available for the sampled boreholes are presented in Appendix A. Reports on the three field trips, including pumping conditions, sampling and preservation techniques and the methods used for field measurements are included as Appendix B.

Several boreholes at Kopoasfontein were not accessible for water sampling during the field work phase of this project, although historical data relating to their water composition are available. Boreholes 56 and 74 had been sealed after coring and boreholes 52 and 54B were fitted with pipes for artificial groundwater injection that would not allow access for the sampling equipment.

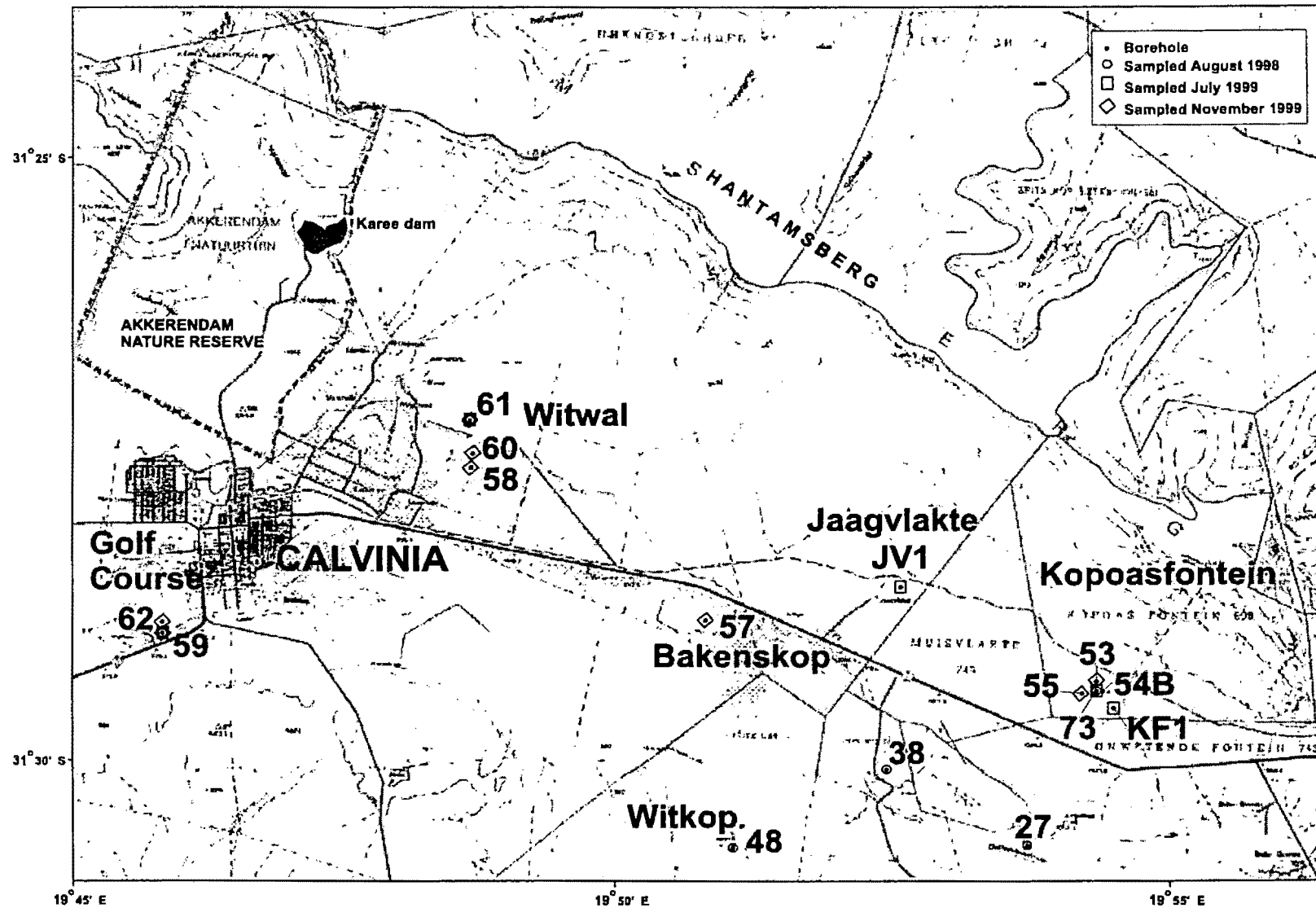


Figure 3.2. Location of boreholes near Calvinia sampled during the field work phase of this project and during a previous investigation (Cavé, 1999).

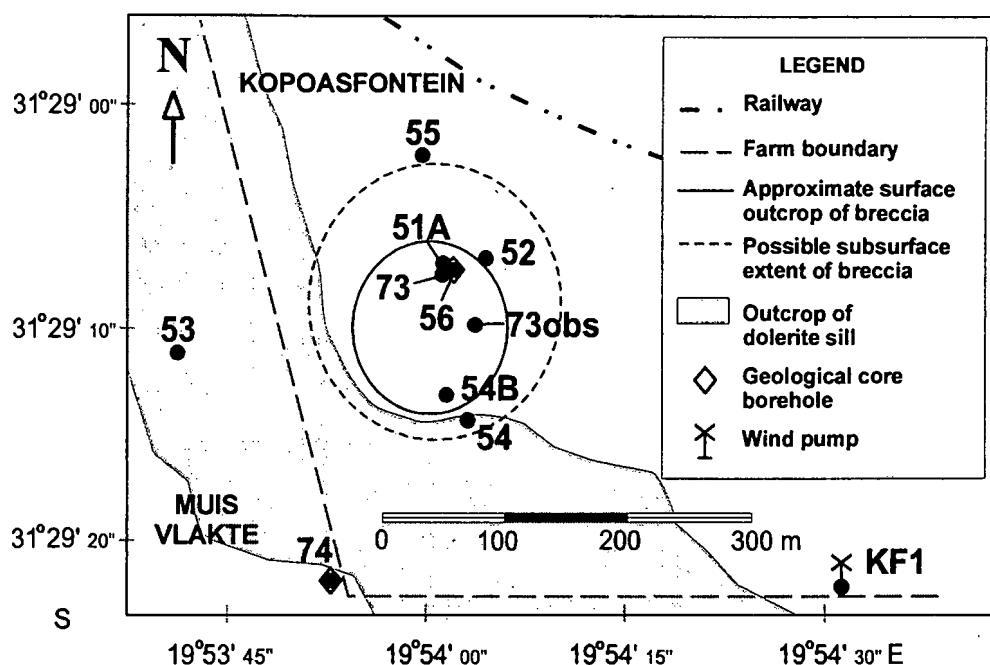


Figure 3.3. Position of boreholes at the Kopoasfontein geohydrological research site.

Additional groundwater samples from borehole 73 were also collected by the CSIR (Murray, pers. comm.) on 26 May 1998, during preliminary artificial recharge investigations, 24 May 1999, at the start of breccia pipe dewatering and 27 September 2000, at the end of the dewatering exercise. Murray has also supplied measurements of pH and EC logged down boreholes 73 and 73obs in February 2000, before injection began and down boreholes 51A and 54B in July 2001, after the pipe was filled with surface water.

3.3.2 Analysis of water samples

All sample preparation and water analyses were conducted by the author using the analytical facilities of the Department of Geological Sciences at the University of Cape Town, with the exception of trace element, dissolved organic carbon and isotope determinations and duplicate Ca and Mg determinations. Three full analyses of samples from borehole 73 were also conducted by the laboratories of the Water Programme at the CSIR. One of these was analysed as a quality control measure to check the analytical results obtained by the author in July 1999. The other two were samples collected by Murray. The CSIR laboratory is accredited by the National Calibration Services and maintains its own system of internal and external quality control measures.

The methods used for analysis of groundwater samples are presented in Table 3.1. Details of the analytical procedures and data reliability have been included as Appendix C.

3.3.3 Other sources of groundwater chemistry data

Additional data on the composition of water samples collected from boreholes in the Calvinia area during hydrocensus, drilling and pumping exercises were found in Van Wyk (1981), Seward (1983), Woodford (1994), Murray and Tredoux (1998b) and DWAF's National Water Quality Database (NWQDB). Boreholes 38, 48, 27, 61 and 73 were sampled by Cavé (1999) as part of the feasibility study for artificial recharge at the Kopoasfontein site. Some trace metal data for groundwater from breccia pipes near Calvinia have also been presented by Hallbauer *et al.* (1995). Isotope analyses for δD , $\delta^{18}O$, $\delta^{13}C$ and ^{14}C were performed during the investigations of the geohydrological potential of Karoo breccia pipes (Woodford *et al.*, in prep.) and these unpublished data were kindly supplied by the analyst, A.S. Talma of the CSIR.

Table 3.1. Analytical methods used for characterisation of groundwater samples from Calvinia.

Constituent	Method	Instrument	Analyst
pH	combination glass electrode	Metrohm 691 pH meter Radiometer TTT85 titrator & electrode	L. Cavé
Electrical conductivity	conductivity cell	Crison Micro CM 2201	L. Cavé
<i>Alkalinity</i>			
phenolphthalein alkalinity	titration to pH 8.3	Radiometer DTS8000	L. Cavé
total alkalinity	titration to pH 4.5	multi-titration system,	
total alkalinity (repeat)	Gran stepwise titration	and ABU autoburette	
<i>Major cations</i>			
Li ⁺ , Na ⁺ , NH ₄ ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺	ion chromatography	Dionex CS12A column	L. Cavé
Mg ²⁺ , Ca ²⁺ (repeat)	ICP-AES	unknown	Chem. Eng., UCT
<i>Major anions</i>			
F ⁻ , Cl ⁻ , Br ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻	ion chromatography	Dionex AS14 column	L. Cavé
F ⁻ (repeat)	ion selective electrode	Corning 225 ion analyser and F electrode	L. Cavé
PO ₄ ³⁻ (repeat)	phosphomolybdate colorimetry	Sequoia-Turner 340 spectrophotometer	L. Cavé
S ²⁻	iodometric titration	manual titration	L. Cavé
SiO ₂	molybdosilicate colorimetry	Sequoia-Turner 340 spectrophotometer	L. Cavé
Total Fe	phenanthroline colorimetry	Sequoia-Turner 340 spectrophotometer	L. Cavé
<i>Trace elements</i>			
Li, Sr, Ba, B, Al, Cr, Mn, Fe Co, Ni, Cu, Zn, As, Se, Rb, Mo, Cd, Cs, Tl, Pb, U	ICP-MS	Perkin-Elmer ELAN 6000 ICP-MS	A. Späth, Geology, UCT
DOC	persulphate ultraviolet oxidation	autoanalyser	M. Louw, CSIR
<i>Stable isotopes</i>			
δ ¹⁸ O	mass spectrometry CO ₂ equilibration	Finnegan MAT252 dual-inlet gas source	F. Rawoot, Geology, UCT
δD	Zn reduction	mass spectrometer	

3.4 Chemical characterisation of groundwater at Kopoasfontein

3.4.1 Field parameters

Temperature and gas partial pressures are controlling variables in chemical equilibria that may be disturbed by the removal of a sample from the subsurface environment. Atmospheric oxygen may oxidise reduced components in anoxic groundwater, while degassing of CO₂ may cause changes in pH, alkalinity and total inorganic carbon (Appelo and Postma, 1996; p. 14). Field measurements are made at the wellhead in an attempt to quantify certain chemical parameters before such changes occur. Submersible probes lowered down a borehole allow for an even closer approximation of the chemical conditions that drive water-rock equilibria in the aquifer than measurements taken at the wellhead or in the laboratory (Tredoux *et al.*, 2000). Physical and chemical parameters measured at the wellhead for boreholes at the Kopoasfontein research site are reported in Table 3.2.

Table 3.2. Physical and chemical parameters measured at the wellhead at the Kopoasfontein research site.

Borehole	Inside breccia pipe				Outside breccia pipe		
	73	73	54	52	55	53	KF1
Date measured (mm/yy)	07/99	08/98	12/97	12/97	11/99	11/99	07/99
Abstraction method	pump	pump	pump	pump	bailer	bailer	wind pump
Water level (mbgl)	60	13	n.d.	n.d.	61	32	n.d.
Abstraction depth (m)	127	127	96	107	61	32	n.d.
Temperature (°C)	24.9	19.5	25	23	23	22.5	20
pH	9.83	8.7	10.0	8.54	10.0	7.82	7.26
EC (mS/m)	88.6	73	72	93	n.d.	n.d.	117
Alkalinity (mg HCO ₃ /L)	184	n.d.	n.d.	n.d.	n.d.	n.d.	352
Dissolved oxygen (mg/L)	n.d.	0.2	n.d.	n.d.	n.d.	n.d.	n.d.
Odour	H ₂ S	H ₂ S	H ₂ S	H ₂ S	None	None	None
Data source	This study	Cavé, 1999	A. Hön, CSIR	A. Hön, CSIR	This study	This study	This study

Groundwater inside the breccia pipe typically has higher temperature and pH and lower EC and alkalinity than that measured outside. Pumping tests have shown good hydraulic connectivity

between boreholes 73 and 54 inside the pipe, and 52 on the edge of the pipe, which intercepts brecciated material from a depth of 60 m downwards (Murray and Tredoux, 1998b).

3.4.2 Vertical profiles

The difference in physical and chemical properties of groundwater inside and outside of the breccia is also evident from vertical logging of field parameters down the boreholes. Figure 3.4 illustrates how pH, EC, dissolved oxygen, pe and temperature vary with depth in uncased boreholes 53, 54B and 55. The measurements were taken during dewatering of the Kopoasfontein breccia pipe in August 1999. Borehole 54B is located in the breccia pipe, while the other two are outside, 55 in the Tierberg shales and 53 through a dolerite sheet, approximately 100 m and 300 m away from the pumping borehole, 73, respectively (See Figure 3.3).

Temperature

Typical heat flow in continental crust is in the order of 40 to 70 mW/m², which produces temperature gradients that increase with depth at a rate of 20 to 35°C/km, assuming a typical thermal conductivity of 2 W/(m.K). Stable cratons will produce geothermal gradients towards the lower edge of this range, while higher heat flow is found in tectonically active areas (Ingebritsen and Sanford, 1998; p. 178-180). The temperature gradients for boreholes 53 (26°C/km) and 55 (32°C/km) fall within the typical range.

Perturbations of the natural thermal gradient are usually related to groundwater flow (Ingebritsen and Sanford, 1998; p.180) and areas of high recharge may be characterised by isothermal or even negative temperature gradient profiles to substantial depths. The near-vertical temperature profile for borehole 54B is related to the high permeability of the brecciated rock material and suggests that mixing by advection, rather than thermal conduction is controlling the temperature of groundwater inside the pipe. This could be strongly influenced by the pumping at nearby 73. The higher temperature in the breccia pipe groundwater, compared with the near surface temperatures in the other boreholes, is in agreement with the values measured at the wellhead (Table 3.2).

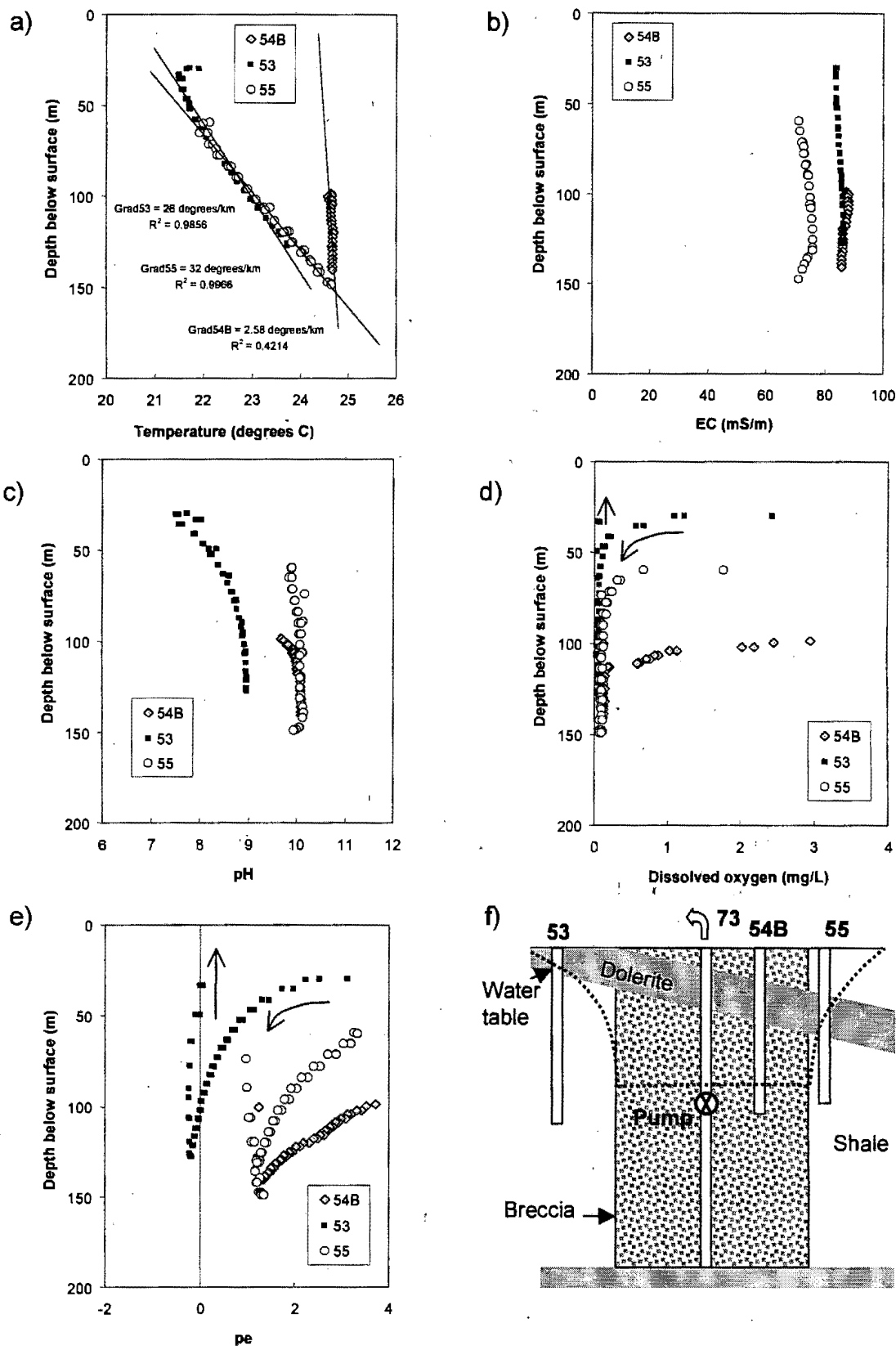


Figure 3.4. Profiles of a) temperature, b) EC, c) pH, d) dissolved oxygen and e) pe with depth in boreholes 53, 54B and 55 during dewatering of the Kopoasfontein breccia pipe in August 1999. A schematic diagram of the water level conditions during logging is given in f) (Diagram not to scale). Bifurcation of DO and pe data series reflects a change in the readings when lowering the probe from those taken when raising it again.

Woodford (pers. comm.) has argued that the elevated temperature of the breccia pipe groundwater is a feature of a deep groundwater flow system which feeds the pipe. From the intersection of the temperature gradient outside the breccia (55) with that of the breccia pipe (54B), it could be argued that the warmer groundwater in the pipe originates at a depth of about 150 m below surface, provided that there is minimal mixing of cooler water recharged from the surface and minimal cooling of the ascending water in the pipe. Major water strikes yielding between 70 and 80 L/s were encountered near this depth at 86 - 133, 140 and 161 m below surface in the breccia pipe when drilling borehole 73.

Electrical conductivity

Observations of electrical conductivity during drilling and test pumping revealed that salinity in the Kopoasfontein groundwater decreases with increasing depth and pumping duration (Woodford, 1994; Murray and Tredoux, 1998b). Figure 3.4 b) shows that electrical conductivity is slightly lower in groundwater from the shale borehole 55, outside the breccia pipe, than inside the breccia or in the dolerite borehole 53. The addition of solutes to the groundwater by water-rock interactions with the breccia minerals may cause the slight rise in EC.

Electrical conductivity is relatively constant with depth in these profiles. Electrical conductivity in the breccia pipe (54B) decreases slightly with depth, but changes are small over the short water column logged here. Marginal increases in EC with depth were noted in 55 and 53 which reach a maximum near 125 m below surface. Detailed geological logs are not available for 55 or 53 that might explain why this occurs. The major water strikes, where a change in electrical conductivity could be expected, are at 60 m (55) and 80 m (53) below surface. Abstraction from borehole 73 may have caused mixing in the groundwater and eliminated some of the stratification that might otherwise have been observed.

pH

pH values show a close similarity between 54B and 55, both of which tend towards pH 10 near the bottom of the borehole. The pH of groundwater in 53 increases from pH 7.7 near the water table to pH 9 at depth, and is thought to show mixing between a shallow component, influenced by the dolerite sill, and high pH deeper groundwater. The grouping of 54B and 55 is different from that of the EC logs, where 54B and 53 have similar values. pH in all three boreholes is

lowest near the water table, which could be a result of equilibration with atmospheric CO₂.

Dissolved oxygen and redox status

Dissolved oxygen profiles show that free oxygen is present in the upper few metres of the water column in each borehole, but subsurface conditions are generally anoxic (Figure 3.4 d). The pe profile diagram (Figure 3.4 e) supports the conclusion that conditions are reducing at depth and shows that groundwater in the dolerite (53) has a more negative redox potential than that in the breccia pipe (54B). Two explanations for this are that lower permeability outside the pipe may restrict the access of oxidising gases such as O₂ and that reducing organic matter is less abundant in the breccia, where it has been lost or transformed to less reactive forms of carbon by thermal alteration.

Figure 3.4 also demonstrates how sluggish response of the electrodes can affect the reliability of redox potential measurements. Measurements made while raising the multiprobe are more negative than those recorded earlier at the same depth values while lowering the probe. This causes bifurcation of the data series in Figure 3.4 d) and e) and complicates the characterisation of the redox status in the breccia pipe.

Water levels

Measurement of groundwater levels during dewatering confirmed that a poor hydraulic connection exists between boreholes inside the pipe and those outside the pipe. Borehole 55 shows a gradual response to pumping at 73, while the drawdown at 53 is minimal, even during heavy abstraction at 73 (See schematic diagram in Figure 3.4 f).

Influence of surface water injection

The Kopoasfontein breccia pipe was dewatered to a depth of about 120 m during 1999 and 2000. Surplus surface water from the Karee dam was then injected via borehole 52 in mid-2001, after an exceptionally good rainfall season. Vertical logging of boreholes inside the breccia was used to monitor the impact of the artificial recharge. Figure 3.5 compares the EC and pH results before and after injection. These measurements were logged under static (non-pumping) conditions. Borehole 51A has been substituted for 73 in the post-injection run, because there was no access for the multiprobe. Boreholes 51 (redrilled as 51A) and 73, about 5 m away, yielded

groundwaters of similar chemistry before injection (See Appendix D).

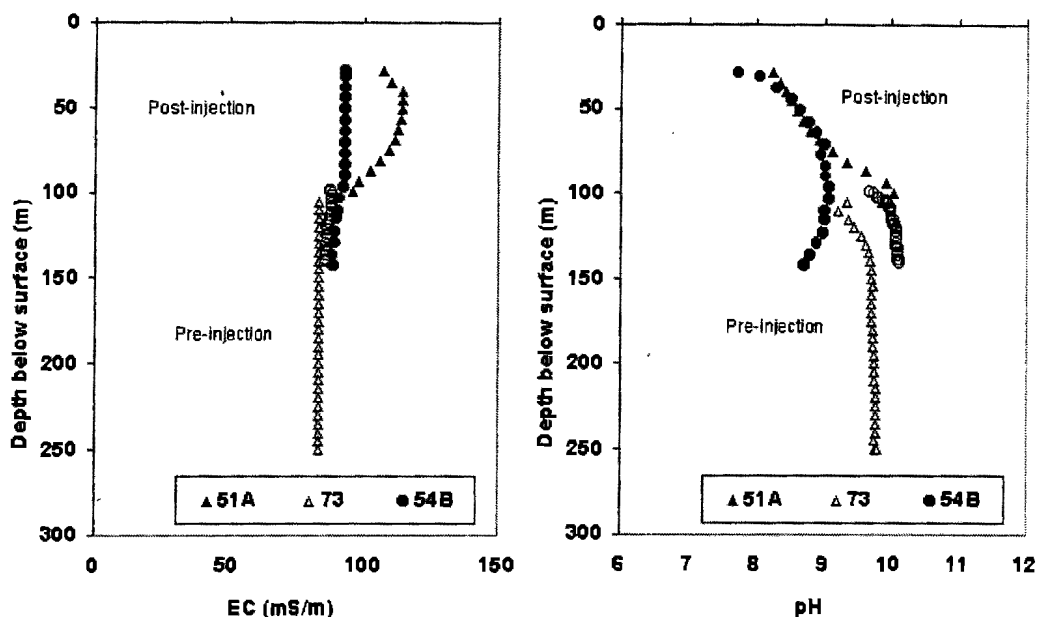


Figure 3.5. Influence of surface water injection on EC and pH in the Kopoasfontein breccia pipe. Open symbols (73 and 54B) indicate conditions after dewatering (pre-injection) and closed symbols (51A and 54B) denote post-injection conditions.

The salinity of the groundwater has increased after injection from natural EC values of 80 to 90 mS/m to over 100 mS/m in the upper portion of the pipe (51A). The increased salinity appears to be less pronounced towards the edges of the pipe (54B). Although the rise in EC represents a slight deterioration in water quality, the water is still acceptable for domestic use (DWAf, 1996).

The recharge water is of low EC (~ 20 mS/m) and so the additional salinity is not brought in by injection. Instead, the rising water table may dissolve mineral salts that have previously been precipitated in the fractures of the breccia near the surface. Secondary calcite is particularly prevalent in the upper 40 m of the pipe. Mineral salts such as halite and gypsum may also precipitate in the capillary fringe above a fluctuating water table. Natural salinity, caused by evaporative concentration, is common in the soils and regolith of semi-arid and arid climate zones and may be flushed downward during injection. A better understanding of the salinity source is not possible at this stage without analysis of the chemistry of the recovered water to establish which ions are responsible for the effect.

Injection of surface water has decreased the groundwater pH from its natural value of approximately pH 10 to near pH 8 in the upper portion of the pipe. The injection water is near pH 7, but mixing with the alkaline breccia water and strong pH buffering reactions cause a steep increase in pH with depth, particularly below 70 m from the surface.

The shift to lower pH represents an improvement in the groundwater quality, since problems such as high F^- concentrations are partly attributable to the high groundwater pH. The pH may continue to rise slowly with time as chemical equilibria disturbed by the injection are re-established.

Summary

Groundwater in the Kopoasfontein breccia pipe is a moderately warm, low salinity, alkaline, mildly reducing solution. The water composition appears to be relatively homogeneous with depth, although only a small portion of the water column was available for logging and pumping of a nearby borehole may have perturbed any stratification of the groundwater. Atmospheric O_2 and CO_2 affect the pH and redox potential near the water table. Conditions at the edges of the breccia show greater variation with depth and are generally slightly cooler, lower in salinity and pH and more reducing than the breccia pipe water.

3.4.3 Major and minor aqueous constituents

Recent data for major cations and anions and minor species in the Kopoasfontein groundwater are summarised in Table 3.3 and 3.4. Unpublished data from the NWQDB and CSIR laboratories are included in the tables. The quality of some of the major ion analyses from other sources appears to be poor, particularly for three older samples (73: 18/10/94, 52: 10/06/92 and 54: 09/12/97), since the calculated charge balance is greater than 10%. An excess anionic charge was calculated for most samples and may be related to overestimation of CO_3^{2-} charge, calculated from alkalinity titrations for these high pH waters.

Major ion chemistry in the breccia pipe changed little during dewatering from May 1999 to September 2000. Although the water table dropped from 15 m below surface to a depth of 120 m, the position of the submersible pump and hence the depth of abstraction remained at 127 m.

Table 3.3. Major and minor species in groundwater from borehole 73 at the Kopoasfontein research site. Data in mg/L unless otherwise indicated.

Date (dd/mm/yy)	27/09/00	18/08/99	07/07/99	24/05/99	19/08/98	26/05/98	18/10/94	10/10/94	28/03/94	15/03/94
Sample depth (m)	127	127	127	127	127	127	160	160	360	26
Water level (mbgl)	120	94.7	33.5	15.0	13.2	n.r.	126.3	66.2	16.1	26
Sample method	pump	pump	pump	pump	pump	pump	pump	pump	air ¹	air
pH (lab, pH units)	9.7	9.59	9.73	9.50	9.8	n.r.	10.0	9.8	8.3	8.2
EC (mS/m at 20°C)	84	81.9	87.6	80.7	71	n.r.	70	73.1	65	95
Na	179	104	157	96	170	159	139	145	144	153
K	0.6	0.6	0.7	0.7	1.7	0.5	<0.3	1.1	2.2	13.3
Mg	0.1	rej ²	1.2	rej.	2.6	0.2	<1	<1	<1	3
Ca	1.6	rej.	3.5	rej.	5.3	1.2	<1	2	2	50
Li	0.29	0.16	0.25	0.16	0.27	0.25	n.r.	n.r.	n.r.	n.r.
NH ₄ as N	1.1	<1	1.3	<1	1.0	1.4	1.62	1.24	1.31	0.88
Cl	100	94	99	99	120	93	85	94	93	93
SO ₄	84	70	64	59	54	40	22	27	20	35
HCO ₃ [#]	147	n.d.	148	n.d.	148	138	138	136	197	340
CO ₃ [#]	30	n.d.	33	n.d.	38	45	56	35	1.6	2.2
F	10.1	9.8	10.6	10	12	11.5	15.8	12.5	15.4	12.8
NO ₂ +NO ₃ as N	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.05	<0.1
Sum cations (m _{eq} /L)	8.01	i.d.	7.28	i.d.	8.05	7.14	6.23	6.57	6.55	9.80
Sum anions (m _{eq} /L)	8.51	i.d.	8.21	i.d.	8.83	7.83	7.81	7.27	7.13	9.72
Cation excess (%)	-3.0	i.d.	-6.0	i.d.	-4.6	-4.5	-11	-5.1	-4.3	0.4
Si	12.1	13.0	13.8	13.7	8.6	12.6	18.0	14.8	16.7	12.8
Total Fe	0.29	n.d.	0.08	n.d.	0.36	0.14	n.r.	n.r.	n.r.	n.r.
Sr	0.09	n.d.	0.11	n.d.	0.19	0.07	n.r.	n.r.	n.r.	n.r.
Ba	n.d.	n.d.	0.01	n.d.	0.02	n.r.	n.r.	n.r.	n.r.	n.r.
B	0.69	n.d.	0.51	n.d.	n.r.	0.8	n.r.	n.r.	n.r.	n.r.
DOC	0.15	n.d.	2.6	n.d.	1	<1	n.r.	n.r.	n.r.	n.r.
Data Source	CSIR	This study	This study	This study	Cavé, 1999	CSIR	NWQDB	NWQDB	NWQDB	NWQDB

¹air = air displacement; ²rej = data rejected due to poor accuracy of IC method; [#] Total alkalinity recalculated as HCO₃⁻ and CO₃²⁻ for high pH samples using HCO₃⁻ = CO₃²⁻ + H⁺, log K = -10.38 at 20°C. See list of abbreviations for others.

Table 3.4. Major and minor species in groundwater from boreholes at the Kopoasfontein research site. Data in mg/L unless otherwise indicated.

Borehole	51	51	51	51	52	52	52	53	53
Date sampled	12/08/92	04/06/92	03/06/92	26/05/92	10/12/97	10/06/92	06/06/92	19/11/99	11/06/92
Sample depth (mbgl)	109	112	84	18	107	150	64	32	84
Sample method	n.r.	air	air	air	pump	air	air	bailer	air
pH (lab, pH units)	9.9	9.7	9.6	7.9	8.9	10.1	8.8	7.91	8.6
EC (mS/m at 20°C)	69.4	63.6	63.9	128.7	105	64.9	67.4	86.3	67.6
Na	149	134	138	140	205	136	142	197	140
K	3.4	1.4	1.5	10.5	1.2	0.6	1.0	0.75	3.8
Mg	2	<1	2	48	3.2	<1	2	0.28	<1
Ca	<1	<1	2	76	10.1	<1	4	0.3	2
Li	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	0.37	n.r.
NH ₄ as N	1.34	1.08	0.99	0.04	0.5	1.53	1.34	<1	1.02
Cl	100	83	80	244	97	82	92	82	78
SO ₄	31	11	19	107	166	13	25	17	21
HCO ₃ [#]	146	153	161	281	181	123	183	316	200
CO ₃ [#]	47	32	26	0.9	2.3	63	4.7	1.1	3.3
F	13.5	15.0	13.8	0.59	8.9	15.6	13.3	6.3	15.7
NO ₂ +NO ₃ as N	<0.1	<0.1	0.11	4.92	<0.1	<0.1	<0.1	<0.1	<0.1
PO ₄ as P	0.07	0.02	0.04	<0.01	<0.01	0.02	0.03	<0.1	0.02
Br	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	0.52	n.r.
Sum cations	6.85	6.01	6.38	14.1	9.75	6.11	6.66	8.68	6.40
Sum anions	7.83	6.94	6.89	14.1	9.70	7.52	6.97	8.21	6.85
Cation excess	-6.7	-7.2	-3.9	0.0	0.2	-10	-2.3	2.8	-3.4
Si	15.9	20.6	20.6	10.8	8.83	20.6	17.4	8.7	5.7
Total Fe	n.r.	n.r.	n.r.	n.r.	0.07	n.r.	n.r.	0.69	n.r.
Sr	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	0.18	n.r.
Ba	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	0.09	n.r.
B	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	0.72	n.r.
DOC	n.r.	n.r.	n.r.	n.r.	<1	n.r.	n.r.	9.8	n.r.
Data Source	NWQDB	NWQDB	NWQDB	NWQDB	CSIR	NWQDB	NWQDB	This study	NWQDB

Table 3.4 (continued). Major and minor species in groundwater from boreholes at the Kopoasfontein research site. Data in mg/L unless otherwise indicated.

Borehole	54	54	55	55	KF1
Date sampled	09/12/97	20/07/92	19/11/99	21/07/92	08/07/99
Sample depth (m)	96	135	61	60	n.d.
Sample method	pump	air?	bailer	air?	wind pump
pH (lab)(pH units)	10	9.7	9.77	9.4	7.32
EC (mS/m at 20°C)	78	66.3	67.4	61.7	120
Na	160	141	135	127	94
K	0.6	2.9	0.56	2.5	1.2
Mg	0.1	1	0.48	<1	47
Ca	1.5	1	0.3	1	90
Li	n.r.	n.r.	0.25	n.r.	0.02
NH ₄ as N	1.4	1.8	1.0	0.10	<1
Cl	93	80	67	70	175
SO ₄	45	15	36	29	78
HCO ₃ [#]	165	159	123	147	319
CO ₃ [#]	68	33	30	15	0.3
F	12	15.5	8.4	14.1	1.4
NO ₂ +NO ₃ as N	<0.1	<0.1	<0.1	1.3	9.4
PO ₄ as P	<0.1	0.03	<0.1	<0.1	<0.1
Br	n.r.	n.r.	0.45	n.r.	<0.1
Sum cations	7.18	6.47	6.07	5.69	12.5
Sum anions	9.16	7.09	6.10	6.33	12.5
Cation excess	-12	-4.6	-0.2	-5.3	-0.2
Si	17.2	19.0	11.1	8.9	12.7
Total Fe	0.22	n.r.	0.48	n.r.	0.41
Sr	n.r.	n.r.	0.05	n.r.	0.68
Ba	n.r.	n.r.	0.04	n.r.	0.07
B	n.r.	n.r.	0.94	n.r.	0.13
DOC	<1	n.r.	n.d.	n.r.	2.2
Data Source	CSIR	NWQDB	This study	NWQDB	This study

The final sample in Table 3.3 represents a water strike (blow yield = 5.1 L/s) intercepted at 26 m below surface during drilling of borehole 73 (as reported by Woodford, 1994). This occurs at the contact between the breccia pipe and a cross-cutting dolerite sill. This water is of a different chemical character from the other samples from borehole 73, having a lower pH and higher EC, Ca, K and alkalinity, and is thought to represent a perched groundwater body above the impervious dolerite. The sample from borehole 51 at 18 m (26/05/97) is also from the shallow groundwater above the dolerite. Further evidence for perched water comes from the observations of the drillers when constructing a new borehole (73obs) in November 1999. Drilling into the Kopoasfontein breccia, groundwater of near-neutral pH was intercepted at a depth of 18 m below surface. The groundwater level in the breccia pipe was then about 100 m below surface because of the dewatering in progress (Murray, CSIR, pers. comm.).

Later samples collected from borehole 73 contain groundwater from the main breccia pipe body, with probably only a minor contribution of perched water. The sample collected on completion of borehole 73 to its final depth of 360 m, shows an increase in F, Si and alkalinity with depth, but decreased EC compared to the samples pumped from higher in the pipe.

Figure 3.6 summarises the EC and pH data, while Figure 3.7 uses a trilinear diagram (Piper, 1953) to compare the relative major cation and anion compositions for the groundwaters in Tables 3.3 and 3.4.

Most of the samples are Na-HCO₃ or Na-HCO₃/Cl dominant. KF1 and the perched sample from 51 are exceptions, having a Na/Ca/Mg-HCO₃/Cl major ion composition, typical of young groundwaters at equilibrium with carbonate minerals. Samples from deeper in the breccia pipe are clustered along the lower right hand edge of the diamond-shaped field in the diagram, except for the perched water sample from 73 (15/03/94). This sample is relatively enriched in Ca and HCO₃ compared with the other points for this deep borehole and appears to contain a mixture of groundwater from above and below the dolerite sill.

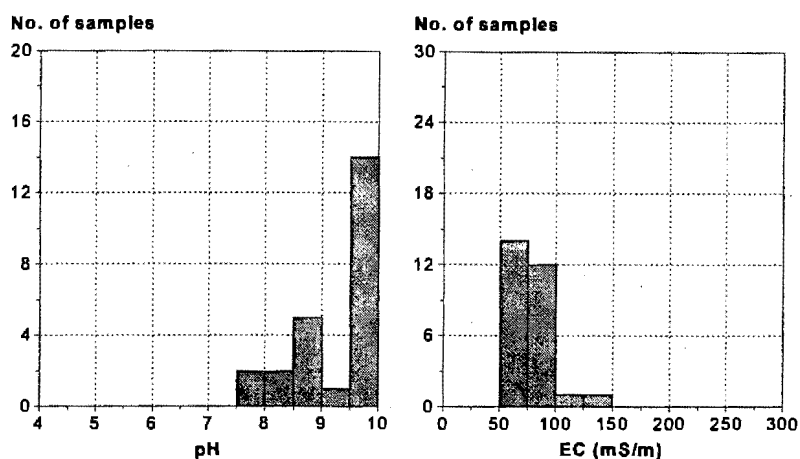


Figure 3.6. Histograms showing the high pH values and narrow distribution of EC values in groundwaters from the Kopoasfontein research site.

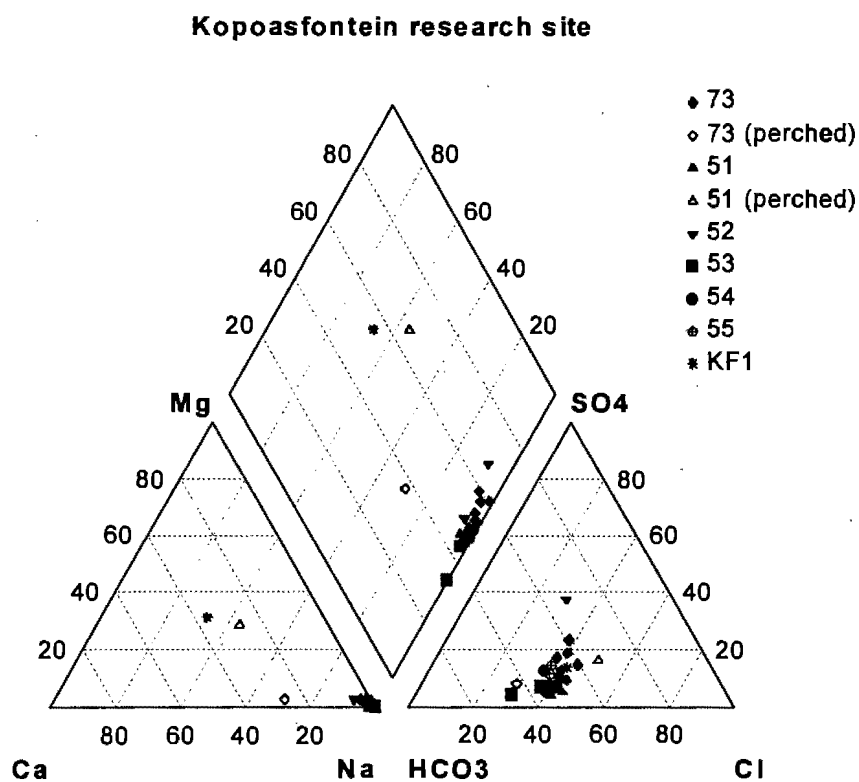


Figure 3.7. Trilinear diagram illustrating the relative proportions of major cations and anions in groundwater samples from Kopoasfontein (After Piper, 1953). Most Kopoasfontein groundwaters are of Na - HCO₃/Cl type.

Major ion data were used to calculate saturation indices for the common mineral phases calcite, quartz, gypsum and fluorite to determine what control, if any, these might be exerting on the groundwater chemistry. The calculations were performed using PHREEQC-2 software (Parkhurst and Appelo, 1999) with thermodynamic data from the default PHREEQC database. The results for the Kopoasfontein groundwater samples are summarised in the histograms on Figure 3.8.

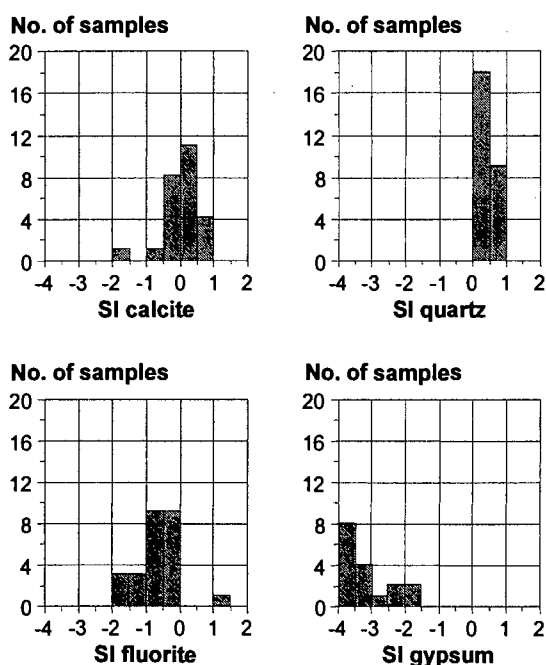


Figure 3.8. Histograms of saturation indices for calcite, quartz, fluorite and gypsum calculated from the composition of the Kopoasfontein groundwaters using PHREEQC (Parkhurst and Appelo, 1999).

Most samples are near equilibrium with calcite and supersaturated with respect to quartz. Precipitation of calcite is expected to limit the concentration of Ca^{2+} that may accumulate in the groundwater under the alkaline conditions in the breccia pipe. The shallow sample from the dolerite sill in borehole 73 (15/3/1994) is supersaturated with respect to fluorite. Mixing of the high Ca^{2+} perched groundwater above the sill with the high F^- water found deeper in the breccia could lead to precipitation of fluorite near the mixing front. It is, however, possible that the Ca^{2+} - or F^- measurement for this sample could be in error. All samples are undersaturated with respect to the gypsum because of the low Ca^{2+} concentrations and gypsum is not expected to limit SO_4^{2-} concentrations in the groundwater.

3.4.4 Trace elements

Table 3.5 presents analytical results for trace elements in the groundwater samples.

Table 3.5 Trace element concentrations for natural groundwater samples from Kopoasfontein. All concentrations measured as total elemental concentrations in $\mu\text{g/L}$ by ICP-MS. Concentrations greater than 0.1 mg/L are shown in bold text.

Borehole	53	55	KF1	73	73	73	73
Date sampled	19/11/99	19/11/99	08/07/99	08/07/99	18/08/98	18/10/94	10/10/94
Al	1580	1180	13	68	85	<40	<40
Cr	<0.1	15	5.7	0.23	2.1		
Mn	19	11	2.3	2.4	4.3		
Co	0.98	0.67	0.24	0.12	n.d.		
Ni	1.2	1.7	2.4	0.61	0.50		
Cu	2.7	1.3	5.8	3.2	2.7	0.51	1.6
Zn	4.2	19	38	3.9	58	2.7	167
As	2.7	37	3.3	258	325	311	412
Se	1.6	1.9	7.1	1.8	2.0		
Rb	4.5	3.9	1.5	1.1	1.5		
Mo	17	70	3.9	60	n.d.		
Cd	<0.1	0.11	<0.1	0.10	0.20		
Cs	2.4	2.9	0.23	0.66	0.60		
Hg	n.d.	n.d.	n.d.	n.d.	n.d.	10.9	48
Pb	1.7	2.1	0.11	0.73	1.4	19.6	35
U	0.25	0.78	8.7	6.7	8.7		
Data source	This study	This study	This study	This study	Cavé, 1999	Woodford, 1994	Woodford, 1994

Most of the divalent, strongly-hydrating trace metal cations, such as Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} and Pb^{2+} , will form insoluble oxide/hydroxide or carbonate species under alkaline conditions (Drever, 1997; p. 189) in the Kopoasfontein groundwaters. Concentrations of these elements in field-filtered samples are consequently relatively low. Zinc data for 73 may be unreliable since the high pH water has corroded the galvanised pipes attached to the submersible pump. A coating precipitate of smithsonite (ZnCO_3) was identified on the pipes by XRD after the pump was removed from the borehole. Elevated arsenic concentrations are consistently found in borehole 73.

3.5 Chemical characterisation of other breccia pipe groundwaters

Breccia pipes at the Golf Course, Witwal, Witkop, Bakenskop, Kopoasfontein, Downes and Airfield sites near Calvinia have been investigated (Chevallier, pers. comm.). Their locations are shown on Figure 3.1. Where available, the drilling logs for boreholes in these pipes are included in Appendix A.

Groundwater at the Golf Course, Witwal, Witkop and Bakenskop breccia pipes was sampled for chemical comparison with the groundwater at the Kopoasfontein research site. The Airfield and Downes boreholes were not included in these field studies because of accessibility problems. Although no breccia pipe has been mapped on Jaagvlakte farm, a private borehole (JV1) sampled there was found to share many of the chemical characteristics of the groundwater from the breccia pipe at Kopoasfontein.

The breccia pipes have been divided into two groups for the purposes of this discussion:

- ▶ *Sodic pipes* yield groundwater with a pH of 9 or above and have a major cation composition dominated by Na (%Na > 80 %).
- ▶ *Calcic pipes* have a pH between 7 and 8 and a mixed Na/Ca/Mg major cation suite (%Na < 60 %).

Under this classification, the Witwal and Jaagvlakte sites fall within the sodic group, along with the Kopoasfontein breccia pipe. Witwal and Kopoasfontein are also classified by Hallbauer *et al.* (1995) as *mineralised breccia pipes*. The Golf Course and Witkop pipes belong to the calcic type.

The Bakenskop sample from borehole 57 falls between the two types. Since this borehole is on the edge the breccia pipe, it is suspected that it intercepts groundwater which is a mixture from a sodic breccia pipe (Bakenskop pipe) and the surrounding weathered Karoo shale aquifer. The Airfield breccia pipe is similar in composition to those in the calcic group, but may also represent a mixed water with a component from the fractured rock aquifer system.

3.5.1 Field parameters

Several physical and chemical parameters were measured on site when groundwater samples were collected, before changes could occur during transport and storage of the samples (Table 3.6). Results for the sample from borehole 48 (Witkop) and one analysis from borehole 61 (Witwal) were reported previously by Cavé (1999).

Table 3.6. Physical and chemical parameters of groundwater measured at the wellhead for breccia pipes.

Sodic breccia pipes		Witwal ¹			Jaagvlakte ²	Bakenskop
Borehole	61	61	61	58	JV1	57
Date measured (mm/yy)	08/98	07/99	11/99	11/99	07/99	11/1999
Abstraction method	pump	pump	pump	bailer	wind pump	bailer
Water level (mbgl)	n.d.	n.d.	n.d.	15.5	n.d.	8.2
Temperature (°C)	22.5	22	21	22	16.4	n.d.
pH	8.6	8.2	9.1	9.3	9.0	7.67
EC (mS/m)	80	157	n.d.	n.d.	76	n.d.
Alkalinity (mg HCO ₃ /L)	n.d.	260	n.d.	n.d.	n.d.	n.d.
Dissolved oxygen (mg/L)	0.5	n.d.	n.d.	n.d.	n.d.	n.d.
Odour	H ₂ S	H ₂ S	H ₂ S	H ₂ S	Slight H ₂ S	None
Data source	Cavé, 1999	This study	This study	This study	This study	This study
Calcic breccia pipes		Golf Course ³			Witkop	
Borehole	59	59	62		48	
Date measured	07/1999	11/1999	11/1999		08/98	
Abstraction method	pump	pump	bailer		pump	
Water level (mbgl)	n.d.	n.d.	11.8		n.d.	
Temperature (°C)	23.8	21.5	24		n.d.	
pH	7.6	7.4	7.8		8.1	
EC (mS/m)	160	n.d.	n.d.		435	
Alkalinity (mg HCO ₃ /L)	307	n.d.	n.d.		n.d.	
Dissolved oxygen (mg/L)	n.d.	n.d.	n.d.		n.d.	
Odour	Slight H ₂ S	H ₂ S	None		H ₂ S	
Data source	This study	This study	This study		Cavé, 1999	

¹ Witwal: borehole 58 in breccia pipe and borehole 61 next to pipe.

² Jaagvlakte: unconfirmed breccia pipe.

³ Golf course: borehole 59 in breccia pipe and borehole 62 next to pipe.

3.5.2 Major, minor and trace aqueous constituents

Results of the analyses of major and minor constituents in these water samples are presented in Tables 3.7 and 3.8 and trace elements in Table 3.9. The major cation and anion compositions of the breccia pipe groundwaters are also plotted on a Piper diagram in Figure 3.9. Data for approximately 50 additional groundwater samples from the Calvinia breccia pipes was obtained from the NWQDB and from Woodford (1994) and these are also shown on the figure. No data were found for the Downes breccia pipe. The reliability of most of these data is not certain, since there is no record of sampling and analytical methods or laboratory precision. A charge balance calculation was performed for the major cations and anions in each sample as a rough test of analytical accuracy and the few samples found to fall above 5% charge imbalance were rejected. Many of the samples were collected during drilling or test pumping of the breccia pipe boreholes. Sample JV1 of unknown geological origin is included in this data set as a possible breccia pipe.

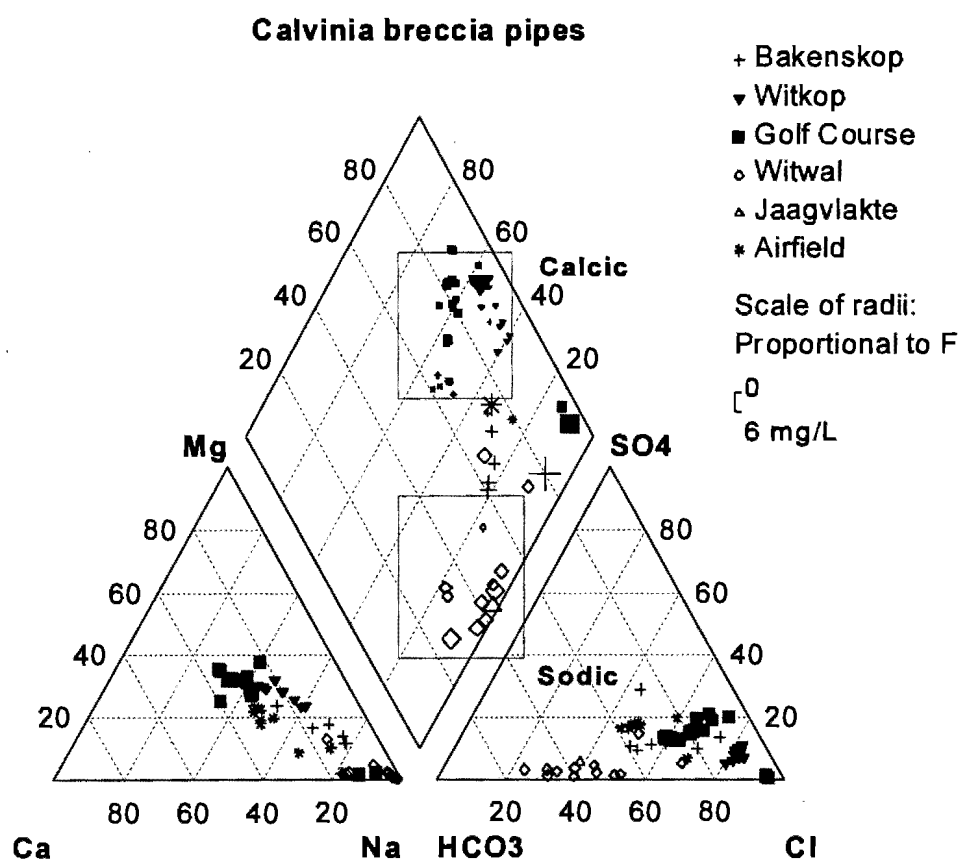


Figure 3.9. Piper trilinear diagram showing the molar proportions of major cations and anions in groundwater samples from breccia pipes near Calvinia. The radius of the symbols in the diamond field have been scaled proportional to the fluoride concentrations of the samples, which have a maximum value of 12 mg/L.

Table 3.7. Major and minor species in groundwater from boreholes in sodic breccia pipes near Calvinia.
Data in mg/L unless otherwise indicated.

Breccia pipe		Witwal				Jaagvlakte ¹
Borehole		61	61	61	58	JV1
Date sampled		17/08/1998	07/07/1999	18/11/1999	18/11/1999	07/07/1999
Sample method		pump	pump	pump	bailer	wind pump
pH (lab)	(pH units)	8.73	8.44	8.81	8.99	9.09
EC (lab)	(mS/m, 20°C)	73	135	92	62	78
Na		180	265	190	143	144
K		0.7	1	1.3	0.7	0.7
Mg		2	7.5	1.8	1	0.15
Ca		4.6	15	2.5	1.2	2
Li		0.18	0.21	0.15	0.09	0.17
NH ₄ as N		<0.1	2.1	<0.1	<0.1	<0.1
Cl		150	317	153	63	93
SO ₄		5.7	33	6.4	3.3	18
HCO ₃ [#]		241	213	233	223	222
CO ₃ [#]		5.3	2.4	1.7	9	11
F		2.7	2.3	1.3	2.2	3.7
NO ₂ +NO ₃ as N		<0.1	<0.1	<0.1	<0.1	<0.1
PO ₄ as P		<0.1	<0.1	<0.1	<0.1	<0.1
Br		<0.1	2.1	0.72	0.38	<0.1
Sum cations	(meq/L)	8.28	13.1	8.59	6.40	6.42
Sum anions	(meq/L)	8.62	13.3	8.39	5.92	7.20
Cation excess	(%)	-2.0	-0.8	1.2	3.9	-5.7
SAR	(meq/L) ^{1/2}	17.6	13.9	8.97	7.99	26.5
Si		5.7	9.1	6.7	9	6.7
Total Fe		0.05	0.06	0.07	0.01	0.09
Sr		0.39	1.15	0.43	0.05	0.15
Ba		0.12	0.21	0.13	0.01	0.08
B		n.d.	0.40	0.63	0.48	0.76
S ²⁻		n.d.	n.d.	1.6	<0.1	n.d.
DOC		<1	2.2	5	6	1.8
Data Source		Cavé, 1999	This study	This study	This study	This study

[#] Total alkalinity recalculated as HCO₃⁻ and CO₃²⁻ for high pH samples using HCO₃⁻ = CO₃²⁻ + H⁺, log K = -10.38 at 20 °C. ¹Jaagvlakte = unconfirmed breccia pipe.

Table 3.8. Major and minor species in groundwater from boreholes in calcic breccia pipes near Calvinia.
Data in mg/L unless otherwise indicated.

Breccia pipe		Golf Course			Wittkop	Bakenskop ¹
Borehole		59	59	62	48	57
Date sampled		07/07/1999	18/11/1999	18/11/1999	17/08/1998	18/11/1999
Sample method		pump	pump	bailer	pump	bailer
pH (lab)	(pH units)	7.57	7.29	7.25	7.27	7.55
EC (lab)	(mS/m, 20°C)	167	252	224	404	335
Na		167	214	412	590	505
K		2.5	3.3	1.8	5.8	3.2
Mg		57	90	3.2	210	89
Ca		98	72	20	220	3.2
Li		0.05	0.04	0.26	0.29	0.04
NH ₄ as N		<0.1	<0.1	<0.1	<0.1	<0.1
Cl		332	544	663	1570	465
SO ₄		103	149	4.4	150	411
HCO ₃ [#]		270	349	50	318	486
F		1.0	<0.1	1.5	1.1	0.1
NO ₂ +NO ₃ as N		<0.1	<0.1	<0.1	<0.1	<0.1
PO ₄ as P		<0.1	<0.1	<0.1	<0.1	<0.1
Br		2.2	2.6	2.4	<0.1	2.9
Sum cations	(meq/L)	16.9	26.7	19.3	54.3	29.5
Sum anions	(meq/L)	16.0	24.2	19.7	53.8	30.0
Cation excess	(%)	2.8	5.0	-1.1	0.4	-0.7
SAR	(meq/L) ^{1/2}	3.32	3.16	15.2	6.83	9.24
Si		9.1	9.7	4.7	5	8.4
Total Fe		0.18	6.2*	0.59	0.07	0.22
Sr		1.18	1.3	0.12	6.6	1.1
Ba		0.03	0.04	0.01	0.29	0.03
B		0.12	0.21	0.51	n.d.	1.5
S ²⁻		n.d.	<0.1	n.d.	n.d.	n.d.
DOC ³		2.4	5.7	5.7	1.5	9
Data Source		This study	This study	This study	Cavé, 1999	This study

¹ Bakenskop: possible sodic breccia pipe mixed with Karoo shale groundwater.

[#] Total alkalinity as HCO₃, CO₃ is negligible at this pH.

* Total Fe may be overestimated by dissolving iron hydroxide after sample acidification. An orange/brown precipitate was present in the groundwater at the time of sampling.

Table 3.9. Trace element concentrations for groundwater samples from Calvinia breccia pipes. All concentrations measured as total elemental concentrations in $\mu\text{g/L}$ by ICP-MS.

Breccia pipe	Witwal			Golf Course			Bakenskop	Jaagvlakte
Sample	61	61	58	59	59	62	57	JV1
Date	07/99	11/99	11/99	07/99	11/99	11/99	11/99	07/99
Al	16	28	14	13	13	8.2	12	37
Cr	3.3	38	84	3.6	48	5.4	20	2.2
Mn	14	7.6	4.0	20	49	63	2.3	3.2
Co	0.12	0.20	<0.1	4.3	3.5	0.24	0.24	0.07
Ni	0.66	3.5	5.1	9.1	4.4	1.0	<0.1	0.71
Cu	1.7	<0.1	2.9	2.9	0.44	3.9	2.8	3.0
Zn	5.0	14	10	24	34	7.8	21	7.1
As	1.9	0.96	1.6	97	182	3.1	3.8	0.5
Se	2.9	2.5	1.1	4.2	10	7.7	34	1.8
Rb	1.6	3.8	1.1	4.4	6.0	2.6	0.97	0.56
Mo	1.2	1.1	1.1	144	67	3.6	11	5.5
Cd	<0.01	0.02	<0.01	0.25	0.08	0.05	0.02	0.04
Cs	0.83	0.77	0.34	0.35	0.44	0.18	0.15	0.73
Pb	0.27	0.67	0.58	0.32	2.7	<0.1	1.9	1.0
U	<0.1	<0.1	0.29	2.6	3.9	0.10	16	<0.1

Samples from the sodic Witwal pipe and Jaagvlakte farm are low salinity fresh waters, but those from the Golf Course and Airfield are slightly brackish and the Bakenskop and Witkop boreholes yield brackish groundwater. No obvious explanation was found for the significant increase in solutes in borehole 61 in July 1999, compared with the samples from November 1999 and August 1998.

The compositions of the sodic (Witwal and Jaagvlakte) and calcic (Golf Course and Witkop) breccia pipes plot roughly in two clusters on Figure 3.9, with the mixed composition of the samples from Bakenskop and Airfield plotting between the two groups in the cation triangle. The two Na-Cl type outliers from the Golf Course are samples from borehole 62, which lies outside the breccia pipe. The size of the symbols on the figure illustrates that higher F^- concentrations are associated with the high pH, low Ca waters of the sodic group.

Elevated Fe, Mn, Co, Cu, Zn, As, Pb and Mo in the groundwater from 59 and Cr, Zn, Pb and Mo in 57, together with relatively high SO_4^{2-} concentrations, suggests that the groundwaters have reacted with metal sulphides in the Golf Course and Bakenskop breccia pipes. These two pipes, along with the one at Airfield, have proportionally higher SO_4^{2-} content than the Witwal, Witkop and Jaagvlakte samples.

The histograms in Figure 3.10 summarise the saturation status of groundwaters from the sodic and calcic group breccia pipes with respect to the minerals calcite, quartz, fluorite and gypsum. Bakenskop samples have been included with the sodic group and Airfield samples with the calcic group in the figure. Calcic pipes are closer to gypsum saturation (because of the higher sulphate content of these samples) and are largely supersaturated with respect to calcite.

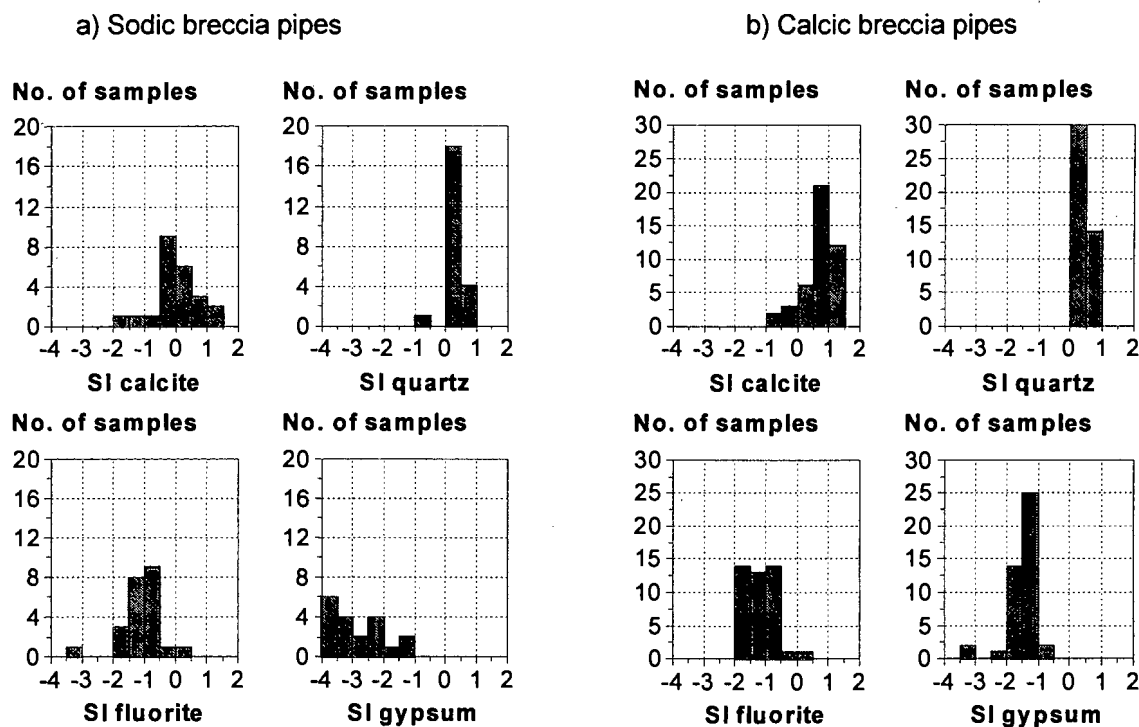


Figure 3.10. Histograms of saturation indices for calcite, quartz, fluorite and gypsum calculated using PHREEQC (Parkhurst and Appelo, 1999) for groundwater samples from a) sodic breccia pipes, Witwal, Jaagvlakte and Bakenskop and b) calcic breccia pipes, Witkop, Golf Course and Airfield.

There is a strong similarity between the major ion chemistry of the Kopoasfontein groundwaters and those of the other sodic breccia pipes. The groundwater from Kopoasfontein, however, has a higher pH and greater concentrations of fluoride and arsenic than other breccia pipes.

3.6 Chemical characterisation of other groundwaters near Calvinia

3.6.1 Primary aquifers

A localised primary aquifer system is associated with the unconsolidated alluvial deposits of the Oorlogskloof River drainage system. Groundwater in this environment is generally located at shallow depths. Chemical data are available for 78 groundwater samples from 48 boreholes located within the alluvial deposits of the Calvinia area. Two of these boreholes (38 and 27A) were sampled and analysed by Cavé (1999) and the rest of the data obtained from the work of Seward (1983) and Woodford (1994) and the NWQDB.

Salient features of the hydrochemistry associated with alluvial deposits near Calvinia are summarised in Figures 3.11 to 3.13. The original chemical data have been included in Appendix D. Records with a charge imbalance of greater than 5% have been omitted from the data set.

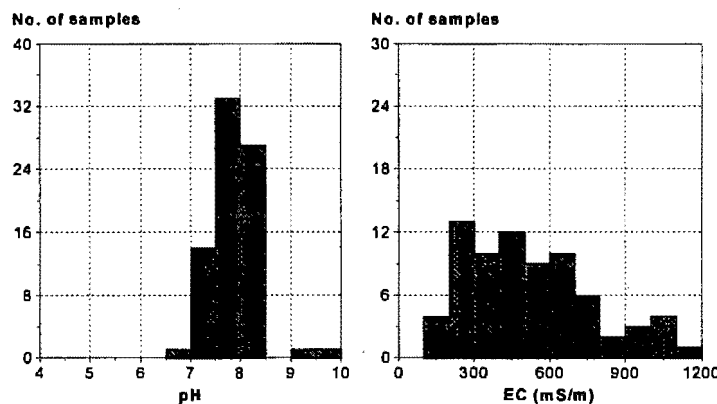


Figure 3.11. Histograms showing distribution of laboratory pH and electrical conductivity values for groundwater samples from alluvial aquifers near Calvinia.

The alluvial waters are generally brackish, ranging from 152 to 1222 mS/m with a mean EC of 710 mS/m. Electrical conductivity is strongly correlated with Cl^- ($R^2 = 0.987$). None of the samples fall within the “no risk” category (below 70 mS/m) under the South African guidelines for domestic water (DWAF, 1996). The lowest EC sample is 80 (EC = 121 mS/m), which is also a sodic outlier on the Piper diagram in Figure 3.12 and may have been incorrectly grouped with the alluvial waters.

The alluvial groundwaters have an average pH value of 7.8. For all but three of the samples (PS26, 80 and 43), laboratory pH is reported to be between 7 and 8.3, probably buffered by equilibrium with calcium carbonate in the alluvial sediments (Figure 3.13).

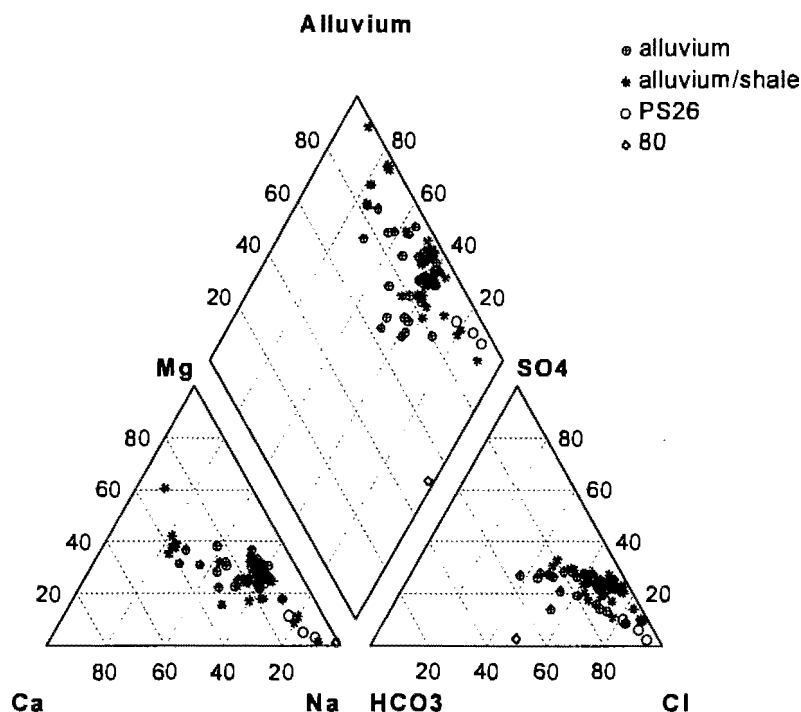


Figure 3.12. Piper trilinear diagram illustrating the relative proportions of major cations and anions in groundwater samples from alluvial aquifers near Calvinia. Open circles show the shift in major ion chemistry with depth for borehole PS26 (G32626) drilled through the alluvium into the underlying shales.

Sodium and chloride are the dominant ions in most of the samples. Roughly equal contributions to the cationic charge in solution are provided by Ca^{2+} and Mg^{2+} , which share the cation dominance with Na^+ in many of the samples.

Four water samples were collected while drilling borehole PS26. The first at a depth of 6.5 m is in alluvium. The remainder are in the underlying shales after the shallow alluvial water was cased off. These were collected at 91 and 117 m and a final cumulative sample after the borehole was developed. The shale samples, shown as open circles on Figure 3.12, show an increase in Na-Cl dominance with depth. At the same time the electrical conductivity of the samples decreased from 626 to 312 mS/m while the pH dropped from 7.4 to 6.8.

Seward (1983), who was involved in the drilling of this borehole, came to the conclusion, later shared by Woodford (1994), that groundwater salinity in the Calvinia area is generally higher in the near-surface alluvial and weathered zone aquifers and decreases with depth, where it occurs in unweathered, fractured hard rocks that are recharged away from the areas of alluvium.

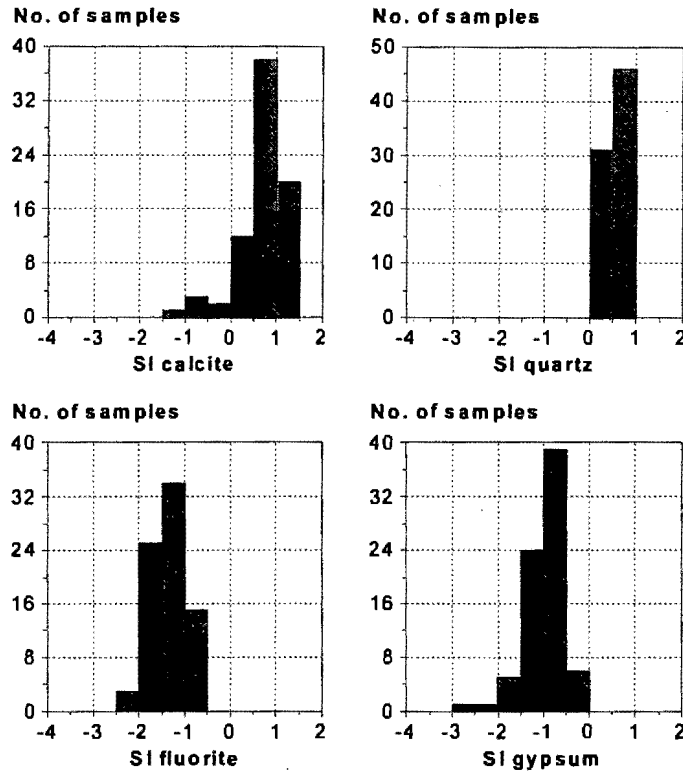


Figure 3.13. Histograms of saturation indices for calcite, quartz, fluorite and gypsum, calculated from the composition of the alluvial groundwater samples using PHREEQC-2 (Parkhurst and Appelo, 1999).

The alluvial groundwaters are undersaturated with respect to gypsum and fluorite and slightly supersaturated with respect to calcite and quartz. Groundwater from the highest salinity borehole, 43, is close to equilibrium with respect to gypsum ($SI_{\text{gypsum}} = -0.5$ to -0.4).

The distribution of saturation indices is similar to that of the calcic breccia pipes in Figure 3.10b), which also share the same major ion patterns. The calcic breccia pipes are generally located in or near the alluvial deposits along the main drainage system of the Oorlogskloof river. Groundwater chemical characteristics indicate that water from the alluvial aquifers is expected to form a major component of the water in the calcic breccia pipes.

3.6.2 Secondary aquifers

Fractured hard rock aquifers near Calvinia comprise faults and contact zones in dolerite, shale and sandstone, as well as several highly localised groundwater-bearing features associated with breccia pipes. Most of the deeper groundwater intercepted in the Karoo occurs in fractured aquifers.

Fifty chemical analyses of groundwater samples from around 30 boreholes drilled in dolerite or shale were found in the reports of Woodford (1994) and Seward (1983) and the NWQDB. The results are summarised on Figures 3.14 to 3.16. Only analyses with a charge imbalance of less than 5% were used.

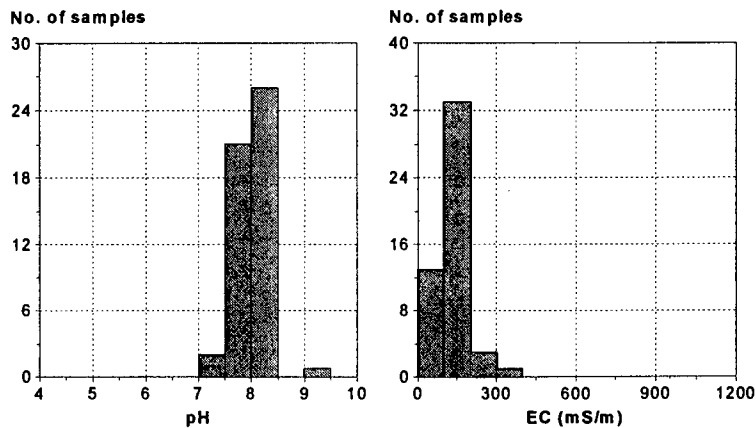


Figure 3.14. Histograms showing distribution of laboratory pH and electrical conductivity values for groundwater samples from fractured hard rock aquifers near Calvinia.

Where pH values have been reported, these range from 7.2 to 9.1 with a mean value of 7.9, slightly higher than the alluvial groundwaters. In general groundwater from the boreholes intersecting faults and dolerite contact zones is of lower salinity than the alluvial aquifers, being fresh to slightly brackish. Electrical conductivity ranges from 52 to 383 mS/m with only one sample (EW29) exceeding the South African “low risk” target of 300 mS/m (DWAF, 1996).

Major ion chemistry in the fractured rock groundwaters (Figure 3.15) ranges from Ca/Mg-HCO₃ type to a mixed Na/Ca/Mg-Cl type, similar to that found for the alluvial samples. The former is typical of freshly recharged groundwater that has equilibrated with CO₂ and soluble carbonate

minerals under open system conditions in the soil zone. The Na/Ca/Mg-Cl water type is characteristic of stagnant groundwater zones or of groundwater at some distance along a flow path. Five surface water samples from the town dam and reticulation system have been added for comparison, as an indication of possible recharge water chemistry in the area. These also tend to plot in the Ca/Mg-HCO₃ region of the piper diagram.

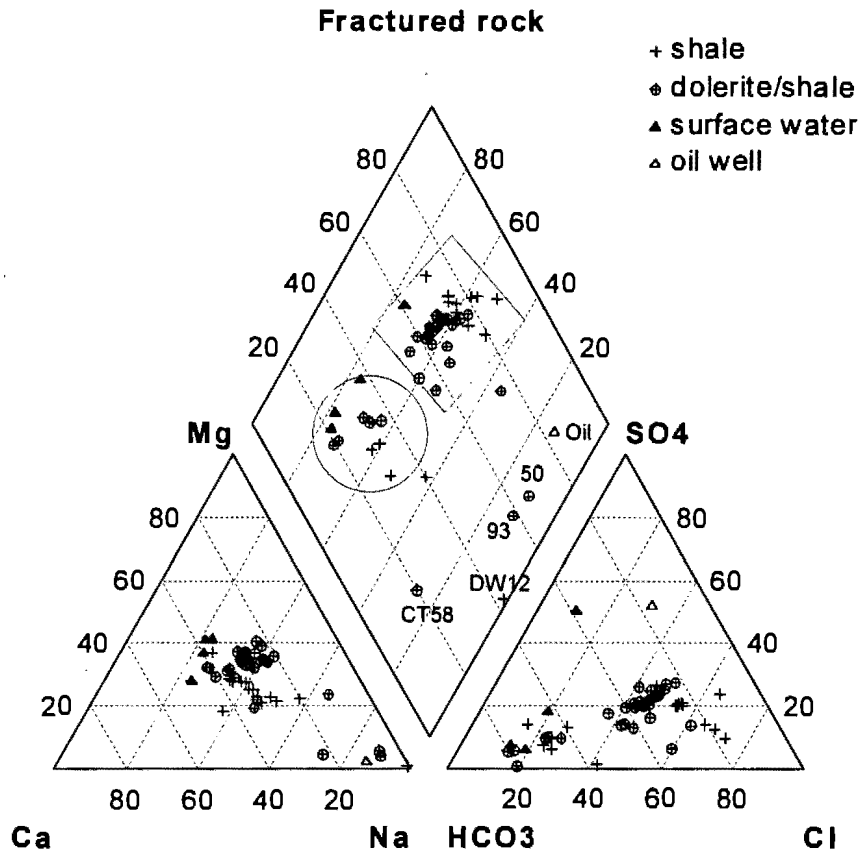


Figure 3.15. Piper trilinear diagram illustrating the relative proportions of major cations and anions in groundwater samples from fractured hard rock aquifers near Calvinia. The circle indicates a small cluster of Ca/Mg-HCO₃ type waters and the diamond the majority of Na/Ca/Mg-Cl type waters.

Several Na-dominant outliers are evident on the piper diagram. Two Na-HCO₃/Cl type samples (50 and 93) tap a groundwater source on the farm Albertfontein Ruggens, to the east of Kopoasfontein, which is possibly another breccia pipe. The deeper of the two, borehole 50 (79 m), also has a F⁻ concentration of 7 mg/L. Other outliers also have elevated F⁻ including DW12, (F⁻ = 3.0 mg/L) and Oil well, a 450 m deep oil exploration borehole at Muisvlakte (F⁻ = 2.1 mg/L). All the other fractured rock groundwater samples from this area have F⁻ concentrations of 1.5 mg/L or lower.

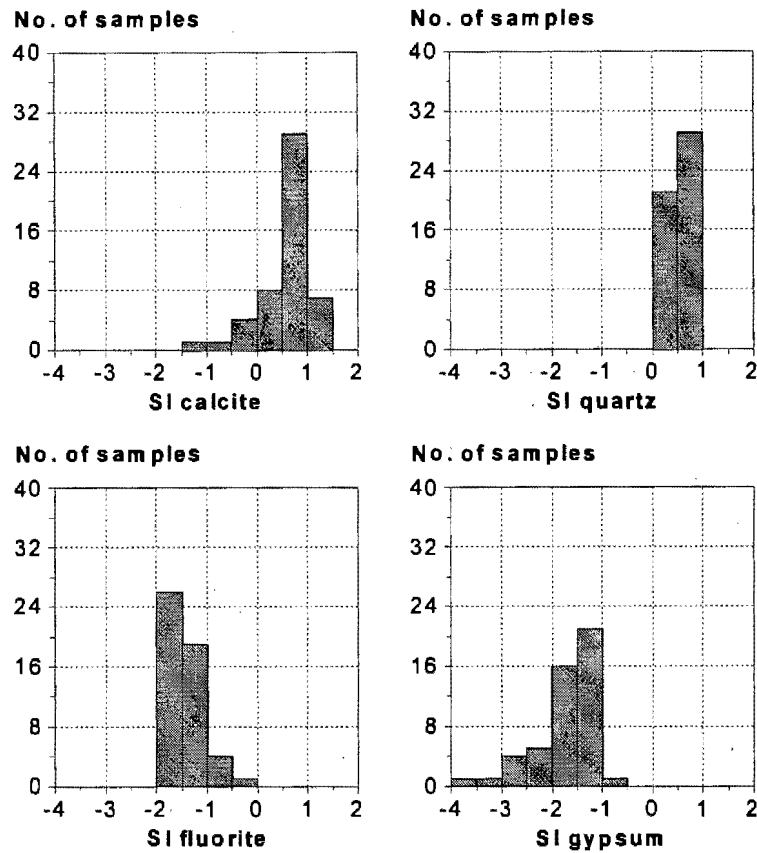


Figure 3.16. Histograms of saturation indices for common sparingly soluble minerals calcite, quartz, fluorite and gypsum, calculated from the composition of the fractured rock groundwater samples, using PHREEQC-2 (Parkhurst and Appelo, 1999).

Saturation index calculations show that the composition of these waters is slightly supersaturated with respect to calcite and quartz and slightly undersaturated with respect to fluorite and gypsum. The high fluoride sample, 50, is near equilibrium with fluorite ($SI_{\text{fluorite}} = -0.18$).

3.7 Isotope characterisation of groundwaters from the Calvinia area

The naturally occurring stable isotopes, hydrogen (H), deuterium (D), oxygen-16 (^{16}O), oxygen-18 (^{18}O), carbon-12 (^{12}C) and carbon-13 (^{13}C) and the radioactive forms, tritium (T) and carbon-14 (^{14}C) provide useful tools in hydrogeology. Ratios of the stable hydrogen and oxygen isotopes, δD and $\delta^{18}\text{O}$, are useful tracers for characterising different water sources, identifying mixing of water types and calculating the proportion of end members in the mixture. Deuterium and

δD and $\delta^{18}O$, are useful tracers for characterising different water sources, identifying mixing of water types and calculating the proportion of end-members in the mixture. Deuterium and oxygen-18 ratios may also be used for providing information about the source and conditions of groundwater recharge, tracing isotope exchange processes during water rock interaction or estimating palaeotemperatures (Drever, 1997; p. 314 - 320). The most important application of $\delta^{13}C$ data is in process identification in the context of the carbonate system, while ^{14}C is a popular age dating tool in hydrogeology and many other branches of science. Carbon-14 can also be used to determine groundwater travel times and flow velocities.

3.7.1 Stable isotopes of hydrogen and oxygen

Stable isotope ratios of hydrogen and oxygen for groundwater samples from boreholes at the Kopoasfontein geohydrological research site and other breccia pipes in the Calvinia area are given in Table 3.10. Limited data for surface water samples, collected by the author and other boreholes in alluvial and fractured rock aquifers are also included. Most of the data from 1994 were obtained from water samples collected at the beginning and end of constant discharge pumping tests (Woodford, pers. comm.).

The most important physical process causing variation of hydrogen and oxygen isotope composition in natural waters is vapour-liquid fractionation during evaporation and condensation. The vapour pressure of water containing the light isotopes (^1H and ^{16}O) is greater than that of water containing the heavier isotopes (D and ^{18}O). When liquid water and water vapour are in equilibrium, the vapour is isotopically lighter with respect to both D/H and $^{18}O/^{16}O$ than the liquid, and hence water vapour in the atmosphere is isotopically lighter than water in the ocean. Water vapour which evaporates from the ocean is depleted by 10 - 15 ‰ in ^{18}O and by 80 - 120 ‰ in D with respect to SMOW (Standard Mean Ocean Water) (IAEA, 1973; Drever, 1997; p. 314).

When water vapour condenses to form rain, fractionation takes place in the reverse direction, with the liquid being isotopically heavier than the vapour. The fractionation during evaporation is thus largely reversed during condensation and the first rain to fall from water vapour over the ocean would have an isotope composition of about -3 ‰ (Drever, 1997; p. 314). If this rain again

forms a vapour, ^{18}O will be selectively removed from the vapour phase and the $\delta^{18}\text{O}$ of the vapour will become progressively more negative as the rain continues to fall. By this process of Rayleigh fractionation, rainfall becomes progressively lighter in both δD and $\delta^{18}\text{O}$ as it occurs further from the ocean source. Calvinia is over 100 km from the coast and its rainfall is expected to be isotopically light. Issar (1995) cites a range of $\delta^{18}\text{O}$ values of -4.5 to -5.7 ‰ for average rainfall in the western Karoo.

Table 3.10. Isotope ratios relative to standard mean ocean water for hydrogen and oxygen in groundwaters from Kopoasfontein and other investigation sites in the Calvinia area.

Location	Borehole	Date sampled	$\delta\text{D}_{\text{SMOW}}$ (‰)	$\delta^{18}\text{O}_{\text{SMOW}}$ (‰)	Data source
Kopoasfontein	73	08/07/1999	-34	-5.96	This study
	73	18/08/1998	-31	-5.8	Cavé, 1999
	73	18/10/1994 ^e	-31.7	-5.73	Talma, CSIR
	73	10/10/1994 ^b	-30.6	-5.72	Talma, CSIR
	KF1	08/07/1999	-33	-5.58	This study
Witwal	61	07/07/1999	-32	-5.66	This study
	61	18/08/1998	-31	-5.5	Cavé, 1999
	61	17/09/1994 ^e	-30.2	-5.29	Talma, CSIR
	61	14/09/1994 ^b	-32.3	-5.5	Talma, CSIR
Jaagvlakte	JV1	07/07/1999	-37	-5.88	This study
Witkop	48	18/08/1998	-24	-3.2	Cavé, 1999
	46	23/09/1994 ^e	-26.2	-3.11	Talma, CSIR
	46	21/09/1994 ^b	-25.7	-3.21	Talma, CSIR
Golf Course	59	07/07/1999	-25	-2.92	This study
	59	26/09/1994 ^e	-22.8	-2.55	Talma, CSIR
	59	20/09/1994 ^b	-22.5	-2.53	Talma, CSIR
Bakenskop	35	13/09/1994 ^e	-30.2	-5.26	Talma, CSIR
Alluvial aquifers	38	18/08/1998	-25	-4.7	Cavé, 1999
	27	18/08/1998	-24	-4.2	Cavé, 1999
Fractured rock aquifers	95	10/09/1994	-29.9	-4.31	Talma, CSIR
	72	16/09/1994 ^e	-30.8	-3.95	Talma, CSIR
	72	10/09/1994 ^b	-28	-4.01	Talma, CSIR
Surface water	Dam	18/08/1998	-2	-1.3	Cavé, 1999
	Plant	07/07/1999	-2	-1.2	This study

^b beginning of pumping test ^e end of pumping test Dam = sample from Karee Dam
Plant = Karee dam water from public reticulation system, sampled at the municipal purification plant.

The δD and $\delta^{18}O$ values in precipitation generally plot close to a straight line (the meteoric water line) with the equation (Craig, 1961):

$$\delta D = 8 * \delta^{18}O + 10 \quad \dots\dots\dots (3.1)$$

Water with an isotope composition falling on the meteoric water line is assumed to have originated from the atmosphere and to be unaffected by other isotope processes. Evaporation from open water and exchange with rock minerals are two of the more commonly observed processes causing deviations from the meteoric water line (Domenico and Schwartz, 1990).

As temperature has a dominant effect on isotope fractionation, variations in isotope concentrations in precipitation can relate to climate, season and altitude (Lloyd and Heathcote, 1985). Temperature dependent isotope variations, however, are more pronounced in temperate and polar regions, than in areas with hotter climates. As a result, isotope variations commonly observed in northern Europe and America can be difficult to distinguish in Southern Africa.

Isotopes of oxygen and hydrogen are, in a certain sense, ideal geochemical tracers of groundwater because their concentrations are not subject to changes by interaction with the aquifer material at low temperature (IAEA, 1973). When precipitation infiltrates to feed groundwater, mixing in the unsaturated zone smoothes the isotope variations, so water in the saturated zone has a composition corresponding to the mean isotope composition of infiltration in the area. This may differ slightly from the mean isotope composition of precipitation due to the fact that not all precipitation during the year infiltrates in the same proportion (IAEA, 1973).

Analyses of δD and $\delta^{18}O$ can be used to identify the probable source of an underground water. If the isotope composition of an underground water plots close to the meteoric water line in a position similar to that of present-day precipitation in the same region, the water is almost certainly meteoric. Although the isotope composition of precipitation at a particular location is approximately constant, it varies from season to season and from one rainstorm to another. The variations can sometimes be used to identify the season at which most of the recharge takes place (Drever, 1997; p. 315).

Groundwater recharged by seepage from surface waters such as rivers or lakes should reflect the isotope signature of the surface water body eg. a river may collect water which originates at higher altitudes and is depleted in heavy isotopes while seepage from lake waters which have been evaporated will be enriched in heavy isotopes. Isotopic imaging of surface water/groundwater interactions is a useful application of δD and $\delta^{18}O$ data.

Hydrogen and oxygen stable isotope data for Kopoasfontein is compared with data from other groundwater sources in the Calvinia region and in the Karoo basin in Figure 3.17.

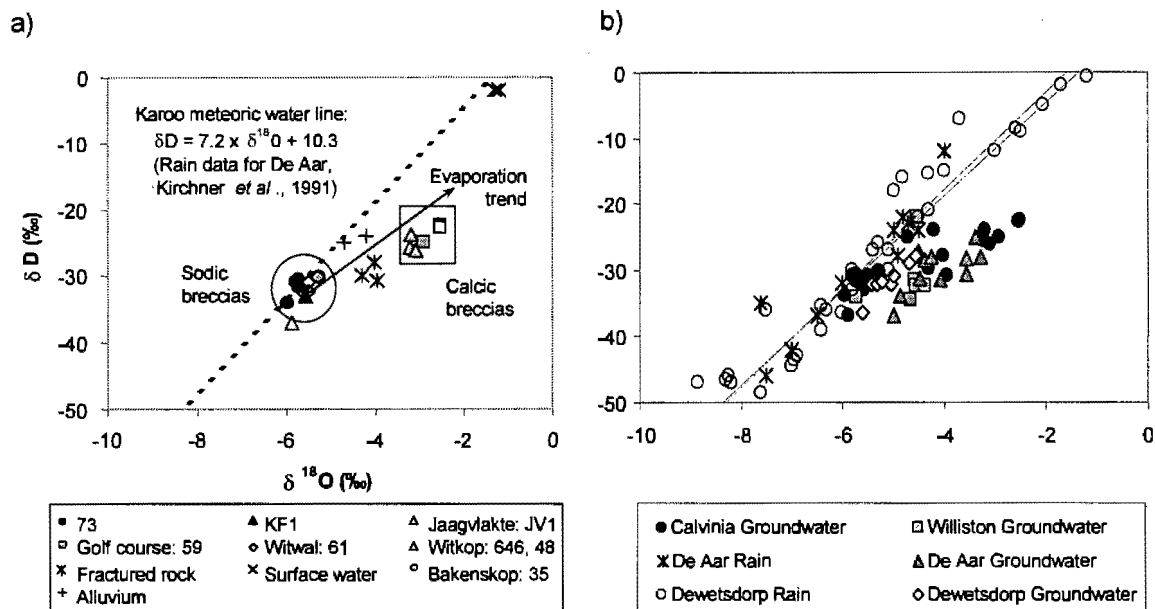


Figure 3.17a). Stable isotope ratios δD versus $\delta^{18}O$ for groundwater samples from Kopoasfontein (filled black symbols) compared with other water sources in the Calvinia area. The dashed line is a local meteoric water line for De Aar, which is characteristic of rainfall in the Karoo climatic region. b). Deuterium versus oxygen-18 ratios for rain water and groundwater samples from four sites in the Karoo basin, showing the meteoric lines for Dewetsdorp and De Aar (Williston data from Talma, pers. comm.; Dewetsdorp and De Aar data from Kirchner *et al.*, 1991).

Groundwater samples from Calvinia show stable isotope trends which fit well with other areas in the Karoo. Sodic groundwaters plot along the meteoric water line, while the samples from calcic breccia pipes plot away from the line, as do the fractured rock samples. The data suggest that sodic breccia pipes are recharged directly by meteoric waters, while groundwater in the other aquifers has undergone some degree of evaporation before infiltration. The samples from the Karee dam are significantly enriched in ¹⁸O and D, but plot surprisingly close to the meteoric water line, considering that evaporation takes place from this open surface water body.

A plot of $\delta^{18}\text{O}$ against Cl^- (Figure 3.18) indicates that the groundwater from the Golf Course breccia pipe and fractured rock boreholes has been recharged by evaporated waters, while the Bakenskop breccia pipe and alluvial groundwater samples are enriched in chloride by leaching and mineral dissolution in the aquifer, rather than by evaporation. The groundwater at Witkop has a composition intermediate between the calcic golf course samples and the high salinity alluvial groundwaters and may be a mixture of the two water types.

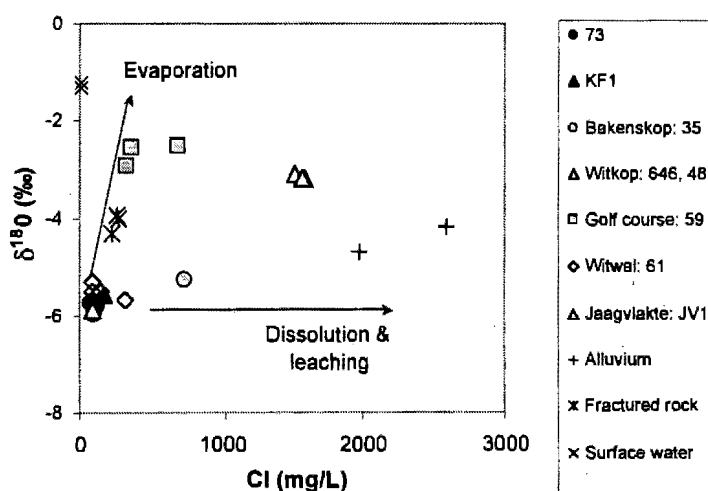


Figure 3.18. Stable isotope ratios $\delta^{18}\text{O}$ versus chloride for water samples from the Calvinia area, showing evaporation and chloride dissolution trends.

3.7.2 Carbon isotopes

The $\delta^{13}\text{C}$ ratio of groundwater is controlled by dissolution, precipitation and fractionation processes. Initially ^{13}C chemistry in recharge water is controlled by the $\delta^{13}\text{C}(\text{CO}_2)_{\text{gas}}$ in the atmosphere, which falls near -7‰ with respect to the carbonate standard (a marine calcite from the Pee Dee belemnite of South Carolina) (Drever, 1997; p. 320).

Changes in $\delta^{13}\text{C}$ occur when carbon is added to, or removed from, the water during its transit through the aquifer. Possible sources of carbon are:

- ▶ dissolution of solid carbonates, e.g. calcite, aragonite, or dolomite, which introduces relatively heavy carbon;
- ▶ transport of CO_2 gas from the soil atmosphere. This introduces relatively light carbon, the isotope ratios of which vary depending on climatic conditions and vegetation type;
- ▶ oxidation of organic matter, which introduces relatively light carbon;
- ▶ anaerobic fermentation of organic matter which fractionates the light carbon isotopes into CH_4 and heavy carbon into CO_2 . The CO_2 may dissolve in water introducing relatively heavy carbon; or
- ▶ dissolution of mantle-derived, volcanic or metamorphic CO_2 , which introduces relatively heavy carbon.

Carbon may be lost from the water by precipitation of a carbonate mineral or by loss of CO_2 gas. In general ^{13}C is used to identify sources of carbon and is particularly valuable for distinguishing between (light) carbon derived from primary biogenic CO_2 from soil organic matter and (heavy) carbon derived from marine carbonate minerals.

Radiocarbon (^{14}C) is produced in the atmosphere by interaction of cosmic rays with nitrogen and was introduced in large amounts by nuclear weapons testing. Carbon-14 has a half-life of 5730 years, making it a useful tool for dating waters as old as 50 000 years (Drever, 1997; p. 322). The ^{14}C generated in the atmosphere is carried down to the earth's surface by precipitation, and becomes incorporated into the biomass or transported into water bodies such as lakes, the ocean and groundwater.

Measurements of ^{14}C activity are normally reported in terms of per cent modern carbon (pmC) where:

$$A = \frac{(^{14}\text{C}/^{13}\text{C})_{\text{sample}}}{(^{14}\text{C}/^{13}\text{C})_{\text{modern}}} * 100 \text{ pmC} \quad \dots\dots\dots (3.2)$$

If there are no processes that alter total inorganic carbon after infiltration, the initial ^{14}C activity after infiltration (no decay), A_0 , and the observed ^{14}C activity at the time of sampling (with radioactive decay), A , can be combined to determine the ^{14}C age of the water sample, which is an estimate of the time since recharge occurred.

$$\text{Age} = -8270 \ln \frac{A}{A_0} \dots\dots\dots (3.3)$$

There are some complications in the behaviour of ^{14}C during recharge, so the “absolute” age of a groundwater cannot always be determined reliably. However, if the ^{14}C concentration is measured at several points along a flow line within an aquifer, the differences in age between the points and hence the flow velocity can be determined.

One complication is that dissolution of carbonate minerals or organic matter within the aquifer may add “old” or “dead” (no detectable ^{14}C) carbon to the water, giving an erroneously old age. The contribution of carbon from these sources can sometimes be estimated from the $\delta^{13}\text{C}$ measurements and chemical arguments, so corrections can be made. Another complication is mixing. A low ^{14}C concentration may mean relatively “old” water, or it may mean a mixture of relatively “young” water and “dead” water. Measurements of ^{14}C can be interpreted as ages only where mixing is insignificant. (Drever, 1997; p. 323).

Carbon isotope data from Talma (pers. comm.) for some of the Calvinia groundwater sources, including several breccia pipes, and two solid samples of secondary calcrete deposits are presented in Table 3.11. Total inorganic carbon, on which the isotope measurements were made, was also quantified to provide an indication of carbonate system reactions that could affect the isotope values.

Disregarding possible mixing or addition of dead ^{14}C , the data appear to show two separate generations of groundwater recharge. Older waters are found in the sodic breccia pipes, Witwal and Kopoasfontein, and younger waters in the Witkop pipe and fractured rock borehole. The final water from pumping tests at boreholes 73 and 646 is slightly older than that abstracted at the start. The Golf Course borehole initially yielded water that appears to belong to the younger generation, but the groundwater at the end of the pump test gave a much older relative ^{14}C age. The two

calcrete samples, unexpectedly, show no recent precipitation of carbonates.

Table 3.11. Carbon isotope data measured by Talma (pers.comm.) for total inorganic carbon in groundwater samples and calcretes from the Calvinia area.

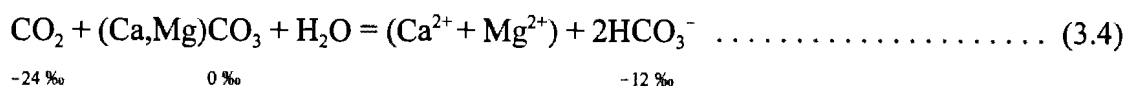
Location	Borehole	Date sampled (dd/mm/yyyy)	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	TIC (mmol/L)	^{14}C (pmC)	Age ¹ (years)
Kopoas- fontein	73	18/10/1994 ^e	-3.58	1.618	23.74±0.46	11900±160
	73	10/10/1994 ^b	-5.18	1.715	25.43±0.43	11320±140
Witwal	61	17/09/1994 ^e	-5.78	3.735	21.13±0.30	12810±120
	61	14/09/1994 ^b	-7.58	3.519	n.r.	n.r.
Witkop	646	23/09/1994 ^e	-8.36	4.426	65.64±0.42	3640±50
	646	21/09/1994 ^b	-7.23	4.432	66.72±0.47	3540±60
Bakenskop	35	13/09/1994 ^e	-10.12	3.430	n.r.	n.r.
Golf Course	59	26/09/1994 ^e	-12.01	4.410	33.61±0.35	8960±90
	59	20/09/1994 ^b	-11.25	5.633	71.72±0.46	2890±50
Fractured rock aquifer	95	10/09/1994	-11.53	6.133	n.r.	n.r.
	72	16/09/1994 ^e	-11.12	5.777	79.36±0.56	2070±60
	72	10/09/1994 ^b	-11.13	6.39	n.r.	n.r.
Calcrete samples	72	n.r.	-12	-	0.07±0.16	44700
	J*	n.r.	-14.5	-	0.55±0.06	45700

¹ uncorrected age of ^{14}C fixing, calculated from half-life = 5730 years with initial activity of ^{14}C = 100 pmC.

^b beginning of pumping test ^e end of pumping test * Sample J, location unknown.

Carbon-13 ratios for dissolved inorganic carbon in the fractured rock aquifer and Golf Course breccia pipe range from -11 to -12‰. These values are typical of groundwaters that have evolved by the dissolution of marine carbonates by CO_2 developed in the soil zone. Marine carbonate minerals typically have $\delta^{13}\text{C} \approx 0$ to -6‰, while soil carbonate precipitating in an open system has a signature close to $\delta^{13}\text{C} \approx -15$ ‰. Biogenic CO_2 has $\delta^{13}\text{C} \approx -23$ to -25‰ for respiration of vegetation that photosynthesises under a C_3 pathway (Salomons and Mook, 1986). The C_3 metabolic pathway is used by most woody plants including non-succulent Karoo plants, while grassland vegetation tends to have C_4 photosynthetic pathways which produce soil CO_2 with $\delta^{13}\text{C} \approx -14$ to -12‰ (Bond *et al.*, 1994).

The reaction:



combines plant-derived carbon dioxide with $\delta^{13}\text{C} \approx -24\text{‰}$ and marine carbonate with $\delta^{13}\text{C} \approx 0\text{‰}$ in equal proportions to produce dissolved inorganic carbon with a mean value of $\delta^{13}\text{C} \approx -12\text{‰}$. Elevated TIC concentrations provide additional evidence for carbonate dissolution in the Golf Course and fractured rock groundwater.

The sodic groundwaters from Kopoasfontein and Witwal breccia pipes are enriched in heavy carbon isotopes in relation to the calcic water samples. The cause of the enrichment is unknown, but could be related to different soil CO_2 conditions, carbon isotope fractionation during methanogenesis, or the addition of magmatic or metamorphic CO_2 during the hydrothermal history of the breccia pipes. Van der Kemp *et al.* (2000) have shown that the $\delta^{13}\text{C}$ of soil CO_2 produced by microbial activity increases with decreasing CO_2 partial pressure. The high $\delta^{13}\text{C}$ values for Kopoasfontein could be related to lower microbial activity at this particular site, and hence low $p\text{CO}_2$, in the soil zone where this water was recharged. This is not the most plausible explanation, however, for the following reasons: The Karoo shrub vegetation cover is similar for the whole study area, so it is unlikely that the soil CO_2 conditions will vary widely from one site to the next. It is also doubtful whether differences in microbial activity would produce a large enough difference in $\delta^{13}\text{C}(\text{CO}_2)_{\text{soil}}$ to explain the shift in $\delta^{13}\text{C}(\text{TDIC})$ in the groundwater between the Golf Course and Kopoasfontein sites. From equation 3.4, the soil CO_2 $\delta^{13}\text{C}$ would need to increase from about -24‰ to about -10‰ from the Golf Course to Kopoasfontein, assuming the water at both sites has reacted with the same marine carbonates. Witkop and Bakenskop have $\delta^{13}\text{C}$ ratios intermediate between the sodic breccias and the Golf Course and fractured rock boreholes and could contain mixed water types.

The chemical and stable isotope composition of these waters suggests that all samples have undergone some degree of reaction with “dead” carbon from carbonates or organic matter which will dilute the ^{14}C signature. All but one of the samples (73, 18/10/94) is supersaturated with respect to calcite. The uncorrected ages in Table 3.11 would, therefore, be maximum ages for these waters, unless mixing has occurred.

Three different approaches were attempted to correct groundwater ages for the effects of chemical reactions. The assumptions in the models used for the corrections are not all valid for the conditions at Calvinia and these often give negative results, shown as “undefined” in Table 3.12. This illustrates the difficulties in establishing absolute recharge ages for the Calvinia groundwaters. Some of the samples (e.g. 646) also appear to contain mixtures of water sources of different ages, which complicates age determination.

The empirical approach relies on a statistical estimate of initial ¹⁴C activity in equation (3.3), which is taken as A₀ = 85 pmC in these calculations. This value is considered to be a reasonable estimate for sediments with fine-grained carbonate and has been applied to other studies in Southern Africa (Vogel, 1970). Although this model, unlike the other two, is not based on theoretical principles, it does give positive results for all the samples.

Table 3.12. Adjusted ¹⁴C ages (years) for Calvinia groundwaters based on empirical, chemical and isotopic corrections of initial ¹⁴C activity. Undefined ages indicate that negative values were obtained.

Sample	Date sampled	Empirical (Vogel, 1970)	Chemical (Tamers, 1969)	Isotopic (Fontes & Garnier, 1979)
73	10/10/94	9990	5600	2940
73	18/10/94	10560	6170	2460
61	17/09/94	11520	7190	2170
646	21/09/94	2000	undefined	9855
646	23/09/94	2140	undefined	12180
59	20/09/94	7670	undefined	31160
59	26/09/94	1410	3370	undefined
72	16/09/94	560	undefined	undefined

For chemical correction, the speciation of total inorganic carbon in the samples was calculated using WATEQ4F (Ball and Nordström, 1991) and then used to adjust the initial ¹⁴C activity in the age calculations to account for the dilution by “dead” ¹⁴C in carbonates. The adjustment uses equation (3.5), where *m*CO₂ and *m*HCO₃⁻ are the molal concentrations of CO₂ and HCO₃⁻ in the water. The assumption is made that soil CO₂ is modern and the ¹⁴C activity of soil CO₂, *A*_{soil}, is 100 pmC (Tamers, 1967).

$$A_0 = \frac{mCO_2 + 1/2 mHCO_3^-}{mCO_2 + mHCO_3^-} \times A_{soil}$$

..... (3.5)

Tamers' model also contains the implicit assumption that all carbon added to the water by carbonate dissolution will be "dead ^{14}C " from very old carbonates i.e. with $A = 0$ pmC. The two calcrete samples from the area that were analysed by Talma fit this description, but there is no information on whether these samples are representative of the carbonate in the local soils and aquifers. The supersaturation of most groundwater samples with respect to carbonate species suggests that there are also modern secondary carbonates forming in soil zone in the area. These minerals will not have a 0 pmC signature and the model assumptions will break down if young secondary carbonates react with the groundwater, as is suspected to have occurred for the non-sodic samples 646, 59 and 72.

Isotopic adjustments based on the $\delta^{13}\text{C}$ data (Fontes and Garnier, 1979) were also attempted, but are largely considered to be unreliable. The calculations give highly variable ages, depending on the input values for carbonate minerals and soil CO_2 , neither of which were properly quantified for the area. Talma (1981) reported difficulties in using isotope corrections for Karoo sandstone aquifers because of the uncertainties in the isotope content of soil CO_2 .

The values reported in Table 3.12 were calculated using the equation:

$$A_0 = \frac{\delta^{13}\text{C}_{\text{TIC}} - \delta^{13}\text{C}_{\text{cc}}}{\delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{cc}}} \times A_{\text{soil}} \quad \dots\dots\dots (3.6)$$

with $\delta^{13}\text{C}_{\text{TIC}} = \delta^{13}\text{C}$ of water sample and $\delta^{13}\text{C}_{\text{cc}} = \delta^{13}\text{C}$ of aquifer carbonate, taken as -12‰ from the calcrete sample data. The $\delta^{13}\text{C}_{\text{CO}_2}$ value = $\delta^{13}\text{C}$ of soil gas CO_2 , which was calculated from a mass balance without isotopic fractionation using NETPATH (Plummer *et al.*, 1994). This method gives more positive age results than mass balance with fractionation or open system equilibration calculations, but still gives negative ages for two of the samples and unreasonably old ages for waters that are known to have a shallow alluvial component.

The isotopic approach is still oversimplified, since it ignores the contribution of organic matter and other potential sources of CO_2 in the aquifer. It is also hampered by large uncertainties in the input $\delta^{13}\text{C}$ data.

3.8 Summary of findings and conclusions

A naturally-occurring high pH, fluoride-rich water is found in the Kopoasfontein breccia pipe near Calvinia. Natural waters of pH 9.5 and above have not been previously reported from any other site in the Karoo basin to the author's knowledge. Groundwater samples from inside the breccia pipe have pH values up to 10.1 and moderate salinity, ranging in EC from 62 to 88 mS/m. No evidence of seasonal fluctuations in water quality has been observed over a six year period, but multilevel samples, collected during drilling and down-hole logging, have revealed minor vertical variations. Salinity decreases slightly with depth while concentrations of F and Si increase. Calcite saturation also decreases with depth, the deepest samples being undersaturated with respect to calcite.

The Kopoasfontein groundwater is characterised by a slightly elevated temperature of 24 to 25°C inside the pipe, compared with samples from outside the pipe which are typically 20 to 23°C, and those in alluvial aquifers which average 19°C. The warmer temperature is thought to indicate relatively deep transport of the groundwater that feeds the breccia pipe.

Major cations show a dominance of Na^+ and very low concentrations of Ca^{2+} and Mg^{2+} , leading to the classification of Kopoasfontein as a sodic breccia pipe in this study. Chloride is the major anion in solution while both HCO_3^- and CO_3^{2-} have an appreciable contribution to the anionic charge at this high pH. Sulphate concentrations show greater variability than the other major ions and are expected to be influenced by redox changes and the presence of sulphide minerals in the breccia pipe. The groundwater composition is undersaturated with respect to gypsum, near equilibrium with respect to calcite and fluorite and slightly supersaturated with respect to quartz.

The Kopoasfontein groundwater contains high concentrations of F^- (10 to 16 mg/L), the source of which will be discussed in following chapters. Concentrations of Si are also elevated (26 to 44 mg/L as SiO_2) probably as a consequence of long residence times and warmer temperatures associated with deep groundwater transport. Dissolved oxygen and NO_3^- are typically absent, while 1 to 1.6 mg/L NH_4^+ is present, indicating reducing conditions in the subsurface. Despite the presence of iron, lead and copper sulphides in the mineralised breccia pipe, trace metal concentrations in solution are generally low because of the reducing environment and the low

solubility of their oxide, hydroxide and carbonate minerals at high pH. Oxyanions of arsenic are, however, mobile under these conditions and concentrations of 0.3 to 0.4 mg/L As are observed in the deepest borehole.

Shallow groundwater at the Kopoasfontein site is perched above an impervious dolerite sill and has a chemical character which appears to have evolved independently from that of the water below the dolerite. This groundwater has a lower pH (7.3 to 8.2) and higher salinity (95 to 130 mS/m) than the deep groundwater and has higher dissolved Ca^{2+} and Mg^{2+} and lower F^- concentrations. The perched water shares these characteristics with other groundwater samples from fractured shale and dolerite aquifers in the Calvinia area, particularly fresher groundwater in the north of the study area near the Hantamsberg mountain range, and is probably of similar origin. Stable isotopes of hydrogen and oxygen indicate that both the deep and shallow water at Kopoasfontein is derived from meteoric water with little or no evaporation before infiltration.

The natural Kopoasfontein groundwater composition has now been perturbed by dewatering and injection of fresh surface water into the pipe. Injection has decreased the groundwater pH and increased salinity in the upper 100 m of the pipe. This is a pilot experiment to assess the feasibility of using the pipe for underground water storage as a backup supply for Calvinia.

Low salinity, $\text{Na-HCO}_3/\text{Cl}$ dominant groundwaters are also present in the breccia pipe at Witwal and at a small number of isolated boreholes in dolerite or shale environments (JV1, CT58, DW12, 80, 50 and 93). Detailed geological records are not available for most of the other sodic water sources, so it is not known whether these are also associated with breccia pipes. Some of these waters have elevated pH and F^- , but from the available data, the extreme values found at Kopoasfontein are not encountered elsewhere in the Calvinia area.

There are also known breccia pipes in the region which do not yield the Na-Cl/HCO_3 water type found at Kopoasfontein, but instead share a similar composition to that of the groundwater in alluvial and fractured rock aquifers in the area. Examples include the breccia pipes at the Golf Course, Airfield and Witkop, which have been classed as calcic breccia pipes in this study. These are typically waters of near-neutral pH, moderate to high salinity and a major anion composition which is dominated by Cl^- , with $\text{Na}^+/\text{Ca}^{2+}/\text{Mg}^{2+}$ sharing the cation dominance. Alluvial

groundwater appears to be a major component in the calcic breccia pipes near the Oorlogskloof river channel. Bakenskop breccia pipe is probably a mixed water type, since these samples tend towards Na^+ dominance, but do not group with the other sodic pipes.

Deuterium and oxygen-18 relationships indicate that the Witkop and Golf Course pipes, located to the south of the Oorlogskloof river channel, contain evaporated water and may be at least partially recharged by local infiltration of surface water from this drainage system. The Bakenskop pipe, like the Kopoasfontein and Witwal pipes to the north of the Oorlogskloof, contains water of meteoric origin which has not been significantly evaporated.

Groundwater in the western Karoo tends to occur in two main aquifer types: shallow alluvial primary aquifers along drainage courses and secondary fractured rock aquifers, often associated with dolerite intrusions. Around Calvinia, alluvial groundwater tends to be brackish to saline, while the pH is well-buffered between 7.0 and 8.3, probably by reaction with carbonate minerals in the sediments. Calcite saturation indices were found to be above zero for most of the alluvial groundwater samples in the study area. The more mineralised alluvial samples also tend towards equilibrium with respect to gypsum. The majority of these waters are of Na-Cl type. Limited stable isotope data suggests that leaching and dissolution of salts from the sediments are the mechanism for accumulation of salinity, rather than evaporative concentration of solutes in meteoric water.

Groundwater from fractured rocks is similar to the alluvial groundwater, also having a pH between 7.2 and 9.1 and being generally slightly supersaturated with respect to calcite. The groundwater from secondary aquifers, however, has a generally lower solute content than the alluvial samples, with EC mostly below 300 mS/m. Fractured rock groundwaters also have a wider spread of major ion compositions, ranging from a few samples of Ca/Mg- HCO_3 type near the Hantamberg mountains to the more common Na-Cl type shared with the alluvial groundwaters along the valley floors.

Absolute age dating of some of the Calvinia groundwaters with ^{14}C was generally unsuccessful, because of complex reactions with inorganic and organic carbon sources in the subsurface. Carbon-13 ratios indicate that a source of heavy carbon may be contributing to the dissolved

inorganic carbon in sodic breccia pipes and also adding “dead” ^{14}C . Uncertainties in the input values of $\delta^{13}\text{C}$ for soil gas and aquifer carbonates in this environment, however, limited the application $\delta^{13}\text{C}$ ratios for age corrections. Provided no significant mixing of different aged groundwaters occurs, indications are that the water in the sodic breccia pipes is older than the calcic breccias and the fractured aquifer samples. Witwal and Kopoasfontein breccia pipe groundwaters are estimated to be 5000 to 10 000 years old, while the groundwater in the Golf Course breccia pipe and fractured rock borehole 72 may be 500 to 2000 years old. These estimated ages are all maximum ages based on ^{14}C measurements. No tritium data was available to test for the presence of recent recharge water in the area.

The next chapter deals with the characterisation of the rocks and minerals in the Kopoasfontein breccia pipe that may improve the understanding of the local hydrochemistry. Groundwater evolution and the controls on water chemistry will be addressed further in Chapter 6.

CHAPTER 4

GEOCHEMICAL CHARACTERISATION OF ROCKS AND MINERALS IN THE KOPOASFONTEIN BRECCIA PIPE

4.1 Introduction

The groundwater at Kopoasfontein is sodium-dominant, fluoride-rich and has an exceptionally high pH, a composition distinct from that found elsewhere in Karoo aquifer systems, with the possible exception of other sodic breccia pipes. The localised occurrence of this groundwater type suggests that the water chemistry in sodic pipes is strongly influenced by interactions with the minerals at these sites. A detailed study of the composition of the rocks and minerals in the Kopoasfontein breccia pipe has been undertaken, so that an assessment might be made of their contribution to the groundwater chemistry. The study includes a search for possible mineral sources of F, As and N species present in the groundwater.

Drilling logs and hand specimens have been used to investigate the structure, lithology, bulk composition and mineralogy of the Kopoasfontein breccia in comparison with neighbouring, undisturbed shale sequences. The analysis considers minerals in the shale matrix, dolerite intrusions and metal sulphides and other secondary minerals in the fractures and cavities of this fossil hydrothermal system.

This chapter also describes the deposition of the Karoo Supergroup in the western part of the Karoo basin and the intrusion of dolerites during the Gondwana break-up. The magmatic episodes with which the dolerites are associated, are also speculated to be the origin of the Calvinia breccia pipes. The stratigraphy of the Calvinia area was documented in Chapter 1 and maps of the regional and local geology provided in Figures 1.4 and 3.1, respectively.

4.2 Lithology and geological evolution of the Calvinia area

4.2.1 Karoo sedimentation (300 - 150 Ma)

The base of the Karoo Supergroup is formed by Permo-Carboniferous glaciogenic tillite of the Dwyka Group which outcrops in the Nieuwoudville area, to the west of Calvinia. This initial glacial phase of deposition was followed by sedimentation in the vast intra-cratonic Ecça sea as the Gondwana supercontinent moved north westwards from the southern polar region towards tropical latitudes (Tankard *et al.*, 1982). Basin sediments were later buried by fluvial and deltaic deposits, represented by the Permo-Triassic Beaufort Group which outcrops to the east of Calvinia, south of the town of Williston.

The Ecça Group comprises mainly clastic sediments deposited in an extensive, shallow, land-locked basin which experienced only rare marine incursions. The palaeosalinity of the water in the Ecça basin is considered to have been predominantly fresh to brackish. In the Calvinia area, the Ecça Group is subdivided into the Prince Albert, Whitehill, Tierberg and Waterford Formations. The Tierberg Formation outcrops at the surface in the flat-lying areas around Calvinia, but is often covered with alluvium, especially along the floodplain of the Oorlogskloof River, while the Whitehill and Prince Albert Formations are found at depth in boreholes drilled for geological exploration. The Waterford Formation is present at surface on top of the Hantamsberg and Keiskie mountains.

Initially muds accumulated in the Ecça sea under anoxic, starved basin conditions. Postglacial shales and mudstones of the Prince Albert Formation are generally horizontally laminated with sporadic calcareous and ferruginous bands. Fossils in the mudstones indicate a likely marine incursion into the Karoo basin from the west (Tankard *et al.*, 1982). The Whitehill Formation comprises a widespread, thin band of black, carbonaceous, pyritic shale near the base of the Karoo sequence, covering an area of 300 000 km² and varying in thickness from 10 to 80 m. The depositional environment is proposed to be a brackish-water continental shelf, supported by the presence of fossil fish, crustaceans and aquatic reptiles (*Mesosaurus*).

The Whitehill Formation was once contiguous with the oil-producing Irati Formation in South America, but hydrocarbon prospects in the Whitehill have been limited by factors such as heating during diagenesis and the lack of a suitable sandstone reservoir. Oil exploration in the Karoo has now been abandoned (Cole and McLachlan, 1990).

The Tierberg Formation, which overlies the Whitehill Formation, consists predominantly of finely-laminated grey, blue or green shales with thin intercalated calcareous layers and lenses. The shales contain illite as the dominant clay mineral and are fairly rich in pyrite (Viljoen, 1989). The Tierberg shales represent a mud-suspension deposit that accumulated under quiescent conditions in a large shallow basin. They coarsen upwards into the arenaceous delta-front and delta-plain sandstones of the Waterford Formation (Cole and Vorster, 1999).

The overlying Beaufort Group sedimentary rocks are absent along the western margin of the Karoo basin, which includes the area around Calvinia.

4.2.2 Karoo volcanism (200 - 190 Ma)

Karoo deposition was terminated by a violent episode of Jurassic volcanism, associated with the break up of the Gondwana supercontinent (Tankard *et al.*, 1982). An initial explosive episode resulted in volcanic vents, diatremes and tuffs, which appear to be confined to distinct centres, mainly in southern Lesotho and the Eastern Cape (Lock *et al.*, 1974). These diatremes and associated features are ascribed to phreatic activity when hot magma came into contact with groundwater causing violent production of steam. The explosive phase was followed by extrusion of vast sheets of basaltic lava flows, preserved as the Drakensberg plateau.

Dykes and sills

Almost the entire Karoo basin north of the latitude 32° 30' S was intruded contemporaneously by a suite of dolerite (diabase) sills up to 150 m thick and dykes up to 100 m long (Cole and Vorster, 1999). The thickest sills have intruded along preferential horizons such as the contact between the Dwyka and Prince Albert Formations. The composition of the dolerites is mostly tholeiitic, while the host sediments near the intrusions have undergone contact metamorphism to hornfels or been metasomatised into a granophyre-type rock (Walker and Poldevaart, 1941).

Dolerite breccia pipes

Clusters of breccia pipes occur along the western and northern edges of the Karoo basin (Figure 4.1) and several pipes are found in the area around Calvinia (Woodford *et al.*, in prep.). These clusters range in size from two pipes at Williston to a large cluster of over 200 pipes over a 50 km² area north of Loeriesfontein. The documented breccia pipes are mostly restricted to the Ecça Group, with only a few pipes near Muldersfontein being found to have penetrated the base of the Beaufort Group.

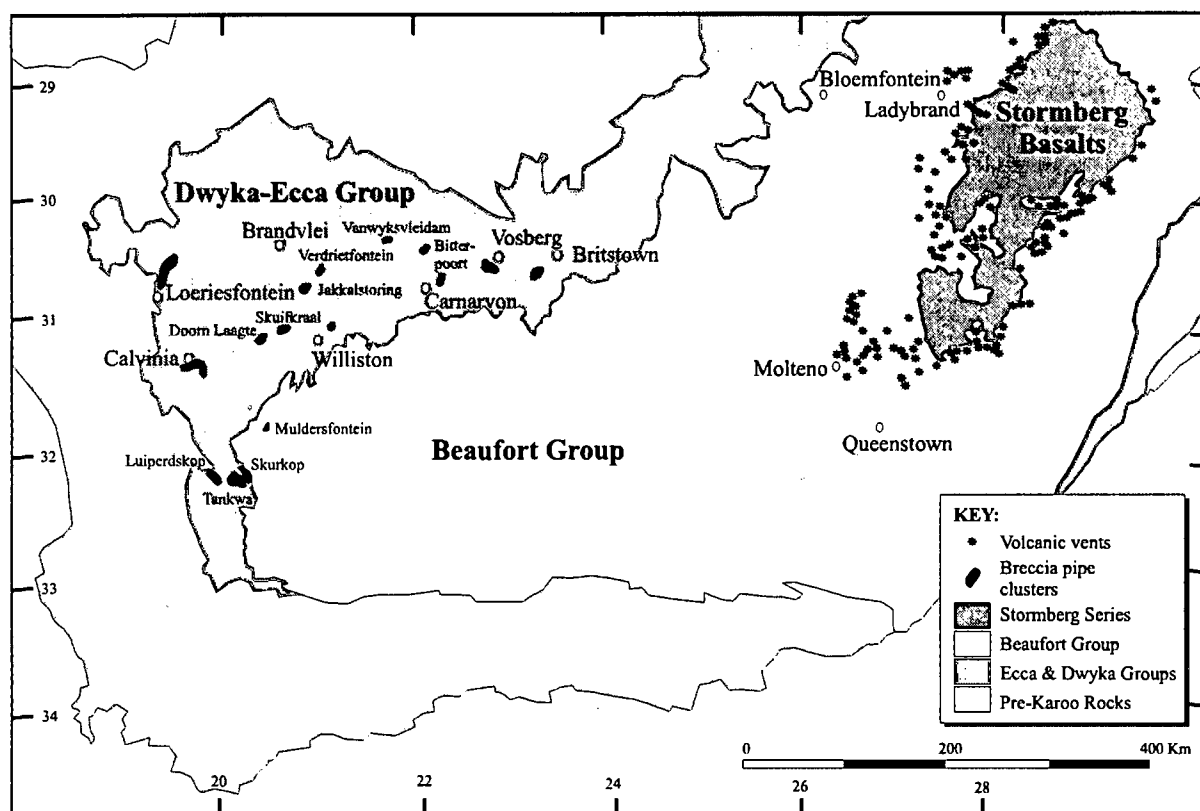


Figure 4.1. Distribution of mapped breccia pipe clusters and volcanic vents in the Karoo Basin (Woodford *et al.*, in prep.).

Karoo breccia pipes were originally thought to be of Cretaceous age, because of their occurrence in proximity to the Salpeterkop volcanics of the Sutherland Suite and their apparent association with swarms of kimberlite fissures in the western Karoo. The Sutherland Suite intrudes the Karoo Supergroup over a small area in the Northern Cape and, at a few localities, also intrudes the older Karoo dolerites. The suite comprises pipes, dykes and sills of lamprophyric, olivine melilititic, carbonatitic and trachytic composition as well as breccia pipes and dykes, all thought to be

related to the same primary magma (Cole and Vorster, 1999). Subsequent work, including the examination of drilling cores (Woodford *et al.*, in prep.), has indicated that the Calvinia breccia pipes are associated with the intrusion of dolerites during the earlier Jurassic phase of Karoo magmatism.

The breccia pipes generally form small, prominent, low-relief, rounded or elongated hills in the outcrops of the Tierberg shales (Viljoen, 1989) or circular depressions with characteristic calcrete development. They can be recognised by their circular relief and white alteration halo on aerial photographs. Breccia pipes are expected to be roughly cylindrical in shape and usually range between 50 and 80 m in outcrop diameter. They vary in geological appearance and mineralogy. Woodford *et al.* (in prep.) recognise two facies of breccia pipes in the western Karoo:

- ▶ *Molten facies*: domed, baked, molten, recrystallised and highly contorted sediment containing xenoliths from the underlying strata. Melting is often accompanied by gas-vugs containing secondary calcite, quartz, zeolites and, to a lesser extent, garnets such as grossular and vessuvianite.
- ▶ *Breccia facies*: true breccia with fractured, broken, shattered, displaced and re-cemented blocks of sediment, often accompanied by mineralisation of quartz, calcite, gypsum, chlorite, apophyllite, barite, siderite, fluorite, pyrite, pyrrhotite, sphalerite, galena, chalcopyrite, marcassite, bornite and traces of gold.

The country rock around the pipes is generally disturbed and foliated. The molten facies is more conspicuous in the field, which may partly account for the fact that this type of breccia pipe is more commonly reported than the true breccia facies. The degree of mineralisation is not always evident from the outcrop, but no economically viable sulphide ore bodies have been found in association with the Karoo breccia pipes. Although molten sediment occurs as the matrix in some of the pipes, the breccia clasts themselves comprise baked and brecciated sandstone and shales and not igneous material, as is the case for volcanic vents or diatremes.

In the Calvinia area, breccia pipes are linked to the intrusion of thick dolerite sills at the Dwyka-Prince Albert and Prince Albert-Whitehill contact zones. Later dolerite sills transect the upper portions of some of the breccia pipes, for example along the contact between the Whitehill and

Tierberg Formations. The lithological units are highly disrupted in the Calvinia breccia pipes, but the stratigraphic succession has not been disturbed.

The Whitehill Formation in the vicinity of the breccia pipes is baked and leached from a black carbonaceous shale to a white, contorted meta-sediment, while the Tierberg shales are often converted to mineralised, clast-supported breccia, with highly disordered clasts and numerous open cavities or vugs. Mineralisation in the Prince Albert Formation is zoned by grossular and vessuvianite garnets, while sulphide mineralisation only occurs above the Whitehill Formation (Woodford *et al.*, in prep.). Calcite, chlorite and apophyllite in the upper Tierberg portion of the Kopoasfontein breccia pipe represent a much lower grade of metamorphism, related to the cooling phase of hydrothermal activity.

The mode of emplacement of the Karoo breccia pipes is not fully understood. Viljoen (1989) suggests that they represent a sudden escape of gas, possibly associated with the intrusion of kimberlite or dolerite. Woodford *et al.* (in prep.) propose that localised, explosive hydrothermal activity occurred when the lowermost dolerite sills intruded into the partially indurated, “wet” Karoo Supergroup sediments during the Jurassic. This resulted in the brecciation and melting of the host sediments, as well as the upward transport of elements from the Prince Albert and Whitehill Formations.

The breccia clasts from the Tierberg portion of the Kopoasfontein pipe, however, dispute this theory. The clasts are angular and preserve the original shale lamination, which can only be explained if whole sedimentary sequence up to the Tierberg had already undergone diagenesis before brecciation. Explosive activity may have been triggered by the rapid generation of steam when deeply circulating meteoric waters came into contact with the intruding magmas.

4.3 Structure and lithology of the Kopoasfontein breccia pipe

The breccia pipe at Kopoasfontein has been investigated by core drilling to 755 m (borehole 56) and correlated with the undisturbed stratigraphy from another core (borehole 74), drilled 500 m away, outside the pipe. The location of these exploration boreholes is indicated on Figure 3.3.

Figure 4.2 shows the facies logged for these two cores by Chevallier¹ and Balaban² (pers. comm.).

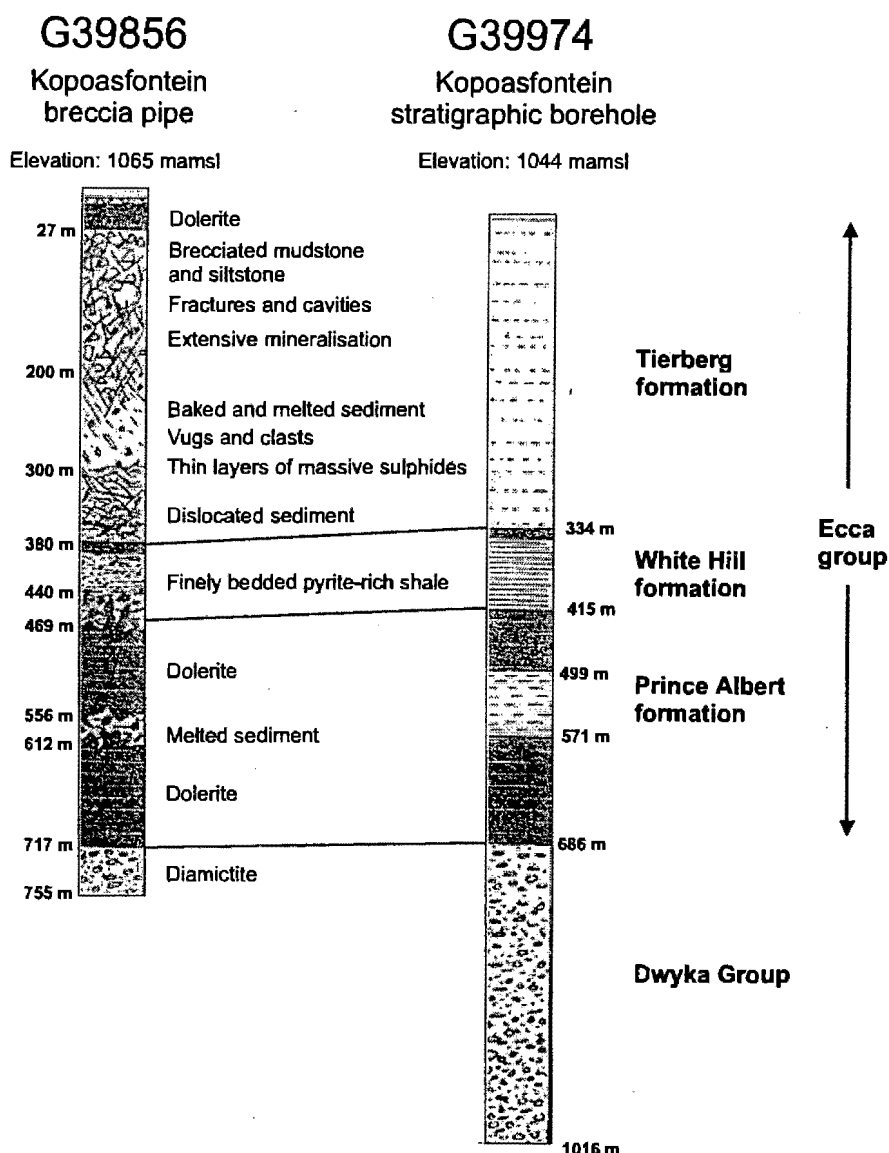


Figure 4.2. Lithological sequence of boreholes 56 and 74 at Kopoasfontein, as logged by Chevallier and Balaban (pers. comm.).

The Kopoasfontein breccia pipe is of the true breccia facies comprising fragmented, displaced and re-cemented blocks of sediment and has weathered to produce a surface depression

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² Institute of Geology and Geophysics, Bucharest, Romania

approximately 100 m in diameter. The southern edge of the pipe outcrop abuts a ridge of dolerite. The sediment at surface appears to be broken and re-cemented, but still homogeneous in composition. Clasts of baked, leached and altered shales and mudstones range in size from several centimetres to less than a millimetre (microbreccia). Ecca and Dwyka Group rocks can be distinguished in the core samples, but their boundary is uncertain and the formations of the Ecca Group are difficult to recognise. Dolerite sills at 380 m and 469 m have been used to locate the Tierberg-Whitehill and Whitehill-Prince Albert boundaries respectively.

The clast-supported breccia in the upper part of the Kopoasfontein breccia pipe contains numerous open cavities. The largest cavity recorded while drilling borehole 56 has a depth of 9 m. This borehole also encountered highly-pressurised methane gas at 109 m below surface in one such cavity (Woodford *et al.*, in prep.). The fractures and cavities in the Tierberg portion of the pipe have been mineralised by hydrothermal activity.

Two early dolerite sills intruded along the Dwyka-Prince Albert and Prince Albert-Whitehill contacts. Alteration features are noted along the interface of these dolerites with the sediments, including: localised magmatic differentiation and layering in the dolerite; extraction of the leucocratic phase; injection of magmatic material into the sediments and partial digestion of sediment material. Based on these observations, Hallbauer *et al.* (1995) concluded that the intrusion of these sills was the cause of the brecciation and subsequent mineralisation. Local hydrothermal, contact metasomatic reactions leached elements from the Whitehill and Prince Albert Formations and deposited sulphides and other secondary hydrothermal minerals in the upper brecciated rock column.

Another two minor dolerite sills have been intruded later at approximately 27 m and 380 m below surface. These sills post-date the brecciation and mineralisation and were, therefore, emplaced during (a) subsequent event(s) of Karoo volcanism.

4.4 Bulk chemical composition of Kopoasfontein rocks

The bulk of the material in the Kopoasfontein breccia pipe comprises very low grade metaclastites, which have been subjected to mechanical disruption, contact metamorphism and hydrothermal alteration. The breccia clasts are frequently coated or cemented with secondary hydrothermal minerals, which are also deposited as veins and fracture-fillings in the breccia pipe. These late stage minerals form only a minor component of the total rock. Dolerite occurs as an intrusive igneous phase at various depths in the breccia pipe.

Rock samples were collected from the diamond drilled geological core, 56, for bulk compositional analysis and drilling chips from percussion-drilled borehole 54B, for preparation of thin sections and apophyllite and sulphide mineral separates. Further core segments were later sampled to investigate geological nitrogen and carbon in the breccia pipe shales. These included brecciated and baked shales from core 56 and unaltered Whitehill Formation and Tierberg Formation shales from core 74. Drilling cores for the exploration boreholes 56 and 74 were housed with the Council for Geoscience and drilling chips provided by DWAF.

4.4.1 Brecciated sediments

Fourteen samples of brecciated and mineralised Tierberg Formation sediments from the upper 350 m of the Kopoasfontein breccia pipe were obtained from the borehole 56 drill core for chemical and mineralogical analysis as described by Cavé (1999). The major oxide and trace element components in the samples, determined by wavelength dispersive XRFS, are reported in Table 4.1. Sedimentary rocks from the Whitehill, Prince Albert and Dwyka Formations in the lower portion of the breccia pipe core were not sampled.

The samples contain a high proportion of Si and Al, reflecting the prevalence of quartz and aluminosilicates in the rocks. Base cations in the brecciated sediments are dominated by K, Mg and Na, but Ca concentrations are low, especially in samples where secondary minerals are absent. The ratio K_2O/Na_2O shows a generally decreasing trend with depth.

Table 4.1. Bulk composition of brecciated sediments from the upper 350 m of the Kopoasfontein breccia pipe. Data from Cavé (1999; n = 14 samples), except for nitrogen and carbon data (This study).

Major oxides (weight %)	Mean	Std. dev.	Trace elements (mg/kg)	Mean	Std. dev.	Trace elements (mg/kg)	Mean	Std. dev.
SiO ₂	60.5	2.13	F	360	340	Rb	170	37
Al ₂ O ₃	18.0	1.58	Sc	16	3	Sr	113	35
Fe ₂ O ₃	7.11	1.38	V	114	14	Y	34	10
MgO	2.00	0.47	Cr	54	11	Zr	150	18
CaO	1.24	1.06	Mn	800	178	Nb	13	1.5
Na ₂ O	2.43	0.98	Co	13	2	Ba	830	117
K ₂ O	3.89	0.73	Ni	20	4	Th	15	2
Minor oxides ¹	1.15	0.85	Cu	12	12	U	3.8	0.8
H ₂ O loss (110°C)	0.31	0.43	Zn	52	25	N [#]	4026	5
LOI (950°C)	3.35	1.00	As	11	6	C [*]	700	
Total oxides	100.0	0.45	Pb	23	22			

¹ Minor oxides = SO₃ + P₂O₅ + MnO + TiO₂

[#] Determined by nitrogen analyser on composite powdered sample, n = 2

^{*} Determined by combustion CHN analyser, sample from 181 m, n = 1

Average trace element concentrations are not dissimilar to the typical concentrations for shales reported by Drever (1997; p. 176). High standard deviations for CaO, F and the chalcophile elements (Ni, Cu, Zn, As, Pb) reflect localisation of these elements in the secondary hydrothermal minerals (e.g. calcite, apophyllite and metal sulphides), which are not distributed homogeneously in the breccia pipe (Cavé, 2000). Unpublished data from Chevallier (pers. comm.) gives maximum concentrations of 3000 mg/kg Zn, 2220 mg/kg Cu, 1200 mg/kg Pb, 106 mg/kg As and 37.2% Fe₂O₃ in selected mineralised samples from the pipe.

Previous leaching tests on the Kopoasfontein rocks mobilised a significant amount of nitrogen species in solution (Cavé, 1999; Cavé and Fey, 2000). Up to 10 mg/L NH₄⁺ was leached by reacting finely-crushed Tierberg shales from the breccia pipe with deionised water for two weeks (solid:water = 330 g/L, pH = 8.3). A composite sample of Tierberg shale material from borehole 56, comprising approximately equal proportions of powdered rock from the fourteen core segments, was submitted to the US Geological Survey for total N analysis (J. Holloway, analyst) to investigate the extent of the geologic nitrogen reservoir. The NH₄⁺ released in the leaching tests represents only a small fraction (0.006) of the 0.4 wt% total nitrogen present in the rock.

Nitrogen and carbon in the rock are discussed further in Section 4.6.

4.4.2 Dolerite

The geochemistry of dolerites (or olivine tholeiites) in the Calvinia area has been studied by Walker and Poldervaart (1941) and Le Roex (1976). A dolerite sample from the core of borehole 56 was also collected and analysed by Cavé (1999) using XRFs.

The chemical composition of the dolerites in the region is fairly consistent, as can be seen from Table 4.2, which compares bulk composition data from Le Roex (1976) and Cavé (1999). The data from Le Roex reflects the composition of dolerite sills classified as “Blaauwkrans type” by Walker and Poldervaart (1941).

Table 4.2. Bulk composition of dolerite samples from the Kopoasfontein breccia pipe core and surrounding area, determined by XRFs analyses (Cavé, 1999; Le Roex, 1976).

Major oxides (weight %)	Core 56 sample ¹	Blaauwkrans type outcrops ²		Trace elements (mg/kg)	Core 56 sample ¹	Blaauwkrans type outcrops ²	
		Mean	Std. dev.			Mean	Std. dev.
SiO ₂	49.9	51.9	0.14	V	240	240	6
TiO ₂	0.84	0.91	0.05	Cr	400	370	21
Al ₂ O ₃	14.7	15.6	0.24	Co	43	51	3
Fe ₂ O ₃	10.7	11.0 ³	0.14	Ni	100	100	9
MnO	0.18	0.16	0.01	Cu	84	95	3
MgO	7.3	7.5	0.16	Zn	67	81	5
CaO	10.0	10.8	0.05	Rb	18	16	11
Na ₂ O	2.4	2.4	0.30	Sr	240	180	17
K ₂ O	0.45	0.54	0.02	Y	22	23	1
P ₂ O ₅	0.13	0.14	0.01	Zr	69	79	5
H ₂ O loss (110°C)	0.60	n.r.		Ba	130	150	38
LOI (950°C)	1.26	n.r.		S	n.d.	660	20
Total oxides	99.4	100.0	0.01	As	4.5	n.r.	n.r.

¹ Sample O, dolerite sill at 380 m in borehole core 56 (Cavé, 1999).

² Dolerite samples from Hantamsberg and Blaauwkrans dolerite sills; n = 9 samples (Le Roex, 1976).

³ FeO + Fe₂O₃ recalculated as Fe₂O₃

Dolerites have lower Si and higher Fe, Mg and Ca than the brecciated shales, related to the absence of quartz and the presence of primary mafic minerals in the dolerite. The K content of

the dolerites is also much lower than that of the shales which host them. Dolerite is classified as a saturated basic igneous rock, having 50-60% total SiO₂.

4.5 Mineralogy of the Kopoasfontein breccia pipe

4.5.1 Shale matrix mineralogy

The shale fragments of the breccia pipe contain weathered, detrital primary minerals from the source rocks and secondary minerals formed during diagenesis and alteration. Thin sections were prepared from hand specimens of the brecciated shales, but positive mineral identification was not possible by optical microscopy, even at 40 times magnification, since the rock materials are extremely fine-grained and have undergone significant alteration.

Quartz, feldspar and phyllosilicate clay minerals were initially identified by powder X-ray diffraction (XRD) analysis as the dominant detrital minerals in the shales of the Kopoasfontein breccia pipe (Cavé, 1999). A more comprehensive characterisation of the individual clay minerals in the brecciated shales has been achieved by isolating the clay size fraction and subjecting this to a series of diagnostic treatments, before XRD analysis.

Brecciated shales from the upper 350 m of the Kopoasfontein pipe were divided into four facies, based on appearance, physical and textural properties and chemical composition. A composite sample of each facies was prepared by combining equal masses of jaw-crushed rock fragments from the original core segments collected from borehole 56 (Table 4.3).

Separation of the <2 µm particles size (using a dispersion-flocculation technique) and treatments for XRD analysis were performed on the samples KF1 to KF4, following the procedures recommended in *Methods of Soil Analysis* (Whittig and Allardice, 1986). Treatments included potassium saturation, magnesium saturation, heat treatment (550°C) and glycerol solvation. The methods of clay separation and diagnostic treatments, as well as the XRD method and instrumental settings, are described in Appendix C.

Table 4.3. Description of composite shale facies samples from the breccia core.

Sample	Core Segments [†]	Depth below surface (m)	Mass of crushed rock fragments (g)	Description of sedimentary rock and Munsell® colour
KF1	A	32.20 - 32.30	20	Mudstone
	B	42.40 - 42.55	20	dark grey N4/ (dry)
	C	65.95 - 66.00	20	black N2.5/ (wet)
KF2	E	119.20 - 119.30	20	Siltstone
	F	133.90 - 134.20	20	light grey 2.5Y 7/1 (dry)
	G	162.40 - 162.55	20	dark grey 2.5Y 4/1 (wet)
	H	169.00 - 169.20	20	
	I	191.40 - 191.50	20	
	J	210.20 - 210.30	20	
KF3	K	242.20 - 242.35	30	Siltstone with dark mottles
	L	261.40 - 261.45	30	greenish grey 5GY6/1 (dry) dark greenish grey 5GY 4/1 (wet)
KF4	M	324.80 - 324.90	30	Shale with dark lamellae
	N	350.90 - 350.95	30	white N8/ (dry and wet)

[†] Segment labels are taken from Cavé (1999), where the individual samples are described.

Expandable layer silicates may retain different amounts of interlayer water when air dried, depending on the nature of the interlayer exchangeable cations. Potassium or magnesium saturation of the clay exchange complex is employed to ensure that expansion as a result of hydration is uniform for all crystals of a particular species. Potassium specifically restricts the interlayer adsorption of water by vermiculites, which collapse to essentially non-expanded structures with an interlayer spacing of 10 Å.

Formation of a stable two-layer water complex in the interlayers of smectite and vermiculite is achieved by Mg saturation and air drying, resulting in an interlayer spacing of approximately 14 Å. The change in interlayer spacing with a change in the exchange cation is what distinguishes the expandable vermiculites and smectites from the non-expandable 2:1 phyllosilicates such as halloysite and mica (illite) (10 Å) and 2:2 phyllosilicates (chlorite, 14 Å). Non-expandable clays have the same d-spacing under either saturation condition. Solvation of Mg-saturated samples with glycerol allows for the positive identification of smectites, which are the only phyllosilicates that can expand the interlayer spacing to 17 to 18 Å under these conditions.

Heating a K-saturated sample to 550°C for 2 hours serves the dual function of collapsing vermiculite structures, which often contain discontinuous, non-exchangeable hydroxy complexes

and destroying kaolin minerals. The first effect allows vermiculites to be distinguished from chlorites, which are generally unaffected by heat treatment, since the continuous hydroxy interlayer (brucite sheet) of chlorites does not collapse. The diagnostic first order maximum for kaolinite at 7.15 Å overlaps with the first order maximum for serpentine and the second order maximum for chlorite. Where heat treatment removes or reduces the intensity of a 7.15 Å peak, the presence of kaolinite is confirmed (Whittig and Allardice, 1986).

X-ray diffraction patterns from the clay mineral samples for the four shale facies in the Kopoasfontein breccia are presented in Figure 4.3. Tables of the relative peak intensities and crystallographic plane spacing (d-spacing) for the major mineral phases can be found in Appendix E. Miller index notation is used to denote the mineral plane causing the X-ray diffraction, for example, {001} and {002} are first and second order reflections off the plane perpendicular to the c crystallographic axis.

Quartz and plagioclase feldspars occur in varying proportions in the shale samples and appear to be most abundant in KF4. They probably represent detrital quartz and feldspar grains in the original siltstones and mudstones. This is a very fine-grained fraction of the relatively hard primary silicates, which should be removed in a typical separation of the clay size fraction. The highly crystalline nature of these minerals produces sharp diffraction peaks, the intensity of which may give an exaggerated impression of the abundance of quartz and feldspar in the samples.

The bulk of the crystalline material in the $< 2 \mu\text{m}$ size fraction is composed of layer silicate clay minerals which have formed by the weathering and alteration of primary minerals. Table 4.4 summarises the minerals observed by XRD analysis and gives a qualitative assessment of the relative proportions present in the $< 2 \mu\text{m}$ size fraction of the Kopoasfontein shale samples.

KF1 Clay fraction (30 - 100 m)
dark grey brecciated mudstone

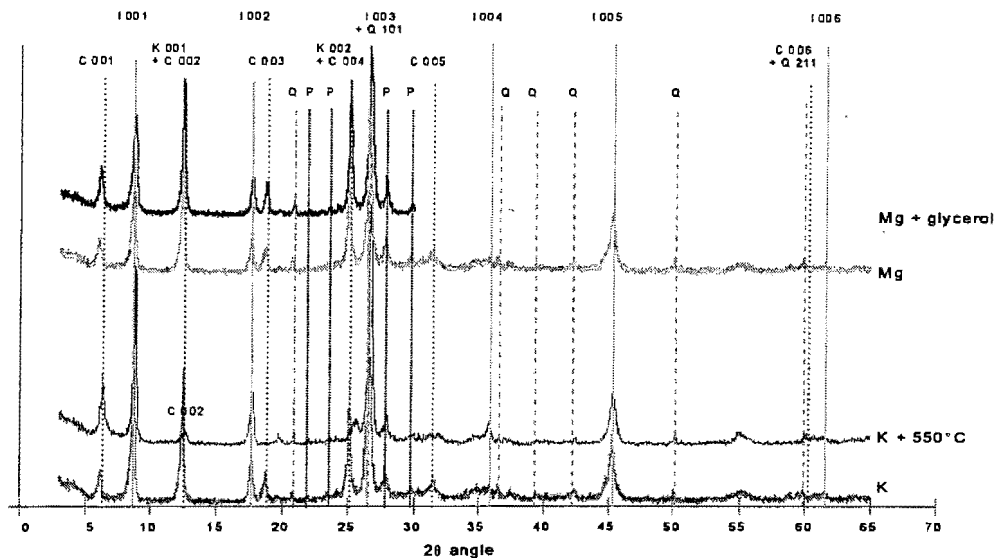


Figure 4.3a). X-ray diffraction patterns for the clay fraction of sample KF1 showing major reflections for chlorite (C), illite (I), kaolinite (K), quartz (Q) and plagioclase feldspars (P). Samples were subjected to four different treatments: potassium saturation (K), heat treatment (K + 550 °C), magnesium saturation (Mg) and glycerol solvation (Mg + glycerol).

KF2 Clay fraction (100 - 220 m)
baked light grey siltstone with vugs

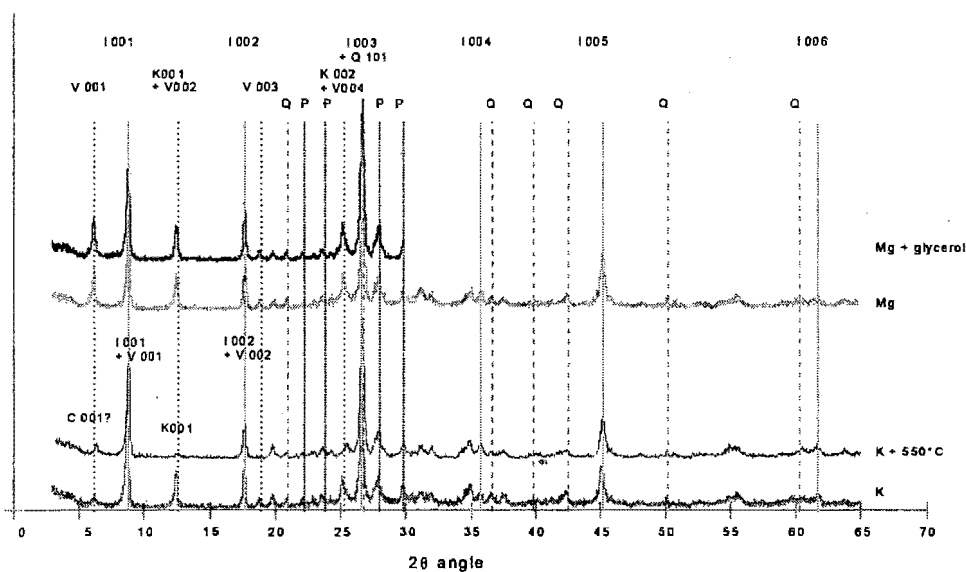


Figure 4.3b). X-ray diffraction patterns for the clay fraction of sample KF2 showing major reflections for vermiculite (V), illite (I), kaolinite (K), quartz (Q) and plagioclase feldspars (P).

KF3 Clay fraction (220 - 300 m)
melted light grey siltstone + clasts

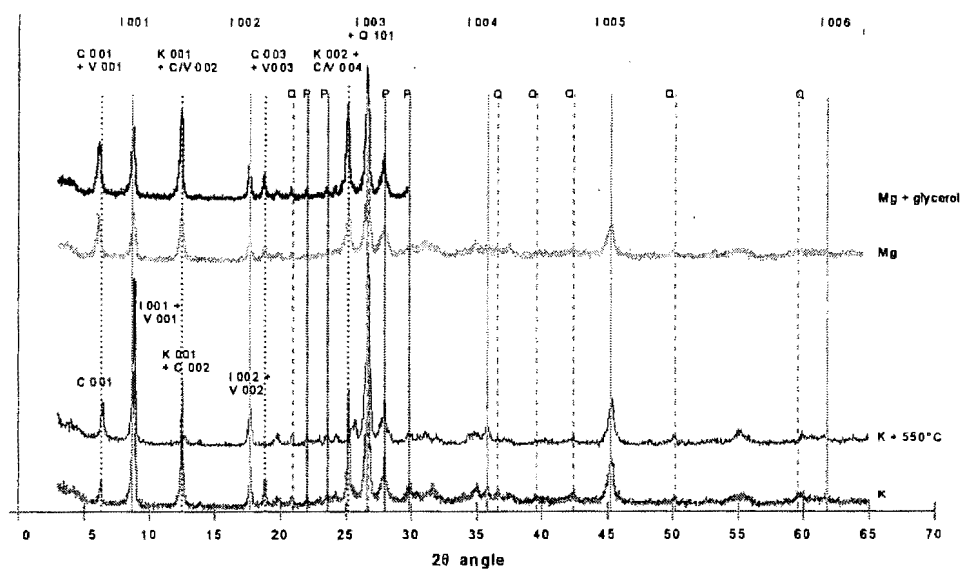


Figure 4.3c). X-ray diffraction patterns for the clay fraction of sample KF3 showing major reflections for vermiculite (V), chlorite (C), illite (I), kaolinite (K), quartz (Q) and plagioclase feldspars (P).

KF4 Clay fraction (300 - 380 m)
dislocated creamy white shales

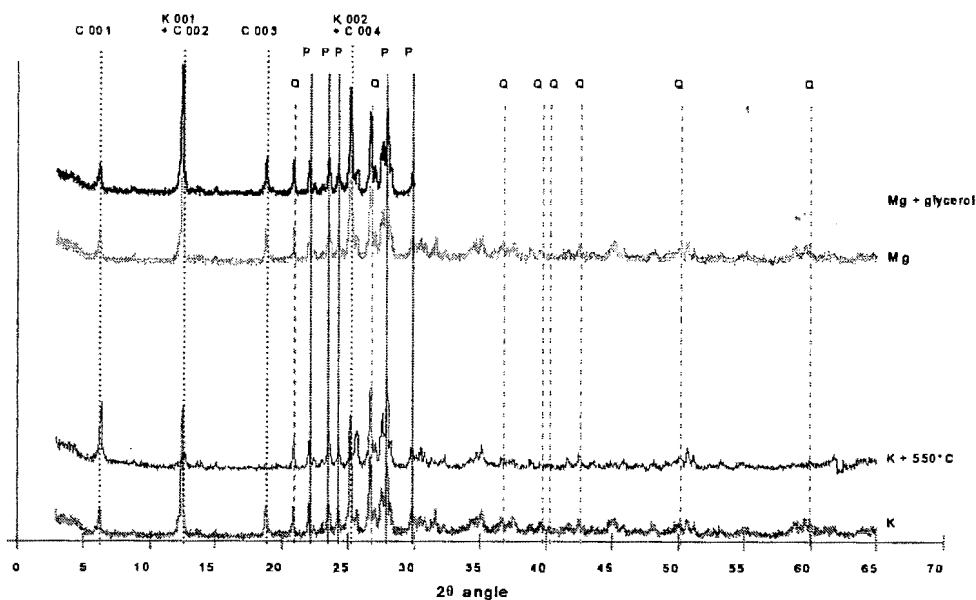


Figure 4.3d). X-ray diffraction patterns for the clay fraction of sample KF4 showing major reflections for chlorite (C), kaolinite (K), quartz (Q) and plagioclase feldspars (P).

Table 4.4 Qualitative abundance of clay minerals identified in the $< 2\mu\text{m}$ size fraction of crushed shale samples from the Kopoasfontein breccia pipe.

Sample	Mineral	Relative abundance ¹
KF1	illite	***
	kaolinite	**
	chlorite	*
	vermiculite	?
KF2	illite	***
	kaolinite	**
	vermiculite	*
	chlorite	?
KF3	illite	***
	kaolinite	**
	vermiculite	*
	chlorite	*
KF4	kaolinite	***
	chlorite	*
	vermiculite	?

¹ Key: *** abundant ** major * minor ? possible trace quantities

Illite is a major component of the clay fraction for samples KF1, KF2 and KF3, but is absent in KF4. Detection of kaolinite is complicated by the overlap of its strongest reflections ($\{001\}$ and $\{002\}$) with major reflections of chlorite ($\{002\}$ and $\{004\}$), but the almost complete collapse of the $7.1\text{ \AA}$ reflection after heat treatment indicates that kaolinite is a major component of the clay fraction in all samples.

The diagnostic peaks for Mg-saturated vermiculite at $14\text{ \AA}$ and K-saturated vermiculite at $10\text{ \AA}$ are shared by the chlorite $\{001\}$ and illite $\{001\}$ reflections, respectively. KF2 and KF3 show increased intensity of the $14\text{ \AA}$ peak and decreased intensity of the $10\text{ \AA}$ peak relative to the K-saturated pattern when samples are Mg-saturated. This indicates that some of the 2:1 layer silicates contain expandable layers. Smectite group minerals are absent, since no large d-spacings ($18\text{ \AA}$) were detected when Mg saturated samples were treated with glycerol.

Sample KF3 contains chlorite and vermiculite, while KF2 has little or no chlorite and the $14\text{ \AA}$ peak in the Mg-saturated sample is that of the expanded vermiculite layers. There is no appreciable vermiculite in sample KF4, where the absence of illite makes determination easier, since there is no overlapping peak for the diagnostic $10\text{ \AA}$ d-spacing of K saturated samples.

4.5.2 Dolerite mineralogy

The dolerites of the Calvinia area comprise plagioclase and pyroxene primary minerals, with minor alkali feldspar (intergrown with quartz) or olivine (when orthopyroxene is absent). Plagioclase is the most abundant of these minerals by volume and is typically of calcic composition ($\pm\text{An}_{70}$). Pyroxene compositions in the lower Hantam dolerite sill are pigeonitic clinopyroxene and sub-ophitic hypersthene-augite, while olivine is not reported for this locality (Walker and Poldervaart, 1941). Ilmenite, biotite and amphibole are other minor constituents.

Bulk composition data from Table 4.2 were used to calculate normative mineral compositions for the dolerites using the CIPW method as described by Kelsey (1965). The results of these calculations for the Kopoasfontein dolerite sill (380 m) and the average composition of the Hantam and Blaauwkrans dolerites is compared with Walker and Poldervaart's (1941) data for the Blaauwkrans and lower Hantam sills, based on optical microscopy (Table 4.5).

Table 4.5. Normative mineral composition, calculated for dolerites in the Calvinia area, compared with observed mineralogy.

Sample	CIPW Norms (wt %)		Observed composition (%)	
	Core 56 sample	Blaauwkrans-type	Lower Hantam sill	Blaauwkrans sill
Raw data source	(Cavé, 1999)	(Le Roex, 1976)	Walker and Poldervaart (1941)	
Plagioclase	49.3	50.4	43.5 (An_{68})	42.5 (An_{68})
albite	20.6	20.3	-	-
anorthite	28.7	30.1	-	-
Pyroxene	27.3	28	45 (Pi, Hy-Au) ¹	47.7 (Pi, Hy-Au) ¹
diopside	16.4	17.5	-	-
hypersthene	10.9	10.5	-	-
Orthoclase	2.7	3.2	-	-
Olivine	0	0	altered	3.9 (Fa_{38})
Biotite + amphibole	-	-	1.5	0.5
Ilmenite	1.59	1.73	5 ²	3.4 ²
Chromite	0.08	0.16	-	-
Magnetite	0	0.45	-	-
Hematite	9.95	8.77	-	-
Quartz	7.1	6.8	5	2
Apatite	0.3	0.3	-	-
Pyrite	0.78	0.14	-	-
Water	0.61	-	-	-
Total	99.7	100	100	100

¹ Pi = pigeonite; Hy-Au = hypersthene-augite

² ilmenite or titanomagnetite

4.5.3 Fracture-filling minerals

Late stage hydrothermal minerals in the Kopoasfontein breccia pipe were identified by Chevallier and Balaban (pers. comm.) during an investigation of the economic potential of the breccia pipe mineralisation. Their qualitative assessment of the relative mineral abundances is summarised in Table 4.6. The presence of the more abundant minerals, quartz, carbonate, chlorite, pyrite, pyrrhotite and chalcopyrite was also confirmed by the author from hand specimens and optical examination of fracture-filling minerals on polished thin sections.

Table 4.6. Fracture-filling minerals in the Kopoasfontein breccia pipe (After Chevallier and Balaban, pers.comm).

Ore Minerals	Relative Abundance ¹	Gangue Minerals	Relative Abundance ¹
pyrrhotite	***	apophyllite	***
pyrite	***	quartz	***
chalcopyrite	**	calcite	***
sphalerite	*	chlorite	**
galena	*	gypsum	**
marcassite	*	siderite	*
arsenopyrite	*	barite	–
bornite	–	fluorite	–
covellite	–		

¹ Key: *** abundant ** major * minor – trace

Although a paragenetic sequence for these minerals was not established during their preliminary study, Chevallier and Balaban did identify the minerals associated with three major phases of mineralisation, which occurred after intrusion of the dolerites:

- ▶ Stage I - Postmagmatic quartz + sulphide stage
pyrite ± sphalerite ± chalcopyrite + quartz
- ▶ Stage II - Postmagmatic carbonate + sulphide stage:
sphalerite ± chalcopyrite ± gypsum ± calcite
- ▶ Stage III - Supergene alteration stage:
gypsum ± calcite ± barite ± secondary Cu minerals ± Fe-hydroxides

Metal sulphides

Four major types of sulphide mineralisation have been recognised by Chevallier and Balaban (pers comm.) in the Kopoasfontein pipe. These are:

- ▶ synsedimentary (pyrite and pyrrhotite in the deep, unaltered Dwyka tillites)
- ▶ authigenic post-sedimentary (pyrite)
- ▶ late hydrothermal (pyrite, sphalerite, chalcopyrite, pyrrhotite and gold)
- ▶ pseudohydrothermal - mineralisation in the wake of tectonic movement (pyrite, sphalerite and galena)

Pyrite is the most abundant sulphide phase in the Kopoasfontein breccia pipe and several generations of this mineral have been recognised. *Pyrrhotite*, *sphalerite*, *chalcopyrite* and *arsenopyrite* occur as late hydrothermal phases, often in aggregates with pyrite. First generation sphalerite contains very rare exsolution droplets of chalcopyrite, suggesting that the exsolution phases formed at fairly high temperatures (350°C), although most sphalerites, do not contain exsolution phases (Chevallier and Balaban, pers. comm). Apophyllite is stable under lower temperatures and would have been deposited during the final cooling phase of hydrothermal activity (Geptner and Petrova, 1988).

Fresh drilling fragments from borehole 54B were used for investigation of the fracture-filling minerals and isolation of metal sulphides and apophyllite mineral separates for detailed studies of mineral composition. The rock fragments (2 to 15 cm size range) were obtained during air rotary percussion drilling in November 1998 and were supplied to the author by DWAF. All the specimens were collected from depths between 20 and 140 m below surface in the breccia pipe, but no record was kept of the origin of individual fragments.

Close examination of hand specimens confirmed at least two generations of brecciation and hydrothermal mineralisation in the Kopoasfontein breccia pipe. First generation breccia clasts are covered with a fine-grained surface coating of black or dark green material, probably chlorite or metal sulphides. Larger, well-formed, single crystals of apophyllite have formed in open fractures and vugs after a second brecciation event, coating clean fractured shale surfaces as well as those on which chlorite or metal sulphides had previously formed. In some specimens, apophyllite is also coated with later secondary chlorite.

Large single crystals, some over 2 cm in diameter, of a metallic, bronze-coloured sulphide mineral with distinctive tabular, hexagonal habit, were isolated by hand from the drilling fragments. These were subjected to mineralogical analysis by random oriented powder mount XRD and arsenic analysis by XRFS. The X-ray analyses and operating conditions are described in Appendix C.

The major sulphide mineral component in these massive crystals was identified as pyrrhotite 4C (JCPDS reference pattern 17-0200) (Figure 4.4). Arsenic concentrations in the sulphide sample were found to be below the analytical detection limit of 4 mg/kg. This is possibly because the pyrrhotite crystal structure does not accommodate As substitution. Arsenic may instead substitute for S in pyrite to give arsenian pyrite with up to 10 wt% As.

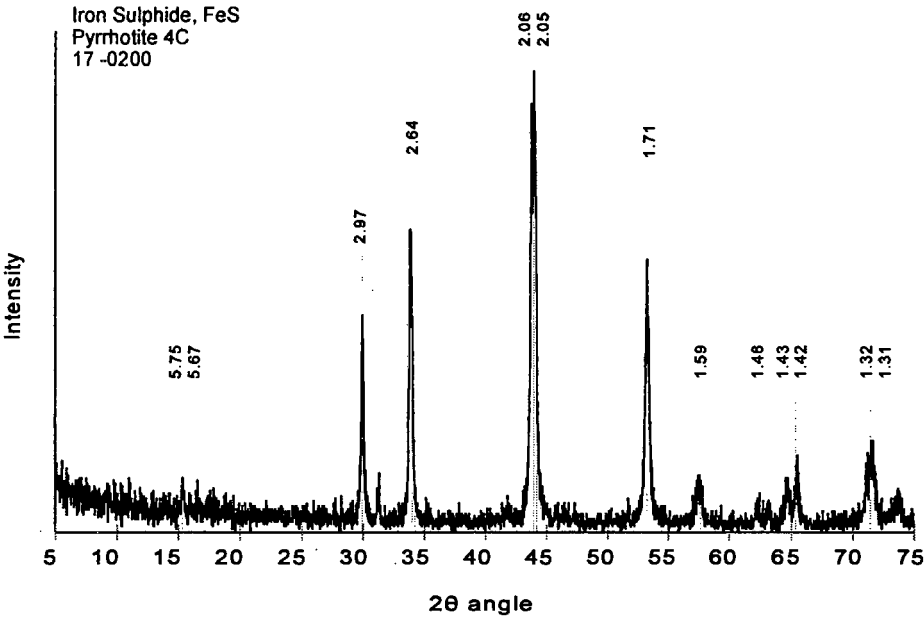


Figure 4.4. X-ray diffractogram for massive pyrrhotite from the Kopoasfontein breccia pipe. Characteristic peaks for the mineral are labelled with the d-spacing values in Ångstrom units.

Although a mineral source of As has not yet been positively identified in this study, metal sulphides are a likely host for As under the reducing conditions of the Kopoasfontein breccia pipe. Chevallier and Balaban (pers. comm.) report minor arsenopyrite as a late hydrothermal phase in the pipe. Pyrite is known to be abundant, both in the shales and the later mineralisation and arsenian pyrite could also be a source of As in the groundwater.

Non-ore minerals

Quartz in the breccia cavities displays cockade structures, typical of epithermal environments. Fine grained quartz grades into coarse crystals inside the vugs.

Calcite is observed in mineral veins at depth in the breccia pipe, where it is suspected to be of hydrothermal origin. It also fills fractures in the upper portion of the pipe, where it is likely to be precipitated at low temperature, particularly near the groundwater table under alkaline conditions.

Several generations of *chlorite* are present in the Kopoasfontein breccia pipe. As well as being a minor constituent of the shale clasts, chlorite is also a commonly recognised secondary mineral in the fractures of the breccia pipe, noticeable by its green colour in hand specimens and thin sections. Chlorite is typically associated with low to medium grade regional (greenschist facies) metamorphism and contact metamorphism. The hydrothermal alteration of almost any rock type may result in the production of chlorite, either from recrystallisation of clay minerals or from the alteration of mafic minerals such as biotite and hornblende (Nesse, 1991; p. 258).

Apophyllite is the most abundant non-ore phase in the late stage fracture filling minerals along with quartz and calcite, and the most conspicuous. It occurs as colourless, equant crystals with perfect basal cleavage, lining the cavities of the breccia. The characterisation of apophyllite from the Kopoasfontein breccia pipe will be discussed in detail in Section 5.4.

4.6 Nitrogen and carbon in the Kopoasfontein breccia

Geologic nitrogen is incorporated into the matrix of rocks during diagenesis or into minerals by hydrothermal fluids. It is estimated that 20% of the global nitrogen inventory is contained in the bedrock (Schlesinger, 1997). Geologic nitrogen has been found to play a significant role in terrestrial biogeochemical nitrogen cycling and to provide a non-point source of nitrate contamination in surface water (Holloway and Dahlgren, 1999). Injection of oxygenated surface water could result in the oxidation of NH_4^+ from the Kopoasfontein rocks by nitrifying bacteria, causing nitrate concentrations to rise in the subsurface reservoir.

Organic-rich shales, such as those of the Whitehill Formation, generally contain more organic

and inorganic nitrogen than other common sedimentary rocks. Ammonium released during organic matter degradation can exchange with the interlayer cations of expandable clay minerals or substitute for K in the structures of feldspars, zeolites, micas and clay minerals (Stevenson, 1962). Ammonium substitution in apophyllite has also been reported (Marriner *et al.*, 1990) and will be discussed further in Chapter 5.

Unusually high fixed-NH₄⁺ concentrations have been found in minerals associated with hydrothermal processes. Ammonium-feldspar (buddingtonite) (Erd *et al.*, 1964), NH₄-illite (Sterne *et al.*, 1982) and NH₄-mica (tobelite) (Higashi, 1982) were reported from hydrothermal environments (> 200°C), where NH₄⁺ is proposed to have been leached from nearby organic-rich shales and precipitated in aluminosilicate minerals. High fixed-NH₄ contents are also found in oil shales in relatively low-temperature (< 150°C) sedimentary basin environments and in clay minerals associated with hydrocarbon reservoirs (Compton *et al.*, 1992).

The relationship between nitrogen and organic matter and the influence of hydrothermal activity at Kopoasfontein was investigated by determining the total N and C concentrations in four composite shale samples from selected locations in the rock cores. The samples represent both unaltered and hydrothermally altered shales from each of the Tierberg and Whitehill Formations.

The results presented in Figure 4.5 show 90% lower C in the Tierberg Formation and 92% lower C in the formerly organic-rich Whitehill Formation in the breccia pipe when compared with the surrounding country rock. Hydrothermal alteration is expected to have caused degradation of most of the organic matter in the sedimentary rocks, changing the colour of the Whitehill shale from black to white. Dissolution by groundwater and escape during second stage brecciation would have allowed for the removal of the resultant carbon gases. Redox potential measurements (Section 3.4.2) have shown stronger reducing conditions outside than inside the breccia pipe, which may be linked to the lower content of oxidisable organic matter in the pipe.

Nitrogen concentrations also appear to have decreased in the Whitehill Formation (38% lower), but increased dramatically (130% higher) in the Tierberg shales when comparing samples of altered and unaltered material. Destruction of the Whitehill organic matter is expected to have released organogenic NH₄⁺, allowing for upward transport by hydrothermal fluids and fixing in

NH₄-bearing minerals higher in the breccia pipe. The nitrogen data from Kopoasfontein also lend support to the theory of upward mobilisation of heavy metals from the organic-rich Whitehill Formation.

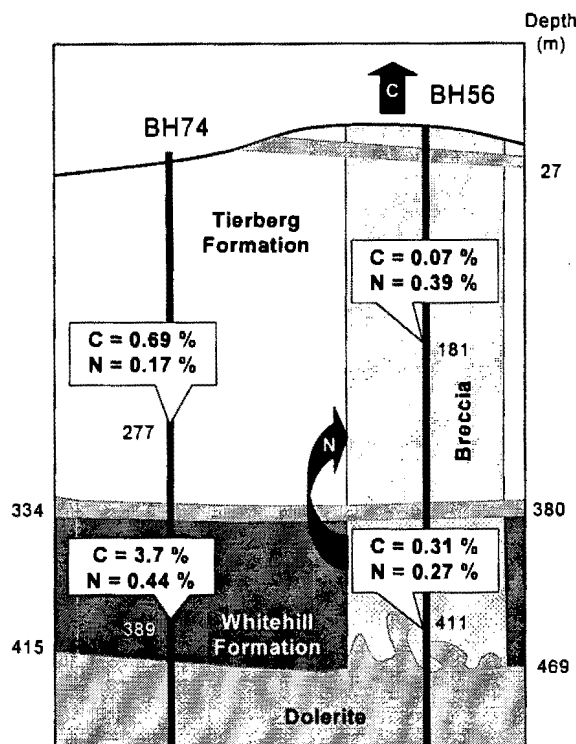


Figure 4.5. Projected loss of carbon and upward migration of nitrogen by hydrothermal alteration of the shales in the Kopoasfontein breccia pipe.

Illite and apophyllite are likely hosts for NH₄ in Kopoasfontein rocks. Analysis of apophyllite in Chapter 5 shows that this mineral has a high degree of NH₄ substitution. Ammonium-illite has a slightly greater interlayer spacing than K-illite, producing a 10.3 Å {001} reflection (Moore and Reynolds, 1989). The XRD analysis of shale samples did not show any 10.3 Å peaks, but the slight splitting of the illite {001} peak in sample KF1 and the shift to 10.1 or 10.2 Å in some of the samples, may be a result of partial NH₄ substitution. The presence of NH₄ in illite is unconfirmed, since this mineral could not be separated for elemental analysis.

4.7 Summary of findings and conclusions

The host rock for the alkaline groundwater at Kopoasfontein is a breccia pipe in which the local shale formations have been fractured, disrupted into angular clasts of varying size and recemented. The sedimentary rock has been baked and even partially melted at depth and the mineralogy altered by contact metamorphism and the passage of hydrothermal fluids. The surrounding rocks consist of relatively undisturbed sedimentary sequences of mudstones and carbon-rich shale. Dolerite sills of olivine tholeiitic composition have intruded the sedimentary sequences before and after brecciation, two younger sills transecting the breccia pipe.

The cause of the brecciation and the subsequent hydrothermal activity is not precisely known, but appears to be associated with magmatic events during the Jurassic, particularly the intrusion of a thick dolerite sheet along the contact zone between the Prince Albert and Whitehill Formations. Explosive brecciation may have been caused by the rapid generation of steam when deeply circulating meteoric waters came into contact with the heat of the intruding magmas.

The clasts of the breccia pipe contain quartz, plagioclase and phyllosilicate clay minerals including illite, kaolinite, chlorite and vermiculite. Chemical analysis of bulk samples showed a relatively low CaO content in comparison with Na₂O, K₂O and MgO. Calcium, fluoride, arsenic and trace metals have a wide range of concentrations in the rock samples and are thought to be associated with secondary mineralisation.

The original sedimentary sequence contains a thin layer of organic-rich, pyritic shale, known as the Whitehill Formation. This layer has been subjected to leaching and thermal alteration in the breccia pipe, decreasing the carbon content from 3.7 to 0.3%. The destruction of organic matter from this layer is thought to have released organic-associated elements such nitrogen, sulphur, heavy metals and possibly arsenic. These would then have been transported upwards by rising hydrothermal fluids and concentrated in sulphide and silicate phases in the upper portion of the breccia pipe. Nitrogen analyses showed a decrease in concentration in the Whitehill and an increase in the overlying Tierberg Formation in the breccia pipe, when compared with unaltered sedimentary rocks from the same strata.

Hydrothermal activity in the Kopoasfontein pipe is thought to have resulted in three stages of mineralisation after the initial brecciation. During the first stage organogenic metals such as iron, zinc and copper were precipitated as sulphides along with quartz on the surfaces of clasts in the breccia. A possible second stage of sulphide deposition was accompanied by the formation of calcite veins. Pyrrhotite, sphalerite, chalcopyrite and arsenopyrite occur as later hydrothermal phases in the pipe. A second generation of brecciation preceded the final stage of mineralisation, where chlorite and apophyllite were precipitated from cooling hydrothermal fluids.

The groundwater at Kopoasfontein has elevated concentrations of F and As which may be derived from the minerals in the breccia pipe. Ammonium in the groundwater may also be derived from a geologic source. Sulphide minerals, particularly arsenopyrite, are the likely source of As, while F and NH_4 are present in the apophyllite and may also have substituted for OH and K in the illites after hydrothermal alteration. The Kopoasfontein apophyllite is a F- and NH_4 -rich member of the mineral series.

Since apophyllite occurs in contact with groundwater in the most porous regions of the breccia pipe, and the aqueous chemistry of this phyllosilicate is poorly understood, the mineral has become a focus area for this study of mineral-water interactions. High fluoride concentrations in the Kopoasfontein breccia pipe groundwater and the absence of measurable quantities of fluorite, suggest the possible involvement of fluorapophyllite in low-temperature water-rock reactions. Chapter 5 is devoted to investigations of apophyllite and its aqueous reactions.

CHAPTER 5

CHEMICAL ATTRIBUTES OF APOPHYLLITES AND THEIR DISSOLUTION IN DILUTE AQUEOUS SOLUTION

5.1 Introduction

This chapter reports the findings of investigations into the composition and aqueous geochemistry of apophyllite from Kopoasfontein. The greater part of the work focusses on experimental observations characterising the dissolution behaviour of apophyllite, for which data are lacking in the scientific literature.

Most apophyllites contain fluoride and these dissolution studies were motivated by the high fluoride content of the Kopoasfontein groundwater and the perceived health threat associated with storage of drinking water in contact with this mineral. Fluorapophyllite has been proposed as a mineral source of fluoride in the Kopoasfontein groundwater (Cavé, 1999) which, once dissolved, cannot be removed efficiently by precipitation of fluorite in the low calcium groundwater environment. A first approximation of apophyllite solubility has been made, using experimental data and published estimation techniques, so that this theory might be tested.

The chemical composition of Kopoasfontein apophyllite has been characterised by wet chemical and X-ray analytical techniques and total nitrogen analysis. Fourteen other apophyllite samples from various localities have also been analysed to investigate the compositional range of the mineral and the effects of substitution of OH for F and of NH_4 for K on the stability of the mineral. This included studies of thermal stability and the rate of dissolution of selected samples in aqueous solution at 25°C.

One of the controlling variables in silicate dissolution reactions is pH and its influence on apophyllite dissolution rate and stoichiometry has also been investigated, as reported in the final section of this chapter.

5.2 Previous findings

Crushed and powdered samples of bulk material from the Kopoasfontein breccia pipe were leached with deionised water under open system conditions for 5 days in batch experiments (Cavé, 1999). The resultant solutions had $\text{pH} > 9$ and Na^+ , K^+ and HCO_3^- dominated major ion chemistry. The proportion of K^+ and NH_4^+ released was increased by decreasing the particle size of the rock sample. Powdering the sample exposes greater surface area of the clay minerals in the baked shales, which were concluded to be a major source of these monovalent cations. Biologically mediated partial oxidation of NH_4^+ to NO_2^- and NO_3^- occurred in aerobic solutions at room temperature. Decreased pH and increased SO_4^{2-} resulted when the leached breccia samples contained greater proportions of hydrothermal sulphides. The highest fluoride concentrations in solution were leached from samples where apophyllite was present.

5.3 Structure, occurrence and properties of apophyllite

The apophyllite group, $(\text{K}, \text{Na}, \text{NH}_4)\text{Ca}_4\text{Si}_8\text{O}_{20}(\text{F}, \text{OH}) \cdot 8\text{H}_2\text{O}$, consists of a series of hydrous sheet silicates, usually found in association with zeolites in zones of low to medium temperature hydrothermal alteration. Apophyllite occurs in basalt amygdalae and in various ore deposits as part of the final phase of vein mineralisation. Physical and optical properties of apophyllite are summarised in Table 5.1.

Table 5.1. Physical and optical properties of apophyllite (Nesse, 1991; Deer *et al.*, 1962).

Crystal system:	Tetragonal	Colour:	Colourless or white;
Space group:	P4/mnc		some varieties are pink,
Unit cell dimensions:	$a = b = 9.00 \text{ \AA}$ $c = 15.84 \text{ \AA}$		pale yellow or green;
Density:	2.33 - 2.37 g/cm ³		white streak
Hardness:	4½ - 5	Relief:	Low negative or positive
Cleavage:	{001} perfect {110} poor	Interference figure:	Uniaxial (+) or (-)
Form:	equant or platy parallel to {001}	Refractive indices:	$n_o = 1.531 - 1.542$ $n_e = 1.533 - 1.543$
Twinning:	uncommon on {111}	Birefringence:	$\delta = 0.000 - 0.003$
		Interference colours:	first order grey; often anomalous

The crystal geometry (Chao, 1971; Colville and Anderson, 1971; Prince, 1971), optical properties (Akizuki and Konno, 1985; Akizuki and Terada, 1998), chemical composition (Dunn *et al.*, 1978; Matsueda *et al.*, 1981; Marriner *et al.*, 1990) and thermal behaviour (Ståhl *et al.*, 1987; Marriner *et al.*, 1990; Ståhl, 1993) of apophyllites have been investigated, but little is known about their reactions in aqueous environments at surface temperatures.

5.3.1 Crystal structure and geometry

Mineralogists have been fascinated by the unusual atomic structure of apophyllites, first described by Taylor and Náray-Szabó (1931) and later refined by Colville and Anderson (1971), Prince (1971) and Chao (1971). The mineral framework consists of four-fold and eight-fold rings of SiO_4 tetrahedra, linked together to form corrugated sheets parallel to the {001} crystallographic plane (Figure 5.1). Apical oxygen atoms on alternate rings point in opposite directions. The sheets are held together by Ca, F and K atoms which lie on horizontal mirror planes between them (Figure 5.2).

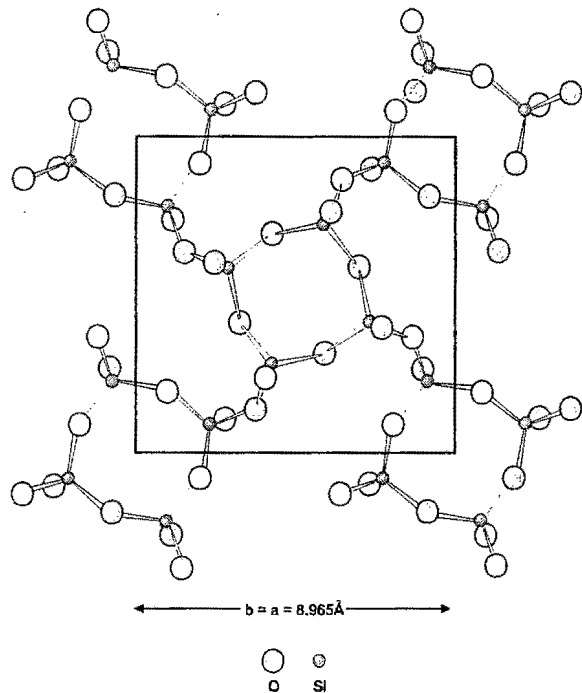


Figure 5.1. Structure of the Si_8O_{20} sheet in apophyllite projected on {001} (Reproduced from Chao, 1971).

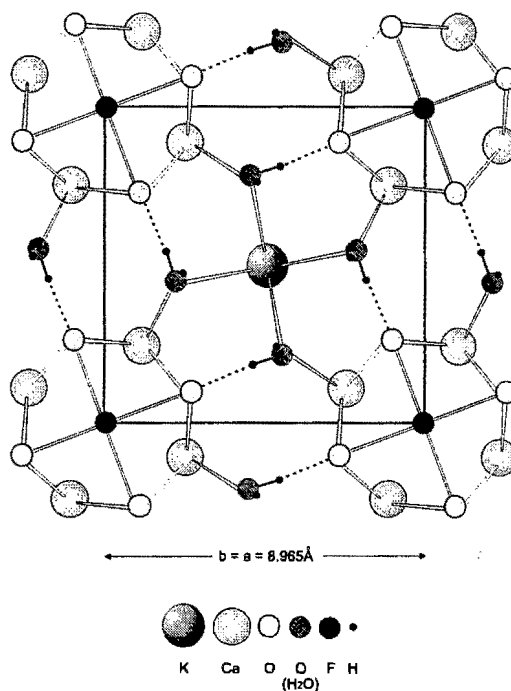


Figure 5.2. Structure of the K, Ca sheet in apophyllite projected on {001} (Reproduced from Chao, 1971).

Each F atom is surrounded by four Ca atoms, while each Ca is seven-fold coordinated by four silicate O atoms, one F atom and two O atoms of the water molecules. The K atoms are eight-fold coordinated by water molecules, four in a plane above and four below (Figure 5.3) (Taylor and Náray-Szabó, 1931).

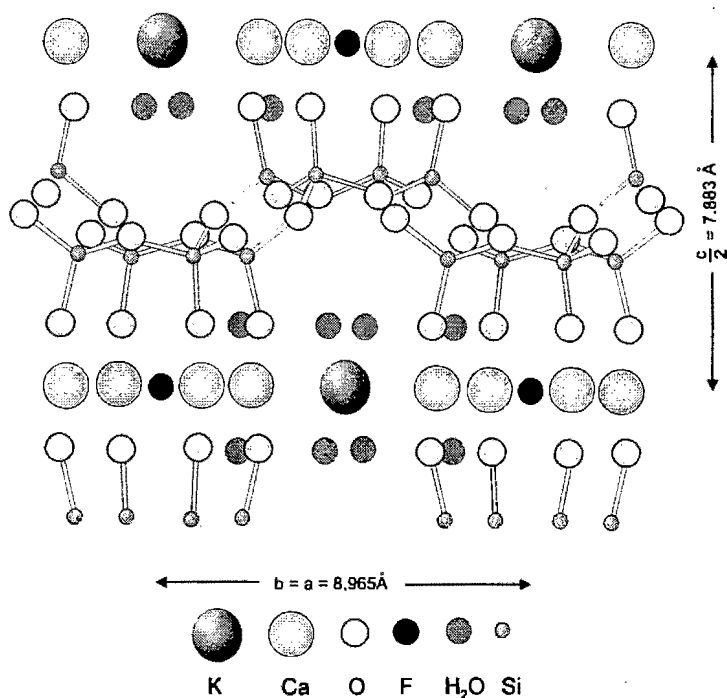


Figure 5.3. The layered silicate structure of the apophyllite crystal, shown by projecting the lattice on {100} (Reproduced from Chao, 1971).

5.3.2 Occurrence and paragenesis

Apophyllites are found in granites, syenites, gabbro, gneisses and various volcanic rocks in association with other hydrothermal minerals (Geptner and Petrova, 1988). Basaltic volcanic rocks are common host rocks for apophyllite, where it is usually found in amygdales, cavities and veins in association with prehnite, zeolites, pectolite, datolite and calcite. The “trap rock” of the Deccan plateau at Poona in India is a classic locality for apophyllite and gem crystals of extraordinary size and beauty are found there. Apophyllite is also occasionally found in cavities in granite or gneiss, in the contact aureole around granitic intrusions, associated with certain ore veins or in metamorphosed limestone or calc-silicate (Dana, 1966; p. 642; Geptner and Petrova, 1988; Nesse, 1991; p. 260). Apophyllite has been reported with stilbite on serpentine at a marble contact, in fractures in aplite dykes and in natrolite veins in an aegerine-alkali amphibole-

nepheline-syenite (Deer *et al.*, 1962 and references therein).

The formation of apophyllite in hydrothermal ore veins, similar to the Kopoasfontein breccia, has been studied with the aim of establishing the conditions of ore genesis (Chukhrov *et al.*, 1973). Apophyllite occurs among the latest phases of mineralisation in what has been described as a “low temperature non-ore association”, typically with quartz, zeolites and calcite. Apophyllite is frequently later than quartz and zeolites, but earlier than calcite. Fluorite and chlorite or smectite are also sometimes found in this quartz-zeolite-calcitic stage.

Although apophyllite is generally accepted to be a product of ascending medium to low temperature hydrothermal solutions (representing the final, cooling stages of a magmatic process), the involvement of deep circulating meteoric waters has also been suggested by several researchers (e.g. Subba, 1967; Chukhrov *et al.*, 1973; Geptner and Petrova, 1988; Merrick, 1995). Hydrous minerals such as zeolites and apophyllites form at relatively shallow depths under low to moderate temperature conditions in silica-rich environments. Thermal decomposition of apophyllite, beginning at 250°C, sets a maximum temperature for its formation at low pressure. Apophyllite occurs predominantly in open spaces including fractures and gas cavities (vugs), indicating that it precipitates from solution (or gels), but it may also form by pseudomorphic replacement of wollastonite or silica glass.

Chukhrov *et al.* (1973) studied the age relationships of apophyllite in several ore deposits of central Kazakhstan, using K-Ar and Rb-Sr dating techniques, and concluded that apophyllite formation occurred in a very late stage, distinct from the formation of the ore mineralisation. These workers proposed that apophyllite was formed at temperatures of 150 to 200°C at normal or low pressures associated with the deep circulation of meteoric waters during a period of uplift. Association with magmatic solutions was ruled out since no magmatism occurred in the area during the Mesozoic when the apophyllite formed.

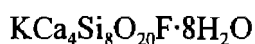
A literature search revealed two reported occurrences of authigenic apophyllite, both cited by Chukhrov *et al.* (1973), but the original sources are very old and their reliability uncertain. These are the precipitation of apophyllite below 100°C on the floors of the Roman baths at Plombière, France (from the handbook of Hintze, 1896) and small quantities (<5%) of authigenic apophyllite

formed at around 30°C in the Eocene lacustrine deposits of the Green River Formation, Utah, Wyoming and Colorado, USA (from Bradley, 1929).

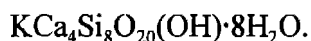
Occurrences of apophyllite and associated minerals have been compiled as a table in Appendix F, based on literature reports and mineral specimens from museum collections.

5.3.3 Compositional variations of apophyllite

While most apophyllites are fluorine-rich, OH may substitute for F and there is a complete solid solution between fluorapophyllite,



and hydroxyapophyllite (Dunn *et al.*, 1978),



Substitution of Na (Matsueda *et al.*, 1981) and NH_4 (Marriner *et al.*, 1990) for K is also found. Natroapophyllite, an orthorhombic sodium end-member apophyllite, was identified in white skarns in Japan by Matsueda *et al.* (1981), but no ammonium end-member has yet been reported.

Characteristic impurities in apophyllite include Mg, Cu, Ti and Mn, while some samples contain Sr, Mo, V, Ba, Ga, Nb, Be or Pb. Small amounts of Al may replace Si and Sahama (1965) and Belsare (1969) have reported apophyllite samples which contain significant Al. Green varieties of apophyllite from Poona, India were found to contain trace quantities of vanadium (Rossman, 1974), as VO^{2+} ions substituting in the Ca(II) site (Ramakrishnan *et al.*, 1991).

5.3.4 Documented reactions of apophyllite

No rigorous investigations of the behaviour of apophyllite in low temperature aqueous solutions have been undertaken and thermodynamic data for the mineral are lacking. Isolated studies of the reactions of apophyllite in acid and calcium or fluoride solutions that have been reported in the literature, are discussed here.

Observations of natural samples indicate that apophyllite may alter to clay minerals e.g. chlorite, (Wolfe and Vilks, 1960), calcite, opal or quartz (Nesse, 1991; p. 260) in weathering

environments. Apophyllite is decomposed by hydrochloric acid, leaving a solid silica residue (Dana, 1966; p. 642). Frondel (1979) and Sogo *et al.* (1998) report the preparation of crystalline layered silica hydrates from apophyllite by leaching with 0.1M HCl. Crystalline material, designated Silica-AP, is produced at 25°C and H-apophyllite at 5°C (Sogo *et al.*, 1998). X-ray diffraction analysis shows these hydrates to have the fundamental silica sheet structure of the original apophyllite. Cross-linking of the leached silica sheets by hydrogen bonds is thought to prevent disintegration of the crystalline structure once the interstitial cations are removed.

The only studies related to the dissolution kinetics of apophyllite, uncovered during an extensive literature search, are those of Pande and Vadrabade (1990) and their predecessors. Following the earlier work of Joshi and Ittayachen (1969), these researchers examined the formation of etch pits on the {001} cleavage surfaces of apophyllite crystals from Poona, India, using a base etching solution of dilute HF, poisoned with varying concentrations of ammonium fluoride. Square pyramidal etch pits were formed at surface defect sites with their sides parallel to {100} at low concentrations of NH₄F (0.6 M), but the pits rotated 45° at higher concentrations (6 M NH₄F) with their sides parallel to {110}. The formation of etch pits demonstrates a surface-controlled dissolution mechanism and the change in pit orientation was attributed by the authors to the preferential adsorption of different aqueous complexes at different surface adsorption sites on the apophyllite. The lateral growth rate of the etch pits was also found to be pH dependent.

The exchangeability of K in apophyllite was tested by Chukhrov *et al.* (1973) to ensure the validity of K-Ar age-dating of their crystals. A 100 mg/L solution of CaCl₂ (intended to be representative of typical groundwater Ca²⁺ concentrations) was infiltrated through a column containing 6.5 g of apophyllite grains (0.25 - 0.5 mm) at a rate of 20 - 25 drops per minute for one month at room temperature. No K⁺ was detected in the eluent after 32 L of CaCl₂ solution had been passed through the sample and the K was concluded to be non-exchangeable. Cation exchange with monovalent ions such as Na⁺ or NH₄⁺ was not investigated. Using isotopically-labelled water, however, Noto *et al.* (1990) found that the water of crystallisation surrounding the K in apophyllite could be exchanged for external water after 10 days under optimum conditions of about 160°C.

Maruthamuthu and Sivasamy (1994) found that apophyllite could be used for the sorption of fluoride in synthetic NaF solutions up to 250 ppm F⁻ and natural fluoride-rich waters. They reported a Langmuir adsorption coefficient of 0.37 dm³/g for fluoride adsorption by apophyllite at 30°C and a maximum of 78% defluoridation of a 10 ppm F⁻ solution at pH 3.7. The intention of their experiments was to compare the behaviour of various zeolite minerals, which were expected to remove fluoride by occlusion of binary salts in zeolite cavities, but this is not a valid sorption mechanism for apophyllite. The authors also did not report the mineral composition.

Reproduction of these findings using the Kopoasfontein apophyllite proved unsuccessful. Sodium fluoride solutions ranging in concentration from 1 to 500 ppm F⁻ were reacted with apophyllite (particle size: 50-100 µm; suspension density: 5 g/L) by shaking horizontally in polyethylene tubes on a reciprocating shaker at approximately 100 cycles/minute for 30 hours at room temperature. After reaction, the samples were filtered through porosity 4 sintered glass crucibles to recover the apophyllite and the solutions analysed for F⁻ by ion chromatography. Fluoride removal was negligible (all < 3%), with measured changes in F⁻ concentrations falling within the range of error for the IC analytical method.

5.4 Characterisation of the Kopoasfontein apophyllite

5.4.1 Powder X-ray diffraction analysis

The X-ray diffraction pattern from a random powder mount of a sample from Kopoasfontein confirmed the mineral identity as apophyllite, with no major crystalline impurities present. The major X-ray diffraction peaks are illustrated in Figure 5.4 using a reference spectrum for apophyllite (75-0913). The perfect basal cleavage of apophyllite produces platy crystals during grinding and it is difficult to obtain a truly randomly orientated powder. Pressing the sample into the holder tended to align the crystals with the c axis perpendicular to the holder. This preferred orientation affects the intensity of the diffraction peaks, which differ somewhat from the various standard reference patterns of apophyllite in the powder diffraction database.

Powder diffraction patterns are not as suitable as single crystal patterns for the determination of unit cell dimensions, especially in this case where no internal standard was used to correct for

errors introduced by poor sample alignment. Nevertheless, the {200} and {004} peaks could be used to estimate the a and c axis dimensions. X'Pert software (Phillips Analytical) was used to search for peaks and calculate d-spacings for the apophyllite spectrum. The spacings for the {200} and {004} peaks were calculated as 0.44904 and 0.39426 nm respectively, giving estimates of $a = b = 8.981 \text{ \AA}$ and $c = 15.770 \text{ \AA}$. Colville and Anderson (1971) report slightly shorter c (15.768 $\text{\AA}$) and a (8.965 $\text{\AA}$) unit cell dimensions for apophyllite from Keweenaw, Michigan.

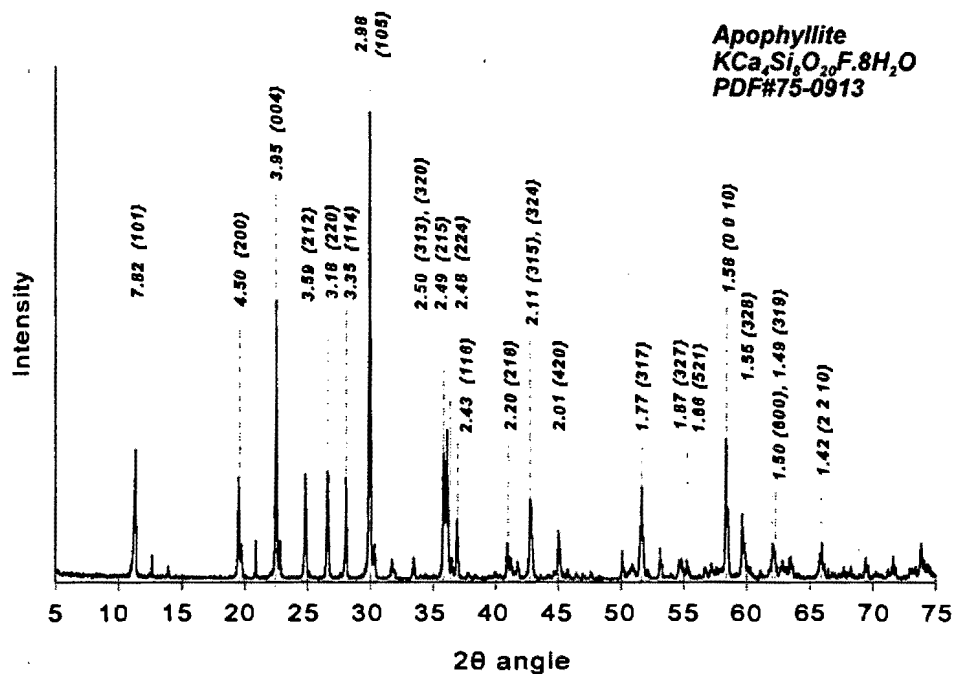


Figure 5.4. X-ray diffractogram for apophyllite from Kopoasfontein, South Africa (random powder mount, Cu K_α radiation) showing peaks for apophyllite reference pattern 75-0913. Peaks are labelled with crystal d-spacings in Ångstrom units and Miller indices in parentheses.

5.4.2 Chemical composition

Several analytical techniques were combined to quantify the chemical components in the apophyllite. Major elements were determined in bulk samples by X-ray fluorescence spectroscopy (XRFS) analysis of solid glass fusion disks or inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of acid digests after lithium metaborate fusion and in polished single crystals by ion microprobe. Fluorine content was determined by XRFS analysis

of a powder briquette, which was also used to analyse sulphur to test for sulphide impurities from the breccia pipe. Fluorine determination was repeated using an ion selective electrode (ISE) method after low temperature sample fusion with NaOH. Loss on ignition (LOI) was measured after roasting overnight at 950°C to determine the volatile content in addition to total mass loss data measured during thermogravimetric analyses. Finally, a total nitrogen analyser was used to determine the ammonium content by pyrolysis of a solid bulk sample at 1050°C. A sample was also submitted to the Sea Fisheries' Research Institute in Cape Town for total nitrogen analysis. Sample preparation and analytical details are given in Appendix C and the results in Table 5.2.

Analysis of apophyllite by standard geochemical techniques is complicated by the high volatile content of the mineral. High fluorine leads to erroneous SiO₂ results by ICP because SiF₄ tends to be lost during sample preparation (Marriner *et al.*, 1990). Two different fusion methods, one from the Union College Geology Department (Union College, current) and the other proposed by Walsh (1980) were used for the ICP-AES analyses. The major oxide results given in Table 5.2 are the average values from these two methods, with the exception of SiO₂, for which only the Union College data are reported. This method uses a 10 minute fusion, during which less SiF₄ would be lost than the 40 minute fusion used in the Walsh method. The latter gave only 47% SiO₂, which is below the expected concentration for fluorapophyllite.

Losses of up to 40% of the F in the sample were also found when comparing the results of short Union College fusions at 980°C with 20 minute NaOH fusions at 500°C, designed to preserve fluorine in the samples (Fabbri and Donati, 1981). The fluorine concentration has, therefore, been used to correct the ICP-AES data for SiO₂ in Table 5.2, assuming 40% of the total F is lost as SiF₄ during sample fusion.

Calcium concentrations appear to be underestimated and potassium overestimated using ICP-AES, but the reason for this is not known. The precision of major cation measurements such as Ca, Si and K by ICP-AES was not as good as for the other two techniques.

The sample analysed by XRFS initially gave high SiO₂ (57.85%) from which it was concluded that the sample may contain minor impurities of quartz from the breccia pipe or crystalline silica hydrate formed by leaching of the apophyllite. The latter is indistinguishable from apophyllite

on a powder X-ray diffraction spectrum (Fron del, 1979). The SiO₂ concentration was recalculated based on an estimated 10% silica impurity and the major oxide concentrations adjusted accordingly to produce a composition closer to that of pure fluorapophyllite. The XRFS method has poor precision in the determination of fluoride and the ion selective electrode results are favoured for this element.

Table 5.2. Chemical analyses of Kopoasfontein apophyllite.

Technique	XRFS	ICP-AES	Ion Microprobe	Fluor- apophyllite ¹
Major oxides (wt%)				
SiO ₂	53.17 ± 0.25	51.18 ²	51.26 ± 1.61	52.99
Al ₂ O ₃	0.51 ± 0.02	0.53 ± 0.04	0.29 ± 0.12	
CaO	25.28 ± 0.06	20.5 ± 1.6	23.14 ± 0.83	24.74
Na ₂ O	<0.12	0.12 ± 0.02	0.13 ± 0.06	
K ₂ O	2.09 ± 0.01	2.74 ± 0.14	1.83 ± 0.27	5.19
MgO	0.11 ± 0.00	0.08 ± 0.01	0.00	
Fe ₂ O ₃	0.21 ± 0.01	0.30 ± 0.03	0.02 ± 0.04	
TiO ₂	0.014 ± 0.001	n.d.	0.01 ± 0.01	
MnO	0.004 ± 0.001	0.006 ± 0.000	0.01 ± 0.01	
P ₂ O ₅	0.003 ± 0.001	n.d.	n.d.	
LOI	19.3 ³	17.73 ⁴	17.73 ⁴	17.96
Total	100.3	92.2	94.4	100
Other analyses				
		Method		
N (wt %)	1.583 ± 0.007 1.06	Total N analyser Measured by Sea Fisheries Research Inst.		0
F (wt %)	2.18 ± 0.07 1.232 ± 0.008	ISE: NaOH fusion XRFS*		2.09
Trace elements (mg/kg)		ICP-AES: LiBO ₂ / HCl digest		
As	< 25	Ni	< 2	
Ba	17.7 ± 1.7	Pb	< 5	
Be	< 0.05	Se	< 25	
Cd	< 2.5	Sr	45.2 ± 4.5	
Co	< 10	V	< 10	
Cr	3.8 ± 2.4	Zn	24.5 ± 22.7	
Cu	16.7 ± 11.7	S*	65.6 ± 1.5	

Notes: Concentrations reported as mean ± 1 standard deviation. Duplicate samples were analysed by XRFS and ICP-AES and 20 spot analyses conducted on 5 single crystals by ion microprobe. Samples for N and F were analysed in triplicate.

¹ Values in *italics* are theoretical values for pure fluorapophyllite, KCa₄Si₈O₂₀F·8H₂O.

² SiO₂ by Union College digestion method was corrected for 40% loss of SiF₄.

³ Mass loss after roasting overnight at 950°C, adjusted to remove 10% non-volatile impurity.

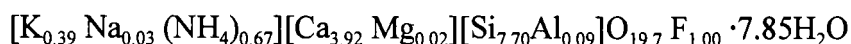
⁴ Total mass loss during thermal analysis from 20 - 1000°C at 1°C/minute heating rate

* F and S measured on unroasted powder briquette by XRFS.

The K content of the Kopoasfontein apophyllite was observed to be much lower than the theoretical 5.19% as K₂O. The low Na₂O content ruled out Na substitution as the cause of K-deficiency. Potassium was not lost during sample roasting, since peak counts by XRFS showed no significant difference in the K content between roasted and unroasted powder briquettes. It was concluded that another monovalent cation must occupy a high proportion of the K sites in the apophyllite, and N analyses were conducted to confirm that NH₄⁺ is the responsible cation.

XRFS major oxide results for SiO₂, CaO, MgO, Al₂O₃, and K₂O, the ICP-AES value for Na₂O and the ISE (NaOH fusion) and Sea Fisheries' nitrogen analysis results for F and N, respectively, were used to derive the mineral formula. The stoichiometry was normalised to 46 mmol cation or anion charge per g apophyllite, as shown in Table 5.3.

The mineral formula for the Kopoasfontein apophyllite was calculated as:



which classifies it as an ammonian fluorapophyllite.

Table 5.3. Calculation of mineral stoichiometry for Kopoasfontein apophyllite.

	mmol/g wt % oxide	mmol/g	Stoichiometry mmol/g × 40
	100* formula wt oxide		46 mmol _c /g
Si	8.848	35.39	7.70
Al	0.100	0.300	0.09
Ca	4.508	9.016	3.92
Na	0.037	0.037	0.03
K	0.444	0.444	0.39
Mg	0.027	0.055	0.02
NH ₄	0.757	0.757	0.67
Total cations		46.00	
O (framework)*	22.62	45.25	19.7
F	1.147	1.147	1.00
Total anions		46.39	
H ₂ O**	8.071	0	7.85

* The sum of the oxygen associated with SiO₂, Al₂O₃, CaO, Na₂O, K₂O and MgO was taken as the framework O.

** Structural water determined by subtracting F and N from the LOI value, using 1.15 mmol apophyllite/g.

Kopoasfontein apophyllite is exceptionally NH₄-rich, containing less K than any of the other apophyllite samples analysed (Section 5.5.2). The maximum NH₄ content reported in the

literature to date is 37% substitution of K by NH_4 (0.7 wt % as $(\text{NH}_4)_2\text{O}$) in samples from Mexico analysed by Marriner *et al.* (1990). The analytical results show that the Kopoasfontein apophyllite is likely to have over 50% substitution of NH_4 for K, which would classify it as an ammonium end-member of the apophyllite mineral series.

5.4.3 Thermal analysis

Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to characterise the apophyllite sample from Kopoasfontein (S.Vasic, analyst: Chemical Engineering, UCT). The analyses were performed on 25 mg samples (50-100 μm). Three analyses were performed using temperature ramps of 2, 5 and 10 degrees per minute, over a temperature range from 45 to 600°C. The thermal analysis curves are shown in Figure 5.5.

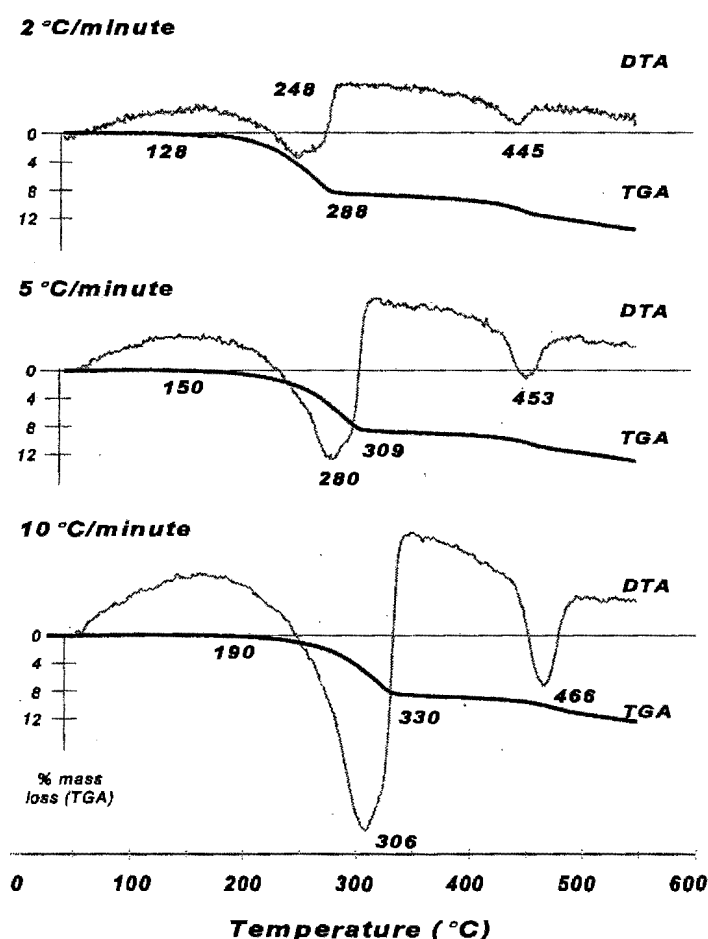


Figure 5.5. Thermograms showing gravimetric mass loss (TGA) and differential thermal analysis (DTA) curves at heating rates of 2, 5 and 10 degrees per minute.

Two distinct stages of mass loss occur below 600°C, the first between 150 and 350°C and the second between 400 and 500°C. TGA curves show that 8.7 % of the sample mass is lost in the first step for all three heating rates and a further 5.3 to 6 % in the second stage.

The corresponding DTA curves show two marked endothermic peaks near 250 and 450°C. Decreasing the heating rate causes a shift in these peaks to lower temperature values, especially for the more intense first endotherm. The DTA peaks indicate a loss of structural water from apophyllite, often interpreted as a two-step dehydration reaction involving a partially-dehydrated apophyllite intermediate (Chao, 1971; Ståhl *et al.*, 1987).

After the first endotherm, X-ray diffraction patterns of the heat-treated apophyllite are reported to have decreased intensities, but the material is still mostly crystalline (Marriner *et al.*, 1990). This is a mixture of the original mineral and a partially dehydrated form in which one water molecule is expelled from the potassium coordination shell, leaving an average of approximately seven water molecules per formula unit (Ståhl, 1993). Continued water loss after the second endotherm causes a collapse of K coordination and, in turn, also of Ca coordination and the structure becomes X-ray amorphous. The remaining volatiles are trapped inside the amorphous structure and expelled on further heating. This may explain why only 14% of the mass is lost by 600°C when the theoretical water content of apophyllites ranges from 15.9 to 16.9%.

A sample was submitted to the USGS thermal analysis laboratory for a repeat of the TGA-DTA analyses to higher temperatures, coupled to a quadrupole mass spectrometer for simultaneous qualitative analysis of the evolved gases (J. Hammarstrom, analyst: USGS, Reston, Virginia). Twenty milligram samples of finely ground apophyllite (50 - 100µm) were used in the analyses. The analytical procedure is described in Appendix C and results of these analyses presented in Table 5.4.

The mass spectra for a 10°C/minute run show three sets of peaks corresponding to the three endotherms on the DTA curves (Figure 5.6). The size of the peaks is approximately proportional to the intensity of the related endotherms. These results show that water, fluorine and ammonia are likely to be evolved during both the major dehydration steps, and that fluorine is not released only after collapse of the structure at 370°C as suspected by Chao (1971) and Marriner *et al.*

(1990). There is, however, an indication that additional loss of species with a mass to charge ratio of 19 (F⁺) occurs above 900°C, at which sintering of the material is expected to occur.

Table 5.4. Thermal analysis results for Kopoasfontein apophyllite (USGS thermal analysis laboratory).

Run conditions				
Heating rate (°C/minute)	10	10	10	1
Temp. range (°C)	20-1000	20-1000	20-1050	20-1000
DTA peaks (°C)				
1 st endotherm	275*	280*	280*	220*
2 nd endotherm	435	435	430	420
3 rd endotherm	790	790	790	740
Relative intensities (%)				
1 st endotherm	100	100	100	100
2 nd endotherm	32	30	33	33
3 rd endotherm	11	10	8	8
TGA steps				
Temp. range (°C)	30-337	37-338	not measured	112-280
Mass loss (%)	9.115	9.476		8.301
Temp. range (°C)	337-474	338-477		283-453
Mass loss (%)	2.889	3.060		4.965
Temp. range (°C)	474-886	477-891		471-947
Mass loss (%)	4.220	4.385		3.354
Total mass loss (%)	16.231	16.970	17.166	17.733

*The first endotherm for the 10°C/minute runs is asymmetric, with a tail on the low temperature side. The peak sharpens and becomes symmetrical at 1°C/minute.

The evolved gases suggest that the third weak endotherm on the DTA curves is related to a transformation involving ammonia, since water and fluorine are not involved. This is supported by the fact that apophyllite samples which do not contain ammonium fail to produce a third peak under the same conditions (Section 5.5.3).

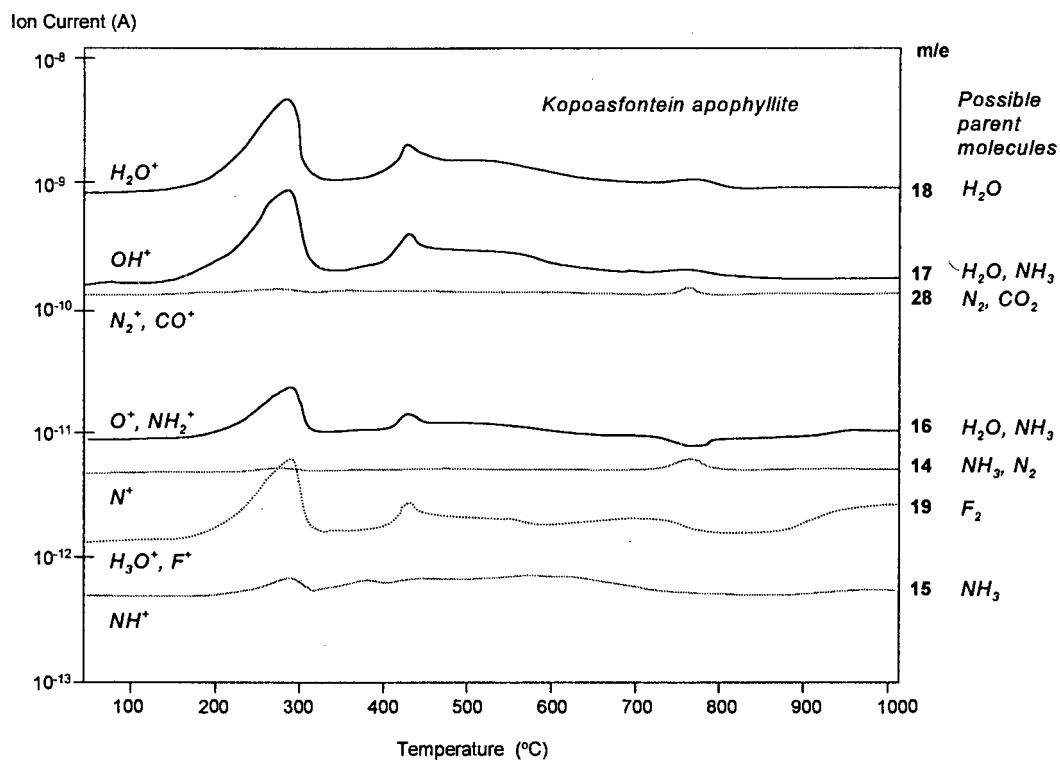


Figure 5.6. Mass spectra for particles of mass to charge ratio 14, 15, 16, 17, 18, 19 and 28, evolved during thermal decomposition of apophyllite from Kopoasfontein from 30 to 1050°C at a heating rate of 10°C/minute.

5.5 Characterisation of apophyllite samples from other localities

Apophyllite samples were donated by museums and universities or purchased from mineral dealers for study. Fourteen specimens provided sufficient material for investigation using the same methods as the Kopoasfontein sample, which is included as sample LC13 in Table 5.5.

Table 5.5. Sources of apophyllite samples investigated in this study.

Sample name	Supplier's identifier	Donor/Supplier	Sample location	Comments
LC1	83.256	Colorado School of Mines, Golden, CO	Murdochville, Quebec, Canada	
LC2	TM11116	Colorado School of Mines, Golden, CO	Centerville, VA, USA	Associated with prehnite & taumasite
LC3	-	Colorado University, Boulder, CO	French Creek, PA, USA	
LC4	DMNH #7386,	Denver Museum of Natural History, Denver, CO	Centerville, VA, USA	Ass. with stilbite
LC5	#31222	Stanford University Mineralogy Collection	Khadrakvasla, Poona Maharastra, India	Green fluor-apophyllite
LC6	#4276	Stanford University Mineralogy Collection	Guanajuato, Mexico	On amethyst
LC7	#29820	Stanford University Mineralogy Collection	Paterson, Passaic Co, NJ, USA	
LC8	-	Kristall Ocean Export Pty. Ltd., India	Jalgaon, India	Single crystal points, ass. with stilbite
LC9	DMNH #13046	Denver Museum of Natural History	Poona, India	With zeolites
LC10	#29960	Stanford University Mineralogy Collection	Sweet Home Mine, Linn Co. OR, USA	
LC11	#1074	Stanford University Mineralogy Collection	Seiser Alps, Tyrol, Austria	
LC12	DMNH #15147	Denver Museum of Natural History	Poona, India	Pale green Apophyllite
LC13	Borehole G39854B	Department of Water Affairs and Forestry	Kopoasfontein Farm, Calvinia, South Africa	Breccia pipe, ass. chlorite & sulphides
LC14	435:1:3	Colorado School of Mines, Golden, CO	Guanajuato, Mexico	On amethyst
LC15	49-5856	Wards Earth Science (research mineral)	Poona, India	

5.5.1 X-ray diffraction analysis

Apophyllite samples analysed by powder X-ray diffraction to determine whether other mineral impurities were present. Samples were prepared as random powder samples mounted in brass sample holders or oriented samples from a methanol suspension on a silicon wafer. The sample preparation and analysis are described in Appendix C. X-ray diffractograms were compared with reference spectrum 77-1730 for apophyllite. Sample LC9 was found to contain possible impurities of clinoptilolite and LC14 contained minor quantities of quartz.

Although unit cell dimensions were refined from the powder X-ray data using a cell-refinement software program, accurate cell dimension data is difficult to obtain from powder X-ray spectra. Single crystals of apophyllite were, therefore, also submitted for measurement of cell dimensions (J. Basca and H. Su, analysts: Chemistry, UCT). Reflections were collected on a NONIUS Kappa CCD with 1.5kW graphite monochromated Mo radiation. The data collection parameters are specified in Appendix C. Cell dimension data for the apophyllite samples are presented in Table 5.6. All data were indexed on a primitive tetragonal unit cell.

Table 5.6. Unit cell dimensions for apophyllite samples from powder and single crystal X-ray diffraction.

Sample	a (Å)	c (Å)	Volume (Å ³)	Data source
LC1	8.945(3)	15.828(5)	1267	Single crystal, 1845 reflections
LC2	8.970(1)	15.887(2)	1277	Single crystal, 981 reflections
LC3	8.979 ±0.007	15.786±0.006	1272.7	Oriented powder on Si wafer
LC4	8.970(3)	15.877(5)	1277	Single crystal
LC5	n.d.	n.d	n.d	Not analysed
LC6	8.986(2)	15.795(3)	1275	Single crystal, 1433 reflections
LC7	8.969(2)	15.804(3)	1270	Twinned crystal, 517 reflections
LC8	8.962(1)	15.775(2)	1267	Single crystal
LC9	8.986±0.010	15.814±0.019	1277	Single crystal, 275 reflections
LC10	8.974(2)	15.847±0.003	1276.3	Single crystal, 278 reflections
LC11	8.980(5)	15.851±0.006	1278.3	Single crystal, 269 reflections
LC12	8.964(2)	15.795±0.0015	1269.2	Single crystal, 281 reflections
LC13	8.990±0.003	15.790±0.003	1276.2	Random powder in brass holder
LC14	8.976±0.007	15.788±0.012	1272	Oriented powder on Si wafer
LC15	8.972(3)	15.765(5)	1269	Single crystal, 6234 reflections

5.5.2 Chemical composition

The chemical composition of the apophyllite samples, expressed as weight percent oxide components, is given in Table 5.7. Major elements were determined by ICP-AES analysis of acid digests after fusion with lithium metaborate, fluoride by ion selective electrode analysis of samples dissolved in water after fusion with sodium hydroxide, nitrogen by total nitrogen analyser and water content derived from mass loss during thermogravimetric analysis. Sample preparation and analytical methods are described in Appendix C. Sample LC13 has been omitted from the table since it was described earlier in Section 5.4.2.

As with the Kopoasfontein apophyllite, adjustments have been made to the silica content to correct for loss of SiF_4 during sample fusion. The totals in Table 5.7 are all below 100%, which could be partly attributable to underestimation of CaO by the ICP-AES method. CaO content is consistently lower than the theoretical value of 25% for apophyllite.

The chemical analyses were used to derive mineral formulae for classification of the samples (Table 5.8), using a similar calculation to that for the Kopoasfontein apophyllite in Table 5.3. Most of the samples are fluorapophyllites, with only LC2 and LC4 from Centerville, Virginia, containing less than 50% F in the anion site. Samples LC6 and LC14 from Guanajuato, Mexico are NH_4 substituted, in agreement with the findings of Marriner *et al.* (1990). Two samples from Poona, India, LC9 and LC12, contained high Al and low Ca (especially LC12) and it is suspected that these may contain other mineral impurities, although Al-substituted apophyllites have been reported from this location (e.g. Belsare, 1969). The X-ray diffraction pattern for LC9 showed that clinoptilolite may be present in the sample.

The sum of the stoichiometric coefficients for the monovalent cations ($\text{K} + \text{Na} + \text{NH}_4$) in the mineral samples was determined to be greater than 1, the total number of ions that can be accommodated in this cation site. It is suspected that the ICP-AES method of analysis may be consistently overestimating the potassium concentrations and the nitrogen analyser the NH_4 concentrations in samples LC6 and LC14.

Table 5.7. Chemical analyses of apophyllite samples.

Sample	SiO ₂ ^a (%)	Al ₂ O ₃ (%)	CaO (%)	Na ₂ O (%)	K ₂ O (%)	MgO (%)	Fe ₂ O ₃ (%)	F ^b (%)	NH ₄ ^c (%)	LOI (%)	H ₂ O ^d (%)	Total (%)	Trace elements ^e (mg/kg)
LC1	48.92	0.96	21.78	0.09	5.52	0.006	0.003	1.50	n.d.	16.92	15.43	94.31	Cr = 55
LC2	48.37	1.56	21.83	<0.06	5.51	0.006	0.173	0.40	n.d.	16.00	15.60	93.48	Cr = 50, Ni = 30
LC3	48.88	1.72	21.61	0.11	5.49	0.014	0.078	1.54	n.d.	n.d.	n.d.	78.02	Cr = 100, V = 60
LC4	50.54	0.64	22.87	<0.06	5.77	0.004	0.061	0.42	n.d.	16.26	15.84	96.20	
LC5	50.86	1.11	22.78	0.17	5.36	0.007	0.002	1.61	0.008	16.37	14.76	96.78	V = 540
LC6*	52.16	0.24	23.75	<0.06	4.80	<0.004	0.017	1.64	0.78	18.17	15.74	98.09	
LC7*	51.90	0.27	23.29	<0.06	5.92	<0.004	0.019	2.22	0.073	17.42	15.13	98.70	Zn = 30
LC8*	52.49	0.17	23.31	0.09	6.10	<0.004	0.011	1.54	0.005	16.58	15.04	98.68	
LC9	53.13	2.41	20.06	0.31	4.91	<0.004	0.039	1.33	0.009	17.22	15.89	97.67	Cr = 40, Cu = 20, Ni = 20
LC10*	52.13	0.33	22.73	0.13	5.78	<0.004	0.010	1.90	0.018	16.78	14.86	98.04	Cu = 25
LC11*	53.21	0.22	22.93	0.12	5.69	<0.004	0.016	2.21	0.028	16.74	14.50	99.11	Sr = 25, V = 40
LC12	55.07	6.36	16.52	0.45	3.86	<0.004	0.015	1.23	<0.005	17.37	16.14	99.76	Co = 20, V = 100
LC14 [#]	51.34	0.52	23.11	<0.06	4.53	0.005	0.016	1.39	0.89	18.21	15.94	97.73	Cr = 30
LC15	52.66	0.24	22.72	<0.06	5.71	<0.004	0.013	1.94	0.012	16.51	14.55	98.09	Pb = 20

* Duplicate samples of LC6, LC7, LC8, LC10 and LC11 were prepared using a 10 minute LiBO₂ fusion and HCl digestion (Union College, current) and LC6, LC7 and LC8 were also digested using a 40 minute fusion method (Walsh, 1980). Values reported for major oxides are the means for these duplicate (LC10, LC11) or triplicate (LC6 - 8) analyses.

[#] Values recalculated to remove 8% SiO₂ impurity. XRD pattern shows quartz contamination.

^a SiO₂ values adjusted for 40% loss of F as SiF₄ for 10 minute fusions and 100% loss of F as SiF₄ for 40 minute fusions.

^b Fluoride values are means for duplicate analyses of a single NaOH fusion, except LC6 and LC8 were fusions were carried out in duplicate.

^c Ammonium was calculated from total nitrogen measured on solid samples. Values reported are means for duplicate analyses, except LC6, LC10 and LC11, which were analysed in triplicate.

^d Water content was calculated from LOI - (F + NH₄)

^e Samples were analysed for As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Sr, V and Zn. Only those elements with concentrations above 20 mg/kg are reported.

Table 5.8. Classification of apophyllites, based on mineral composition.

Fluorapophyllites		Location
LC7	$K_{1.17} Na_{0.02} Ca_{3.86} Si_{8.03} Al_{0.05} O_{20} F_{1.09} \cdot 7.8H_2O$	Paterson
LC11	$K_{1.11} Na_{0.04} Ca_{3.74} Si_{8.10} Al_{0.04} O_{20} F_{1.06} \cdot 7.4H_2O$	Tyrrol
LC15	$K_{1.12} Ca_{3.74} Si_{8.10} Al_{0.04} O_{20} F_{0.94} (OH)_{0.06} \cdot 7.5H_2O$	Poona
LC10	$K_{1.14} Na_{0.04} Ca_{3.77} Si_{8.07} Al_{0.06} O_{20} F_{0.93} (OH)_{0.07} \cdot 7.7H_2O$	Sweet Home
LC3	$K_{1.13} Ca_{3.74} Si_{7.89} Al_{0.33} O_{20} F_{0.79} (OH)_{0.21} \cdot xH_2O$	French Creek
LC5	$K_{1.07} Na_{0.05} Ca_{3.81} Si_{7.94} Al_{0.20} O_{20} F_{0.79} (OH)_{0.21} \cdot 7.7H_2O$	Khadrakvaslar
LC1	$K_{1.15} Na_{0.03} Ca_{3.80} Si_{7.96} Al_{0.18} O_{20} F_{0.77} (OH)_{0.23} \cdot 8.4H_2O$	Murdochville
LC8	$K_{1.19} Na_{0.03} Ca_{3.83} Si_{8.06} Al_{0.03} O_{20} F_{0.75} (OH)_{0.25} \cdot 7.7H_2O$	Jalgaon
Hydroxyapophyllites		
LC2	$K_{1.14} Ca_{3.81} Si_{7.87} Al_{0.30} O_{20} F_{0.21} (OH)_{0.79} \cdot 8.5H_2O$	Centerville
LC4	$K_{1.16} Ca_{3.87} Si_{7.98} Al_{0.12} O_{20} F_{0.21} (OH)_{0.79} \cdot 8.4H_2O$	Centerville
Ammonian apophyllites		
LC6	$K_{0.94} (NH_4)_{0.40} Ca_{3.91} Si_{8.01} Al_{0.04} O_{20} F_{0.80} (OH)_{0.20} \cdot 8.1H_2O$	Guanajuato
LC14	$K_{0.90} (NH_4)_{0.46} Ca_{3.86} Si_{8.00} Al_{0.10} O_{20} F_{0.69} (OH)_{0.31} \cdot 8.3H_2O$	Guanajuato
LC13	$K_{0.39} Na_{0.03} (NH_4)_{0.67} Ca_{3.92} Mg_{0.02} Si_{7.70} Al_{0.09} O_{19.7} F_{1.00} \cdot 7.9H_2O$	Kopasfontein
High aluminium samples		
LC9	$K_{0.95} Na_{0.09} Ca_{3.26} Si_{8.05} Al_{0.43} O_{20} F_{0.64} (OH)_{0.36} \cdot 8.0H_2O$	Poona
LC12	$K_{0.71} Na_{0.13} Ca_{2.55} Si_{7.92} Al_{1.08} O_{20} F_{0.56} (OH)_{0.44} \cdot 7.7H_2O$	Poona

The substitution of OH for F and NH_4 for K causes slight changes in the unit cell dimensions of apophyllite. Marriner *et al.* (1990) showed a contraction of the a and c axis spacings and a reduction in unit cell volume with increasing fluorine content of apophyllite samples. Unit cell measurements in this study are not as accurate as those of Marriner *et al.* (1990), but the data in Figure 5.7 also suggest a decrease in c-axis spacing with increasing fluoride concentration. Ammonium-rich samples do not fit the general trend of the other fluorapophyllite samples, but produce an increase in the a dimension with increasing N content.

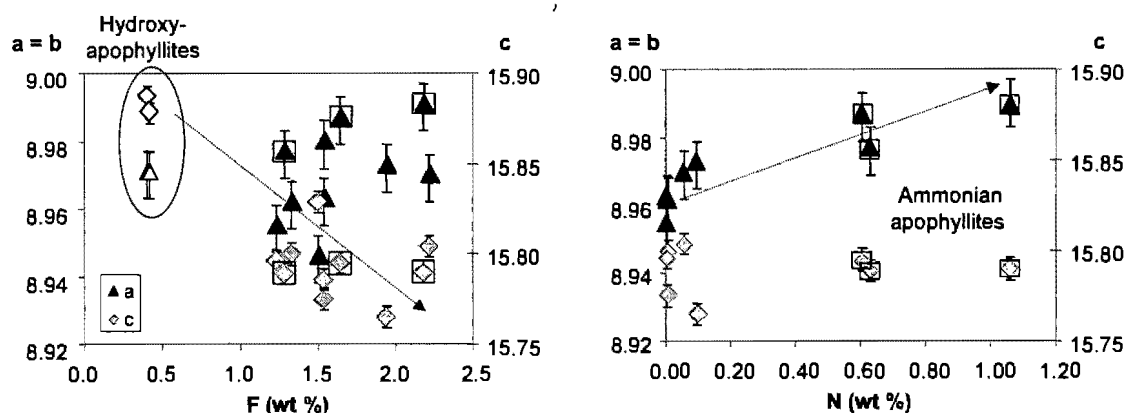


Figure 5.7. Influence of mineral F and N concentrations on unit cell dimensions of apophyllite. Triangular symbols show unit cell a dimensions and diamond symbols, c dimensions in Ångstrom units. Hydroxyapophyllites are shown with open symbols in the first plot and ammonian varieties with squares. The arrows indicate a general decrease in c dimension with increasing F and an increase in a dimension with increasing N.

5.5.3 Thermal analysis

All the apophyllite samples (except LC3, for which insufficient material remained after the digestions) were submitted to the USGS thermal analysis laboratory for simultaneous TGA/DTA coupled to qualitative mass spectrometric analysis of the evolved gases. Twenty milligram samples were run in argon at a heating rate of 10°C/minute from 22 to 1050°C. The spectra for all samples are included as Appendix G.

The TGA curves all show two distinct stages of mass loss below 600°C as well as a gradual loss of mass at higher temperature. DTA curves all have two prominent endothermic peaks near 300 and 450°C, but LC9 and LC12 have an additional low temperature endotherm at 150°C. This agrees with the suggestion that these two samples may be contaminated with some compound of lower thermal stability. The ammonian apophyllites LC6, LC13 and LC14 may also display a weak third endothermic peak at 760, 790 and 690°C, respectively although this is very broad for the Guanajuato samples (LC6 and LC14) and difficult to distinguish from baseline drift. Thermal data for the apophyllite samples are summarised in Tables 5.9 and 5.10.

Table 5.9. Thermogravimetric analysis data for apophyllite samples.

Sample	Step 1		Step 2		Total mass loss (%)
	Temp. range (°C)	Mass loss (%)	Temp. range (°C)	Mass loss (%)	
Fluorapophyllites					
LC7	60-360	10	360-610	6	17.42
LC11	80-380	10	380-680	6	16.74
LC15	80-360	10	360-700	6	16.51
LC10	60-370	9	370-720	7	16.78
LC5	80-360	9.5	360-700	5	16.37
LC1	100-380	10	380-640	6	16.92
LC8 ^a	60-360	10.5	360-620	4.5	16.47
LC8 ^b	100-390	9.5	390-640	6.5	16.70
Hydroxyapophyllites					
LC2	100-340	6	340-850	10	16.00
LC4	80-340	7	360-700	9	16.26
Ammonian apophyllites					
LC6	80-340	10	340-1000	8	18.17
LC14 [*]	120-360	7	360-580 / 580-840	8 2	18.21 [#]
LC13	40-340	9.5	340-900	7.5	19.07 [#]
High aluminium samples					
LC9	40-380	12.5	380-980	4.5	17.22
LC12	40-380	13	380-1000	4.5	17.37

^{*} LC14 has an additional high temperature step.

[#] corrected for 8% (LC14) and 10% (LC13) non-volatile silica component.

^{a,b} Two different particle sizes analysed for LC8, ^a < 50 μm and ^b 50 - 100 μm .

Marriner *et al.* (1990) report thermal analysis data for a range of apophyllite samples of varying chemical composition (particle size < 75 μm), which were also measured at a heating rate of 10°C/minute. They cite DTA endotherm peaks between 310-334°C and 430-450°C for fluorapophyllite and between 300-310°C and 400-422°C for hydroxyapophyllite.

Lower temperatures are measured for the endotherms in this study, particularly the first endotherm. The pattern of lower thermal stability, however, persists for hydroxyapophyllite compared with fluorapophyllite. Endotherm peaks occur at 270 and 272°C (1st peak) and 430 and 432°C (2nd peak) for hydroxyapophyllites, LC2 and LC4, while fluorapophyllite peaks range from 288 - 295 and 440-452°C. The high ammonium sample, LC13 is an exception as can be seen in Figure 5.8.

Table 5.10. Differential thermal analysis data for apophyllites.

Sample	1 st Endotherm			2 nd Endotherm		
	T (°C)	Shape	RI ¹ (%)	T (°C)	Shape	RI (%)
Fluorapophyllites						
LC7	288	broad	89	452	sharp	100
LC11	292	broad, high T shoulder	90	450	sharp	100
LC15	295	broad	94	448	sharp	100
LC10	292	broad, high T shoulder	74	448	sharp	100
LC5	293	broad	100	440	sharp	84
LC1	295	broad, high T shoulder	89	448	sharp	100
LC8 ^a	280	broad, high T shoulder	100	448	sharp	72
LC8 ^b	288	broad	90	450	sharp	100
Hydroxyapophyllites						
LC2	272	broad	64	430/ 450	broad, doublet peak	100
LC4	270	broad	67	432	broad, high T shoulder	100
Ammonian apophyllites						
LC6 [*]	292	shoulder at 180°C	100	455	shoulder at 410°C	57
LC14 [*]	285	weak low T shoulder	46	430	shoulder at 410°C	100
LC13 [*]	275	broad, asymmetric	100	445	broad	33
High aluminium samples						
LC9 [#]	285	2 broad (150 & 285°C)	100	445	sharp	86
LC12 [#]	285	2 broad (150 & 285°C)	100	442	sharp	83

Notes: ¹RI = relative intensity of endotherms calculated as a percentage of the peak height for the strongest peak.

^{a, b} Two different particle sizes analysed for LC8, ^a < 50 µm and ^b 50 - 100 µm.

^{*}Additional weak endotherms may be present for ammonian apophyllites, LC6 (760°C; RI = 6%), LC13 (790°C; RI = 8%) and LC14 (690°C; RI = 15%).

[#]Additional strong endotherms are present for LC9 (150°C/RI = 73%) and LC12 (150°C/RI = 81%).

Marriner *et al.* (1990) found that ammonian apophyllites have a first endotherm which is considerably larger than the second, in contrast to fluorapophyllite and hydroxyapophyllite, which generally have a more intense second stage reaction. They proposed that this is because volatile ammonia is largely removed during the first dehydration step. The endotherm intensities in Table 5.10 support this observation for the ammonian samples LC6 and LC13, but not for LC14.

Mass spectra for evolved gases show that particles with *m/e* of 18, 17, 16 (H₂O) and 19 (F₂) are associated with all the endothermic peaks, including the additional low temperature endothermic peaks at 150°C for samples LC9 and LC12. Release of particles with *m/e* = 19 also occurs above 900°C, except for the hydroxyapophyllite samples, LC2 and LC4. This occurs when trapped

fluorine escapes as the sample decomposes. Ammonian apophyllite LC13 shows an additional weak nitrogen-related peak ($m/e = 14$) above 700°C . The high temperature endotherm (690°C) for sample LC14 is accompanied by evolution of species with $m/e = 12$ and 44 , i.e. derived from parent CO_2 molecules. Carbon dioxide may have been trapped in fluid inclusions in the mineral (e.g. Andrusenko and Vasil'eva, 1968).

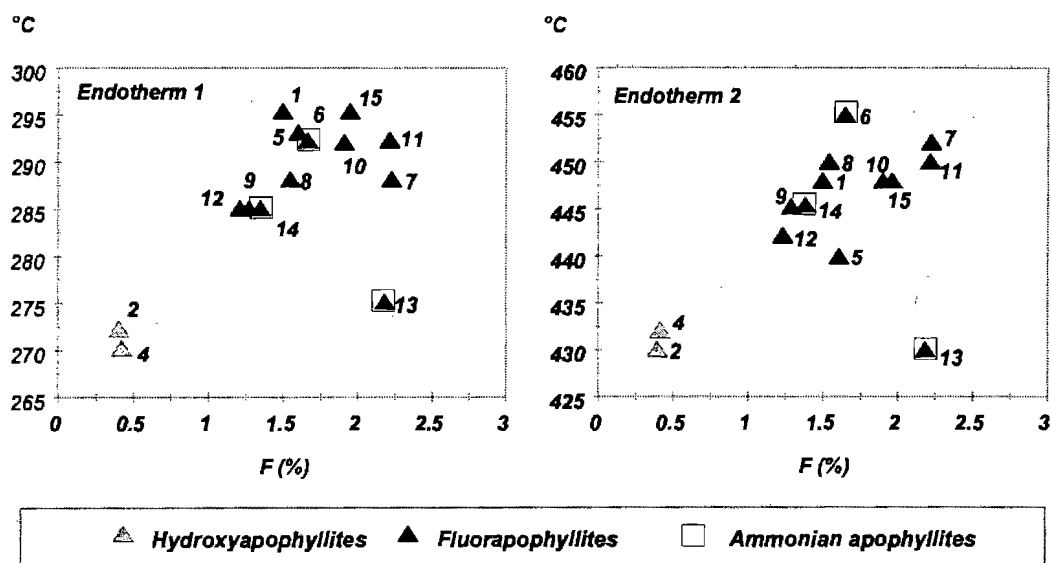


Figure 5.8. Endotherm temperatures versus F content of apophyllite samples, illustrating the influence of F in stabilising the crystal structure.

5.5.4 Apophyllite composition and thermal behaviour: summary and discussion

Apophyllite has a low-density, relatively open structure and a high content of structural water in comparison with the more common rock-forming phyllosilicates. It is expected to form at a reasonably low temperature (below 250°C), a property which is supported by its low thermal stability. At a heating rate of $10^{\circ}\text{C}/\text{minute}$, approximately 10% of the mineral weight of fluorapophyllites is lost before 400°C and the remaining 6 - 7 % before 700°C .

Apart from the structural water, apophyllites may also contain F^- , OH^- and NH_4^+ which volatilise on heating. This high volatile content complicates the determination of mineral composition by the classical methods for rock forming silicates, most of which involve intense heating. Digestion at low temperature is too slow for analytical purposes, except in very strong acid or alkaline solutions, in which case dissolution is incongruent and whole mineral digestion is not achieved.

The presence of F as an analyte also precludes the use of HF digestion techniques. Several fusion, digestion and X-ray or ion beam methods were combined for the analysis of apophyllite samples in this study.

Apophyllite composition is variable, with substitution occurring in the M^+ and X^- sites in the mineral formula: $MCa_4Si_8O_{20}X \cdot 8H_2O$, where $M = K, Na$ or NH_4 and $X = F$ or OH . Minor impurities of Al (for Si) and Mg (for Ca) are also common. A prevalence of fluorine-rich phases of apophyllite was found among randomly selected samples from fifteen localities, while ammonium-rich varieties are relatively rare. The sample from the Kopoasfontein site, South Africa has the composition $K_{0.4}(NH_4)_{0.7}Ca_{4.0}Si_{7.9}Al_{0.1}O_{20}F_{1.0} \cdot 7.7H_2O$, which is remarkably NH_4^- -rich and constitutes, to the author's knowledge, the first reported ammonian apophyllite end-member.

Compositional variations have a measurable effect on the stability of the crystal lattice, with hydroxyapophyllites having larger unit cell dimensions and lower thermal stability than the fluorapophyllites. The ammonium substitution in Kopoasfontein apophyllite also appears to have lowered its thermal stability and increased the c axis spacing. At lower substitution fractions, the stabilising influence of F in the lattice seems to outweigh any destabilisation by NH_4^+ , as was found for Mexican samples with 40% K replacement by NH_4 . This could be expected intuitively from the position of these species in the mineral, F forming a more integral part of the bonding in the lattice than NH_4 , which is coordinated by H_2O molecules. Similar trends based on compositional variations are anticipated for the mineral dissolution behaviour.

5.6 The solubility of apophyllite: A first approximation

Experimental data are lacking for the thermodynamic properties of apophyllite. No published data were found for the Gibbs energy, enthalpy, entropy or heat capacity of the mineral, which would allow the mineral solubility and its variation with temperature to be calculated.

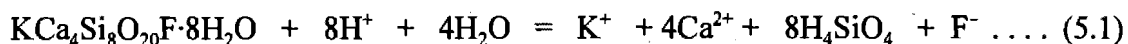
Initial attempts were made to find an approximate value for the solubility of apophyllite at 25 °C and atmospheric pressure, without the use of rigorous phase equilibrium, calorimetric or solubility experiments, which are beyond the scope of the Kopoasfontein study. These involved

the analysis of solute concentration data from long-term batch test samples and the use of thermodynamic estimation techniques developed by Chermak and Rimstidt (1989).

5.6.1 Solubility estimates from dissolution data

Batch tests were conducted for the purpose of measuring the dissolution rate of apophyllite. These experiments are discussed in detail in Section 5.7. While the intention of the experiments was to measure the rate of reaction in dilute solutions, i.e. far from equilibrium with the reacting solid, some of the longer-term samples showed a decrease in the rate with time, which may be expected as the solution approaches chemical equilibrium with apophyllite.

Data from two long-term dissolution batch tests at room temperature have been analysed to determine the ion activity product, as an initial approximation for the solubility product of apophyllite. Using the fluorapophyllite dissolution reaction:



the ion activity product from the mass balance expression for this reaction is given as:

$$IAP_{\text{apoph.}} = \frac{(a\text{K}^+)(a\text{Ca}^{2+})^4(a\text{H}_4\text{SiO}_4)^8(a\text{F}^-)}{(a\text{H}^+)^8(a\text{H}_2\text{O})^4} \dots (5.2)$$

or

$$\log IAP = \log (a\text{K}^+) + 4 \log (a\text{Ca}^{2+}) + 8 \log (a\text{H}_4\text{SiO}_4) + \log (a\text{F}^-) + 8 \text{pH} \dots (5.3)$$

where $(a\ i)$ is the activity of species i in solution. At thermodynamic equilibrium for a particular temperature and pressure condition, the IAP is equivalent to the solubility product, K_{sp} .

Solute concentration data from the batch tests were screened to include only those samples where apophyllite was in contact with the solution for upward of seven days. Experiments where the reacting solution was changed weekly to avoid solute build-up (batch tests 2 and 3, Section 5.7) were excluded. Solute ratios were also checked to make sure these were in agreement with the

stoichiometry of apophyllite and data for non-stoichiometric dissolution were disregarded. This avoided the use of samples in which side reactions such as base cation leaching or the precipitation of calcium carbonate might be occurring. The PHREEQC-1.5 software and thermodynamic database (Parkhurst, 1995) were used to speciate the solute concentrations for apophyllite *IAP* calculations. The results are given in Table 5.11, with values of log *IAP* representing initial estimates of log K_{sp} for apophyllite.

Table 5.11. Solute activities and ion activity product for long-term batch test dissolution of apophyllite.

Test No. ^a	Solution No.	Reaction time (days)	pH	Ca:Si ratio ^b	log (a K^+)	log (a Ca^{2+})	log (a H_4SiO_4)	log (a F^-)	log <i>IAP</i>
1	7	8	9.08	0.56	- 4.53	- 3.86	- 3.80	- 4.44	17.8
	8	12	8.84	0.65	- 4.53	- 3.86	- 3.77	- 4.68	15.9
4	7	15	8.7	0.55	- 4.68	- 3.76	- 3.49	- 4.26	17.7
	8	23	8.7	0.56	- 4.40	- 3.69	- 3.43	- 4.22	18.8
	9	29	8.7	0.40	- 4.26	- 3.80	- 3.40	- 4.29	18.7
	10	38	8.2	0.40	- 4.19	- 3.75	- 3.32	- 4.19	15.7
	12	15	9.2	0.50	- 4.85	- 3.70	- 3.46	- 4.24	22.0
	13	23	8.3	0.52	- 5.06	- 3.72	- 3.41	- 4.27	14.9
	14	29	8.0	0.42	- 4.18	- 3.69	- 3.27	- 4.15	14.7
	15	38	7.9	0.56	- 4.14	- 3.66	- 3.37	- 4.14	13.3

^a Test No. 1: Kopoasfontein apophyllite (LC13, 0.2 g samples, 50 - 100 μ m particle size) reacted with 20 mL of 0.01M LiCl solution in sealed 50 mL polyethylene tubes, shaken horizontally at 100 cycles per minute at 25°C.

Test No. 4: Jalgaon apophyllite (LC8, 0.025 g samples, 50 - 100 μ m particle size) reacted with 5 mL of 1×10^{-4} or 1×10^{-6} M NaOH solution under N_2 in sealed 7 mL plastic tubes, rotated on a thermostatted shaker at 28°C.

^b Ca:Si ratio = molar ratio of Ca/Si in solution. The ratio for stoichiometric dissolution of pure apophyllite is 0.50.

Because of the large stoichiometric coefficients for H^+ , Ca^{2+} and H_4SiO_4 in the dissolution reaction, 5.1, the *IAP* is very sensitive to uncertainties in the pH and the concentrations of Ca^{2+} and Si in solution. Predicted maximum errors of 5% for Si, 30% for Ca^{2+} , 10% for K, 15% for F and 0.1 pH unit give a maximum uncertainty in the value of log *IAP* of 1.5 log units.

5.6.2 Solubility from thermodynamic estimation model

Various methods have been proposed for estimating the thermodynamic properties of silicate minerals where experimental data are lacking (e.g. Tardy and Garrels, 1974; Haas and Fisher,

1976; Robinson and Haas, 1983; Holland, 1989). These are often based on the summation of properties of components from structural analogues. One such model, that of Chermak and Rimstidt (1989), has been applied to apophyllite in an effort to estimate the Gibbs free energy of formation, ΔG_f° , and enthalpy of formation, ΔH_f° , of the mineral at 298 K. The ΔG_f° was then used to calculate an estimated value for the Gibbs energy of the dissolution reaction 5.1, ΔG_r° , and the solubility product, K_{sp} .

Tardy and Garrels (1974) calculated standard Gibbs free energies of formation of layer silicates, based on the assumption that each mineral could be represented by its oxide and hydroxide components. Their method was refined by Chermak and Rimstidt (1989) who included the coordination of the cation in the components and used a multiple linear regression technique to determine the contribution of oxides and hydroxides of specific coordination (polyhedral units). The regression model of Chermak and Rimstidt (1989) is based on ΔG_f° data for 29 minerals and ΔH_f° data for 32 minerals, a more sophisticated approach than Tardy and Garrel's (1974) original solution of a few simultaneous equations.

From their database of thermodynamic values, Chermak and Rimstidt (1989) derived data for the $\Delta G_{f,sil}^\circ$ and $\Delta H_{f,sil}^\circ$ at 298 K of the $^{[4]}\text{Al}_2\text{O}_3$, $^{[6]}\text{Al}_2\text{O}_3$, $^{[6]}\text{Al}(\text{OH})_3$, $^{[4]}\text{SiO}_2$, $^{[6]}\text{MgO}$, $^{[6]}\text{Mg}(\text{OH})_2$, $^{[6]}\text{CaO}$, $^{[8-z]}\text{CaO}$, $^{[6-8]}\text{Na}_2\text{O}$, $^{[8-12]}\text{K}_2\text{O}$, H_2O , $^{[6]}\text{FeO}$, $^{[6]}\text{Fe}(\text{OH})_2$ and $^{[6]}\text{Fe}_2\text{O}_3$ polyhedral units in silicate minerals¹. The values obtained for the oxide and hydroxide units in the silicates are assumed to be constant for silicate minerals of similar structure, but differ from the ΔG_f° and ΔH_f° of the oxides or hydroxides as separate phases. These data could then be employed to estimate ΔG_f° and ΔH_f° for silicate minerals with unknown thermodynamic properties, by summation of the properties for the individual units, weighted according to their stoichiometry.

5.6.2.1 Gibbs free energy and enthalpy of formation estimates

The data of Chermak and Rimstidt (1989) for polyhedral units $^{[4]}\text{SiO}_2$, $^{[6]}\text{CaO}$, $^{[8-z]}\text{CaO}$, $^{[8]}\text{K}_2\text{O}$ and H_2O in silicate minerals have been used to calculate ΔG_f° and ΔH_f° for fluorapophyllite and hydroxyapophyllite end-members of the apophyllite mineral series (Table 5.12). Fluorine-bearing

¹ The superscript [i] refers to the coordination of the cation, with z indicating a zeolite-type structure, while the subscript *sil* refers to the polyhedral units within a silicate framework.

minerals are not included in the database and accounting for the contribution of F in fluorapophyllite is a source of uncertainty in the calculations. Four different schemes have been employed to incorporate the contribution of F in fluorapophyllite, with analogous structural components used for the hydroxyapophyllite calculations.

With the exception of scheme 1, each of the calculations for fluorapophyllite attempts to account for some feature of the mineral structure, although none of these is entirely satisfactory. Scheme 1 is possibly the least appropriate, being based on a simple breakdown of the mineral oxides, with the remaining K and F being assigned to solid KF. Scheme 2 tries to account for the fact that K is coordinated by water molecules, by using the free energy of the aqueous K^+ ion.

Structural determinations by Colville and Anderson (1971) and Chao (1971) suggest that F in apophyllite is bonded to Ca and that K is coordinated by the O atoms of the structural water in the crystal, which has been used as the basis for scheme 3. Both schemes 1 and 3 use data for KF and fluorite (CaF_2) as pure solids phases, since the Chermak and Rimstidt (1989) model does not include data for these components within a layer silicate structure.

Scheme 4 is based on the structural determinations of the hydrogen ion positions by Prince (1971), who found that F was not part of the Ca polyhedron, as suggested by its location between four Ca atoms in square planar arrangement, but rather part of an HF group, so that the chemical formula could be re-written as $KCa_4(Si_4O_{10})_2F_{1-x}(HF)_x \cdot [(H_2O)_{8-x}(OH)_x]$ with $x \approx 1$.

The assignment of one H from the structural water to the HF group is also consistent with a two stage thermal decomposition, which Ståhl (1993) concluded was evidence for one of the water molecules being lost at lower energy than the other seven. This structural determination has, however, been disputed by Rouse *et al.* (1978), who claim that Prince (1971) had unwittingly analysed an OH-rich sample, before the discovery of hydroxyapophyllite.

Scheme 5, like scheme 1, has little structural basis for hydroxyapophyllite, while scheme 6 includes aqueous K^+ as an estimate for the hydrated K in the mineral. Scheme 7 uses portlandite properties to estimate the effect if the OH group is coordinated by Ca, as suggested by the structural determinations of Rouse *et al.* (1978).

Table 5.12. Estimated values for ΔG°_f and ΔH°_f for fluorapophyllite (FA) and hydroxyapophyllite (HA) based on the method of Chermak and Rimstidt (1989), using four different approaches to account for contribution of fluoride and hydroxyl ions in the mineral.

Scheme	Polyhedral units	Data used	ΔG°_f (kJ/mol)		ΔH°_f (kJ/mol)	
			Octahedral Ca	Zeolite Ca	Octahedral Ca	Zeolite Ca
1	FA = 4CaO + 8SiO ₂ + 8H ₂ O + KF	a or b, c, d, e	- 11966.4	- 12130.2	- 12981.9	- 13139.5
2	FA = 4CaO + 8SiO ₂ + 8H ₂ O + K ⁺ + F ⁻	a or b, c, d, f, g	- 11991.4	- 12155.2	- 13000.8	- 13158.4
3	FA = 3.5CaO + 8SiO ₂ + 8H ₂ O + 0.5CaF ₂ + 0.5K ₂ O	a or b, c, d, h, i	- 12042.1	- 12185.4	- 13046.6	- 13184.5
4	FA = 4CaO + 8SiO ₂ + 7.5H ₂ O + 0.5K ₂ O + HF	a or b, c, d, i, j	- 11944.3	- 12108.1	- 12908.1	- 13065.6
5	HA = 4CaO + 8SiO ₂ + 8H ₂ O + KOH	a or b, c, d, k	- 11864.5	- 12028.3	- 12892.3	- 13049.9
6	HA = 4CaO + 8SiO ₂ + 8H ₂ O + K ⁺ + OH ⁻	a or b, c, d, f, l	- 11867.1	- 12030.9	- 12895.5	- 13053.0
7	HA = 3.5CaO + 8SiO ₂ + 8H ₂ O + 0.5Ca(OH) ₂ + 0.5K ₂ O	a or b, c, d, i, m	- 11903.1	- 12046.4	- 12925.2	- 13063.1
8	HA = 4CaO + 8SiO ₂ + 8.5H ₂ O + 0.5K ₂ O	a or b, c, d, i	- 11908.8	- 12072.6	- 12927.1	- 13084.7

Data for components (kJ/mol):

a.	$\Delta G^\circ_{f, \text{sil}} [^6]\text{CaO} = -669.13$	$\Delta H^\circ_{f, \text{sil}} [^6]\text{CaO} = -696.65$	for octahedral Ca in silicates (Chermak & Rimstidt, 1989).
b.	$\Delta G^\circ_{f, \text{sil}} [^8\text{-z}]\text{CaO} = -710.08$	$\Delta H^\circ_{f, \text{sil}} [^8\text{-z}]\text{CaO} = -736.04$	for Ca coordination in zeolite structures (Chermak and Rimstidt, 1989).
c.	$\Delta G^\circ_{f, \text{sil}} [^4]\text{SiO}_2 = -853.95$	$\Delta H^\circ_{f, \text{sil}} [^4]\text{SiO}_2 = -910.97$	for tetrahedral Si in silicates (Chermak and Rimstidt, 1989).
d.	$\Delta G^\circ_{f, \text{sil}} \text{H}_2\text{O} = -239.91$	$\Delta H^\circ_{f, \text{sil}} \text{H}_2\text{O} = -292.37$	for water in silicate structures (Chermak and Rimstidt, 1989).
e.	$\Delta G^\circ_f \text{KF}_{(\text{s})} = -539.0$	$\Delta H^\circ_f \text{KF}_{(\text{s})} = -568.61$	(Naumov <i>et al.</i> , 1974); (Westrich and Navrotsky, 1981).
f.	$\Delta G^\circ_f \text{K}^+_{(\text{aq})} = -282.5$	$\Delta H^\circ_f \text{K}^+_{(\text{aq})} = -252.14$	(Nordström and Munoz, 1994).
g.	$\Delta G^\circ_f \text{F}^-_{(\text{aq})} = -281.5$	$\Delta H^\circ_f \text{F}^-_{(\text{aq})} = -335.35$	(Nordström and Munoz, 1994).
h.	$\Delta G^\circ_f \text{CaF}_{2(\text{s})} = -1175.6$	$\Delta H^\circ_f \text{CaF}_{2(\text{s})} = -1228$	(Nordström and Munoz, 1994).
i.	$\Delta G^\circ_{f, \text{sil}} [^8]\text{K}_2\text{O} = -722.94$	$\Delta H^\circ_{f, \text{sil}} [^8]\text{K}_2\text{O} = -735.24$	for K in 8-fold coordination in silicates (Chermak and Rimstidt, 1989).
j.	$\Delta G^\circ_f \text{HF}_{(\text{g})} = -275.4$	$\Delta H^\circ_f \text{HF}_{(\text{g})} = -273.3$	(Nordström and Munoz, 1994).
k.	$\Delta G^\circ_f \text{KOH}_{(\text{s})} = -437.1$	$\Delta H^\circ_f \text{KOH}_{(\text{s})} = -479.0$	ΔG°_f and ΔH°_f for $\text{K}^+_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} = \text{KOH}_{(\text{s})} + \text{H}^+_{(\text{aq})}$ (Nordström and Munoz, 1994).
l.	$\Delta G^\circ_f \text{OH}^-_{(\text{aq})} = -157.2$	$\Delta G^\circ_f \text{OH}^-_{(\text{aq})} = -157.2$	(Nordström and Munoz, 1994).
m.	$\Delta G^\circ_f \text{Ca(OH)}_{2(\text{s})} = -897.5$	$\Delta H^\circ_f \text{Ca(OH)}_{2(\text{s})} = -985.16$	(Nordström and Munoz, 1994).

Scheme 8 is analogous to scheme 4 for fluorapophyllite, where the F or OH is associated with H from one of the structural water molecules. This form of distributing the mineral components into polyhedral units overlooks the likelihood that the hydroxide group and associated H do not have the same energetic properties as the other structural water molecules. Comparing the FA and HA data in Table 5.12 indicates that HA is the less stable form, in agreement with earlier findings on thermal behaviour (Section 5.5.3).

The calculations in Table 5.12 have been repeated using either octahedral $^{[6]}\text{CaO}$ or $^{[8-2]}\text{CaO}$, in which calcium has zeolite-type coordination. The change in the coordination of the calcium polyhedral unit was found to have a more significant influence on the results than any of the schemes for dealing with F in the mineral, because of the large coefficient of 4 (or 3.5) for the calcium unit. The zeolite configuration is possibly a closer approximation for apophyllite, in which Ca is centred in a trigonal prism, than the more stable octahedral configuration.

Estimating the thermodynamic properties of apophyllite using the Chermak and Rimstidt (1989) model is complicated by the unusual atomic arrangement of the mineral, which is inconsistent with the model assumptions. The authors caution that their method is not applicable for minerals with unusual coordination numbers, such as wollastonite and pyrope, because data for polyhedra with these coordination numbers are not specified by their model. Difficulties in applying the model to apophyllite include:

- ▶ Silica tetrahedra linked together in continuous sheets of 4- and 8-membered rings. The properties of the SiO_2 polyhedral units are therefore not likely to be the same as for the 6-membered rings of the mica group or other sheet silicates used in the regression analysis.
- ▶ Interlayer Ca^{2+} ions are hydrogen bonded to two water molecules and contain two O atoms from each of the overlying and underlying silicate sheets in their co-ordination sphere. The Ca is centered in a trigonal prism, rather than the octahedral coordination specified by the model.
- ▶ Potassium is surrounded by 8 water molecules in a tetragonal prism. This arrangement suggests that the interlayer K^+ may be approximated by $^{[8]}\text{K}_2\text{O}$, but the K-O bond energies in apophyllite will not be the same as those in layer silicates where K is coordinated by

framework O atoms from the silicate sheets.

- The nature of the bonding of F in fluorapophyllite is in dispute, with F being variously associated with 4 Ca atoms in a square planar arrangement (Colville and Anderson, 1971; Chao, 1971) or associated with H from one of the structural water molecules in an HF arrangement (Prince, 1971). Prince (1971) also notes that the H-F bond distance in fluorapophyllite (1.03 Å) is much longer than the distance in hydrogen fluoride gas (0.91 Å). The bond in apophyllite may be considerably weaker than it is in the gas and the use of thermodynamic data for HF_(g) may overestimate the mineral stability.

Uncertainties in the thermodynamic properties of the Ca and Si groups have the greatest impact on the estimated ΔG_f° and ΔH_f° values, because of the large stoichiometric coefficients for these two components used in the summation technique.

The lack of common structural analogues for apophyllite also hampers any attempt to extract thermodynamic data from an alternative database of mineral phases, which might give polyhedral units with the same coordination as the components in apophyllite.

5.6.2.2 Solubility calculations

The Gibbs energy of formation of apophyllite can be used to derive the solubility product of the mineral at 298 K and 1 atm, using the dissolution reaction in equation 5.1 for fluorapophyllite or the following reaction for hydroxyapophyllite:



The Gibbs energy of the reaction for fluorapophyllite is:

$$\begin{aligned} \Delta G_r^\circ = & \Delta G_f^\circ \text{K}_{(aq)}^+ + 4 \Delta G_f^\circ \text{Ca}_{(aq)}^{2+} + 8 \Delta G_f^\circ \text{H}_4\text{SiO}_{4(aq)} + \Delta G_f^\circ \text{F}_{(aq)}^- - 4 \Delta G_f^\circ \text{H}_2\text{O}_{(l)} \\ & - 8 \Delta G_f^\circ \text{H}_{(aq)}^+ - \Delta G_f^\circ \text{FA} \dots\dots\dots (5.5) \end{aligned}$$

and for hydroxyapophyllite:

$$\begin{aligned} \Delta G_r^\circ = & \Delta G_f^\circ K_{(aq)}^+ + 4 \Delta G_f^\circ Ca_{(aq)}^{2+} + 8 \Delta G_f^\circ H_4SiO_{4(aq)} - 3 \Delta G_f^\circ H_2O_{(l)} \\ & - 9 \Delta G_f^\circ H_{(aq)}^+ - \Delta G_f^\circ HA \end{aligned} \quad \dots\dots\dots (5.6)$$

Estimated ΔG_r° for the apophyllite dissolution reactions at 298 K has been calculated using tabled free energy data for the aqueous species (Nordström and Munoz, 1994) and the estimates of ΔG_f° from Table 5.12. The ΔG_r° values have then been used to estimate K_{sp} for the dissolution of apophyllite at 298K, using the relation:

$$\log K_{sp} = - \frac{\Delta G_r^\circ}{2.303 R T} \quad \dots\dots\dots (5.7)$$

where R is the molar gas constant, 8.314 J/mol K, T is the temperature at which the Gibbs energy of the reaction was measured, 298 K, and ΔG_r° is converted to J/mol units. The results are presented in Table 5.13.

Comparing the estimated values for $\log K_{sp}$ with the $\log IAP$ values in Table 5.11, the closest agreement is obtained using scheme 3 of Table 5.12, which includes $CaF_2(s)$ as a structural component (to account for the association between Ca and F) and the thermodynamic properties of Ca in a zeolite-type polyhedral unit. Octahedral Ca polyhedral units give ΔG_f° values which appear to be too negative and overestimate the solubility product.

Although apophyllite is a sparingly soluble silicate mineral, a relatively large solubility product is not unreasonable, because of the large stoichiometric coefficients for H^+ , Ca^{2+} and H_4SiO_4 in the dissolution reaction, which become exponents in the expression:

$$K_{sp} = \frac{(a Ca^{2+})^4 (a H_4SiO_4)^8 (a F^-) (a K^+)}{(a H^+)^8} \quad \dots\dots\dots (5.8)$$

where (a i), is the activity of aqueous species i at equilibrium with fluorapophyllite.

Table 5.13. Estimated Gibbs energy of reaction and solubility products for the dissolution of fluorapophyllite and hydroxyapophyllite at 298 K, based on various schemes for estimating the free energy of formation of the minerals using the model of Chermak and Rimstidt (1989).

Fluorapophyllite			Hydroxyapophyllite		
Scheme	ΔG°_f (kJ/mol at 298K)	$\log K_{sp}$ (298K)	Scheme	ΔG°_f (kJ/mol at 298K)	$\log K_{sp}$ (298K)
Octahedral Ca			Octahedral Ca		
1	- 332.2	58.20	5	- 369.8	68.28
2	- 307.2	53.82	6	- 387.2	67.82
3	- 256.5	44.94	7	- 351.2	61.52
4	- 354.3	62.07	8	- 345.5	60.51
Zeolite Ca			Zeolite Ca		
1	- 168.4	29.51	5	- 226.0	39.59
2	- 143.4	25.13	6	- 223.4	39.13
3	- 113.2	19.83	7	- 207.9	36.42
4	- 190.5	33.37	8	- 181.7	31.82

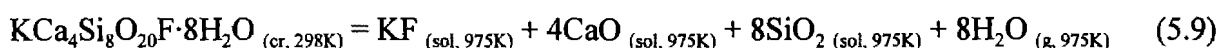
Data used for the aqueous species (kJ/mol):

$$\begin{aligned}\Delta G^\circ_f K^+_{(aq)} &= -282.5 \\ \Delta G^\circ_f H_4SiO_4(aq) &= -1309 \\ \Delta G^\circ_f H_2O(l) &= -237.14\end{aligned}$$

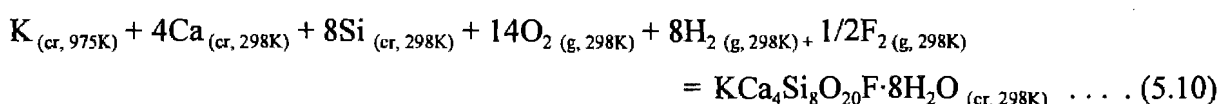
$$\begin{aligned}\Delta G^\circ_f Ca^{2+}_{(aq)} &= -552.8 \\ \Delta G^\circ_f F^-_{(aq)} &= -281.5 \\ \Delta G^\circ_f H^+_{(aq)} &= 0.0 \text{ (standard state)} \\ &\text{(Nordström and Munoz, 1994).}\end{aligned}$$

5.6.2.3 Experimental data for ΔH°_f

A fluorapophyllite sample from Jalgaon, India was submitted for calorimetric measurements (J. Majzlan, analyst: Thermochemistry facility, University of California, Davis). The sample was used to determine an ΔH°_f value of $1\,410.5 \pm 7.1$ kJ/mol for the reaction:



using high temperature oxide melt calorimetry, with lead borate ($2PbO \cdot B_2O_3$) as solvent at 700°C. This value was then used to calculate a value of $\Delta H^\circ_f = -13\,234.8 \pm 12.8$ kJ/mol (Majzlan, pers. comm.) for the enthalpy of formation of apophyllite:



assuming ideal mineral stoichiometry. Uncertainty about the final state of fluorine in the system is a source of error in the determination.

The experimental ΔH_f° value is more negative than any of those estimated in Table 5.12 by the method of Chermak and Rimstidt (1989). The closest value is once again that of scheme 3, using a zeolite configuration for Ca coordination, which gives $\Delta H_f^\circ = -13\,184.5$ kJ/mol. The entropy of formation of apophyllite has not yet been measured and so the Gibbs energy of formation and solubility of fluorapophyllite cannot be calculated from experimental data at this stage.

5.6.3 Conclusions and limitations regarding solubility estimates

The unusual structure of apophyllite limits the applicability of conventional summation techniques for estimating thermodynamic properties, because of the different coordinative arrangement of polyhedra in the apophyllite structure compared with those of the minerals in the databases of the various available models. Major sources of uncertainty are the unusual arrangement of the SiO_4 tetrahedra in 4 membered rings and the 5-fold coordination of Ca. These uncertainties are magnified through the high stoichiometric coefficients of the Si and Ca components in the various calculations. The large number of water molecules in apophyllite and the role of hydrogen bonding in stabilising the structure also make the estimated parameters very sensitive to the values used for the thermodynamic properties of the structural water. Another source of variability is the hydrated arrangement of the potassium and the presence of fluorine in the mineral, which is not accounted for in the model of Chermak and Rimstidt (1989). The effect of these is of less significance, however, since they are minor components.

From preliminary observations of limited dissolution data and rough estimates based on the approach of Chermak and Rimstidt (1989), which is not entirely appropriate for a mineral of this structure, a “best guess” estimate of $\Delta G_f^\circ \approx -12\,185$ kJ/mol and $\log K_{sp} \approx 20$ is proposed for the dissolution of fluorapophyllite.

5.7 Apophyllite dissolution rate experiments

Silicate mineral-water interactions often pose a problem when treating the reactions as equilibrium systems in low-temperature geochemical studies. Activity diagrams showing mineral stability fields for silicates, such as those used by Tardy (1971) and Rogers (1989), may give an overview of stability relations between minerals and waters in complex systems, but they are frequently open to misinterpretation. The positions of the stability boundaries are very sensitive to errors and uncertainties in the values of ΔG_f° used in the calculations (Drever, 1997; p. 210). Solid solutions and variations in crystallinity and grain size in natural minerals create even greater uncertainty than synthetic end-members, because of their effects on dissolution/precipitation behaviour. Because of the slow kinetics and essentially irreversible dissolution, it is also questionable whether true equilibrium is ever attained for many silicate phases (Appelo and Postma, 1996; p. 215). Although the solubility of apophyllite has only been estimated, the lack of reliable reports of low-temperature apophyllite formation suggest that it will not reach equilibrium with respect to its dissolved constituents in natural waters at ambient temperatures.

The problems with thermodynamic treatments have led to the use of alternatives, such as mass balance and kinetic approaches, for describing silicate weathering in natural systems. This section describes investigations into the kinetics of apophyllite dissolution. A series of experiments were performed with the aim of measuring the empirical rate of dissolution of the mineral. Batch test methods were chosen as the simplest means of acquiring dissolution rate data for the purposes of the Kopoasfontein geohydrological study. In these tests mineral composition and pH were varied to test their influence on the rate of release of solutes from the mineral. Batch tests allow many samples to be run simultaneously, providing for faster generation of results than a flow-through system, but sometimes at the sacrifice of data accuracy. Several refinements were introduced in the later batch tests to allow for more reliable data interpretation.

Since apophyllite is a silicate mineral, its dissolution under near-surface temperature and pressure conditions is a very slow process and long-term experiments were needed to measure changes in solute composition as the mineral dissolved. The rate of dissolution of apophyllite at near-neutral pH was anticipated to be around 10^{-12} to 10^{-13} mol/m²/s, the dissolution rate typically measured for other phyllosilicate minerals (Nagy, 1995).

5.7.1 Sample pretreatment

In all the experiments which follow, samples of apophyllite were pretreated following a standardised method which involved crushing, grinding and sieving the material to isolate particles between 50 and 100 μm in diameter. The mineral samples were sonicated in alcohol (ethanol or methanol) to dislodge ultrafine particles from surfaces, which could cause apparent acceleration of initial rates, and washed several times in distilled water to remove any soluble salts. Surface area measurements were made on the pretreated mineral samples using a BET nitrogen multilayer gas adsorption technique (Brunauer *et al.*, 1938) described in Appendix C.

5.7.2 Preliminary investigations

Dissolution in water

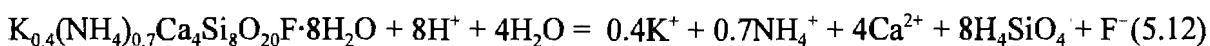
Dissolution experiments began with a simple test to monitor the reaction of apophyllite crystals in pure water, to determine the effect on solution pH and to ensure that changes in solution composition were measurable on a reasonable time scale.

Pretreated Kopoasfontein apophyllite (50 - 100 μm , surface area 0.449 m^2/g) was weighed out in three 0.1 g portions into clean, glass-jacketed reaction vessels and 20 mL of boiled, glass distilled water added to each. After 24 hours of stirring under N_2 gas at 25°C, the pH was measured and the mineral suspensions decanted into glass vials. Two weeks later the solutions were filtered (0.45 μm microporous membrane filter) for analysis of selected ions by ion chromatography. The results of the dissolution of apophyllite in water over 2 weeks are shown in Table 5.14.

The apophyllite dissolution estimates in Table 5.14 are fitted to an assumed linear rate law:

$$\text{Rate} = - \frac{d[\text{apoph}]}{dt} = \frac{d[\text{F}^-]}{dt} = 0.7 \frac{d[\text{NH}_4^+]}{dt} = 4 \frac{d[\text{Ca}^{2+}]}{dt} \quad \dots (5.11)$$

based on the reaction:



where

$$\frac{d[X]}{dt} = \frac{(X)_{t_2} - (X)_{t_1}}{t_2 - t_1} \dots\dots\dots (5.13)$$

and (X) is the molar quantity of F⁻, NH₄⁺ or Ca²⁺ ions in solution per m² of original mineral surface area in the reaction vessel at the start (t₁ = 0) and end (t₂) of the experiment.

Table 5.14. Preliminary determination of dissolution rate, based on NH₄⁺, F⁻ and Ca²⁺ release of Kopoasfontein apophyllite in water near pH 9.

	Vessel 1		Vessel 2		Vessel 3	
Sample mass (g)	0.1020		0.1083		0.1050	
pH (after 24 hours)	8.69		8.69		9.24	
Total time (days)	17		16		14	
	mg/L	mol/m ²	mg/L	mol/m ²	mg/L	mol/m ²
NH ₄ ⁺	0.9	2.2 × 10 ⁻⁵	0.8	1.8 × 10 ⁻⁵	0.6	1.4 × 10 ⁻⁵
Ca ²⁺	32	3.5 × 10 ⁻⁴	36	3.7 × 10 ⁻⁴	29	3.1 × 10 ⁻⁴
F ⁻	1.9	4.4 × 10 ⁻⁵	2.0	4.3 × 10 ⁻⁵	2.1	4.7 × 10 ⁻⁵
Rate _A (mol/m ² /s)	2.6 ± 0.4 × 10 ⁻¹¹		2.5 ± 0.6 × 10 ⁻¹¹		2.8 ± 1.1 × 10 ⁻¹¹	
Rate _{Ca} (mol/m ² /s)	6.0 × 10 ⁻¹¹		6.3 × 10 ⁻¹¹		5.3 × 10 ⁻¹¹	

Notes: Rate_A is the rate of dissolution of apophyllite estimated from the average rate of accumulation of F⁻ and NH₄⁺ in solution using the mineral stoichiometry K_{0.4}(NH₄)_{0.7}Ca₄Si₈O₂₀F·8H₂O, and based on an assumed linear rate law (zero-order with respect to products) over the 2 week period.

Rate_{Ca} is the stoichiometric rate of release of Ca per formula unit of apophyllite during the experiment, again assuming linear kinetics.

Dissolution in acid and basic solution

Longer dissolution trials were also performed in HCl and NaOH solutions. Apophyllite is known to dissolve rapidly in concentrated HCl to give a silica gel (Dana, 1966; p. 642) and the HCl trial confirmed that rapid, incongruent dissolution occurs. Hydrochloric acid addition was originally intended to saturate the mineral surface sites with H⁺ for surface titrations, but rapid dissolution caused continuous drift in the pH reading and the titration was abandoned.

The same apparatus and procedure was used as for the dissolution in water, replacing 20 mL of H₂O with either 20 mL of 0.01M HCl in 0.09M NaCl background electrolyte or 20 mL of 0.001M NaOH. The sample mass used for the NaOH experiment was decreased to 0.05 g.

Samples were stirred overnight, and then transferred to glass vials for storage, before filtering and analysing the solutions after a two month reaction period. The solution composition and estimated dissolution rates in the acid and basic solutions are given in Table 5.15.

Table 5.15. Preliminary estimates of Kopoasfontein apophyllite dissolution rate in HCl and NaOH solutions.

	Acid dissolution		Base dissolution	
Sample mass (g)	0.1007		0.0514	
Solution composition	0.01 M HCl + 0.09M NaCl		1×10^{-3} M NaOH	
pH (start)	2.27		10.66	
Reaction pH	5.76 (after 3.5 hours)		10.77 (after 30 minutes)	
			8.24 (after 45 days)	
Total time (days) ^a	63		62	
	mg/L	mol/m ²	mg/L	mol/m ²
NH ₄ ⁺	19	4.7×10^{-4}	0.25	1.2×10^{-5}
K ⁺	35	4.0×10^{-4}	16	3.5×10^{-4}
Ca ²⁺	284	3.1×10^{-3}	10	2.2×10^{-4}
F ⁻	29	6.8×10^{-4}	0.9	4.1×10^{-5}
Rate (mol/m ² /s)	Linear rate ^b $1.4 \pm 0.3 \times 10^{-10}$		NH ₄	3.2×10^{-11} ^c
			K	16×10^{-11}
			Ca	1.0×10^{-11}
			F	0.7×10^{-11}

^a Total time of mineral contact with solution before filtering.

^b Rate in acid solution is estimated from the average rate of stoichiometric accumulation of K⁺, Ca²⁺, F⁻ and NH₄⁺ in solution using the mineral stoichiometry K_{0.4}(NH₄)_{0.7}Ca₄Si₈O₂₀F·8H₂O, and based on an assumed linear rate law (zero-order with respect to products) over the 2 month period.

^c Dissolution in NaOH solution is non-stoichiometric and dissolution rates calculated from the mineral stoichiometry differ for each solute. It is likely that incongruent dissolution occurs or side reactions such as volatilisation of NH₃ and precipitation of CaCO₃ and/or CaF₂ has caused some loss of solutes. Errors in NH₄⁺ and F⁻ data are likely to be large, since concentrations are near the analytical detection limit.

Acid dissolution is significantly faster than dissolution in pure water. Basic dissolution appears to be non-stoichiometric and, with the exception of K⁺ release, is slower than that in acid.

The results of these preliminary tests have no real significance to the determination of apophyllite dissolution kinetics under acid conditions without information on the final pH. The results under basic conditions are of limited significance because of the strong drift in pH.

5.7.3 Batch dissolution experiment 1

A long-term dissolution batch test was conducted on the Kopoasfontein apophyllite, during which time-dependent solute concentration data were collected. Several workers have cautioned against the use of short reaction times for the measurement of silicate dissolution rates (e.g. Carroll and Walther, 1990; Amrhein and Suarez, 1992), as these often lead to overestimation of the rate. In this experiment, aqueous solutions of constant 0.01M ionic strength were reacted with crushed and cleaned apophyllite for just less than 1000 hours.

5.7.3.1 Method

Preatreated apophyllite from Kopoasfontein (50 - 100 μm ; surface area $0.449 \pm 0.003 \text{ m}^2/\text{g}$) was weighed out accurately in 0.2 g portions into eleven 50 mL polyethylene centrifuge tubes. A stock solution of 0.01 M LiCl was prepared from oven-dried, reagent-grade LiCl in deionised water and a 20 mL aliquot of this solution added to each sample. The tubes were closed with plastic screw-on caps and mounted horizontally on a flat-bed reciprocating shaker which agitated them at approximately 100 cycles per minute for the duration of the batch test. The experiment was conducted in a temperature-controlled laboratory, where the average temperature during the batch test was 25°C.

At increasing time intervals, one sample tube was removed from the shaker, while the remaining samples were left to continue reacting. The solution from the selected sample tube was filtered through an oven-dried, porosity 4 sintered glass crucible, collecting the liquid in a clean plastic sample container for chemical analysis. No attempt was made to buffer the solution pH in the experiments, but each time a sample was removed for filtration, a separate control sample was also removed and the pH measured before returning the control to the shaker.

After filtering, the batch test samples were stored in a refrigerator at 4°C and analysed together once the final sample was removed at 985 hours. Fluoride was determined by IC and molybdate-reactive silica by colorimetry on undiluted samples. The remainder of the solution was diluted ten times and submitted for analysis of K^+ and Ca^{2+} by FAAS (M. Louw, analyst: CSIR, Stellenbosch). Ammonium concentrations were also measured for the first five samples by IC.

5.7.3.2 Results

The raw data collected from the long-term batch dissolution of Kopoasfontein apophyllite are presented in Table H.1 in Appendix H.

Solute release rates are calculated on the basis of the original surface area of apophyllite in the reaction vessel. The mass of solid dissolved at the end of the batch test was calculated from the accumulated mass of dissolved products and was generally found to be less than 0.6%. The change in surface area was, therefore, assumed to be negligibly small.

The control sample had a lower final solution volume than the others and was found to have high concentrations of K^+ and Cl^- . It is suspected that KCl contamination originated from the filling solution of the pH electrode, which was immersed repeatedly in the sample when measuring the pH. The origin of the elevated Ca^{2+} concentration in the third sample is not known.

Potassium, fluoride and ammonium release

Figure 5.9 shows that measured K^+ concentrations in the first two samples were higher than in the remainder of the samples.

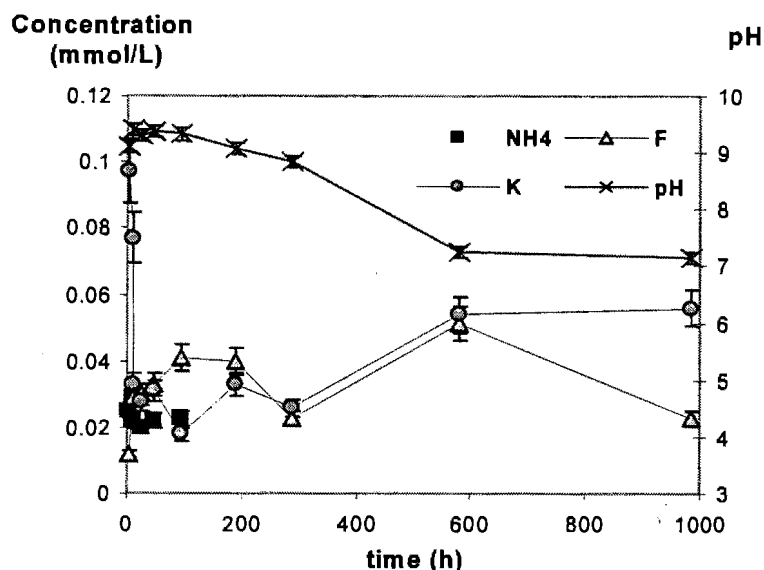


Figure 5.9. Changes in K^+ , F^- and initial NH_4^+ concentrations and pH during batch dissolution of Kopoasfontein apophyllite in 0.01M LiCl. Error bars indicate estimated maximum analytical errors of 20% for K and NH_4 , 14% for fluoride and 0.2 pH units.

Lin and Clemency (1981a) observed a rapid release of K^+ (up to 1 mmol/L) in the first three minutes of their dissolution experiments on muscovites, which they ascribed to an exchange reaction, in which H^+ from acidic solutions displaces the K in the mica. Surface area calculations were used to show that the K was not only exchanged at the surface, but also leached from deeper within the basal planes. An equally rapid rise in pH from 3.8 to 4.7 reflected the removal of hydrogen ions from solution. Little further K^+ release or H^+ removal occurred over the rest of their 1000-hour experiment.

The neutral LiCl solution (start pH = 7.02) would not have provided the same quantities of H^+ ions as those in the acid solutions used by Lin and Clemency (1981a). Ammonium, which occupies the same crystallographic sites as K, also does not show a sufficiently marked increase on the initial day of the experiment to suggest that ion exchange is responsible for the high initial K^+ concentrations in this experiment. Although some ion exchange is likely to have occurred, since NH_4^+ and K^+ are released in higher quantities than F^- , there is also no suitable explanation for the decrease in K^+ concentrations in the later samples. The initial K^+ data are, therefore, considered unreliable.

A small amount of NO_3^- (0.05 to 0.6 mg/L) was observed in samples from 192 hours onwards, in the anion chromatograms. Biological oxidation of NH_4^+ , released from the Kopoasfontein apophyllite, is likely to have occurred produced the NO_3^- in the later stages of the experiment. The oxidation of NH_4^+ to NO_3^- provides a potential mechanism whereby the weathering rate of Kopoasfontein apophyllite could be microbially enhanced. Nitrifying bacteria could promote apophyllite dissolution under aerobic conditions by oxidising NH_4 at the mineral surface, thereby destabilising the mineral structure, or by acting as a sink for NH_4^+ in solution.

Calcium and silicon release

Calcium and silicon data are considered more reliable than the relatively low K^+ and F^- concentrations for monitoring apophyllite dissolution in the long-term batch test. The curves in Figure 5.10 show the rapid initial increase in concentration at the beginning of the experiment, slowing down as the reaction progresses.

Initial dissolution rates in laboratory batch experiments are typically higher than the long-term steady state dissolution rates for the bulk mineral (Rimstidt and Dove, 1986) and are generally disregarded in the more recent literature. One of the reasons for the faster initial rate is the artificially high proportion of reactive surface sites, created by crushing of mineral grains for dissolution experiments (Petrovic, 1981a). Although the samples used in this experiment were sonicated to remove adhering ultrafine particles, the material was freshly crushed (without aging) and rapid initial dissolution suggests that a high proportion of reactive surface sites was still present at the start of the experiment.

Slowing of the reaction rate generally occurs as dissolution reactions reach steady-state. The batch experiment rates may, however, be affected by other factors which decrease the reaction rate with time. Examples include the drift towards neutral pH or towards equilibrium with the dissolving mineral, where rates are generally slower. Possible side reactions such as precipitation of calcium carbonate may also slow the *apparent* dissolution rate, by decreasing measured solute concentrations. These effects may help to explain why concentrations of Si and Ca^{2+} have decreased in the final sample. They also make it difficult to determine the long-term steady-state dissolution rate of apophyllite reliably using the available data.

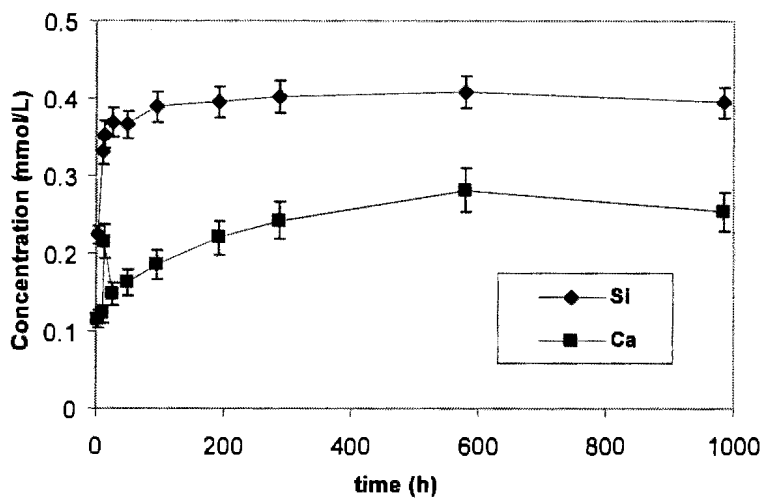


Figure 5.10. Changes in concentration of dissolved Ca^{2+} and Si during apophyllite batch dissolution in 0.01M LiCl. Error bars indicate estimated maximum analytical errors of 10% for Si and 20% for Ca.

The rates of release of Si and Ca^{2+} were estimated from the linear portions of a plot of moles of solute release per m^2 of original surface area of mineral against time (Figure 5.11).

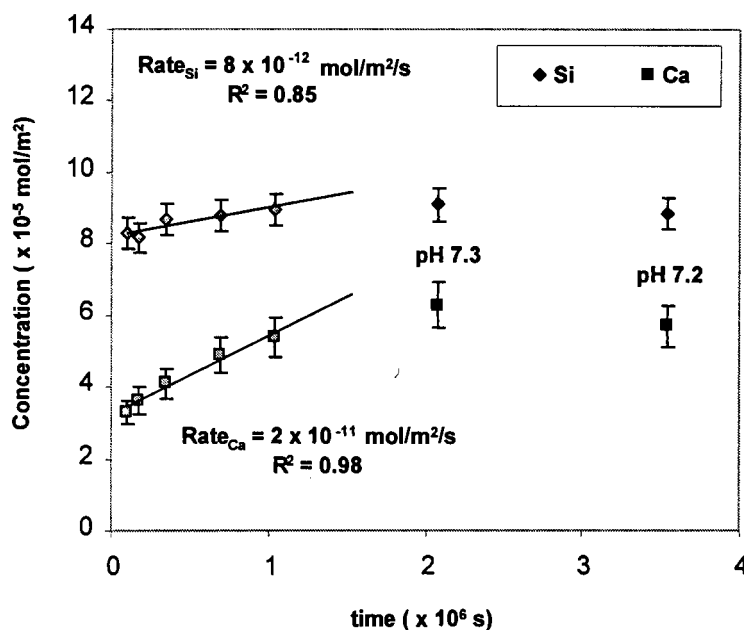


Figure 5.11. Assumed steady state rates of accumulation of Si and Ca^{2+} in solution during batch dissolution of apophyllite at pH 9. Error bars indicate the expected maximum 10% error in Si readings and 20% error in Ca^{2+} .

Rates were determined from the slope of a line created by regression through data points 4 to 8 (26 to 288 hours) from the data set. Data points 1 to 3, measured on the first day of the experiment have been rejected due to initial surface effects on the rate, while points 9 and 10 at the end of the experiment have been excluded due to pH drift. Unfortunately, this means that the reported rate has been calculated for approximately 300 hours, rather than the intended 1000 hour reaction period. Taking account of the analytical error, there is apparently no significant change in the Si concentration with time after the first day of this batch experiment and the calculated rate for silica dissolution may be meaningless.

Overall dissolution rate and dissolution stoichiometry

Since complete disintegration of the apophyllite mineral framework would release 8 silicon atoms per formula unit, the overall rate of dissolution of apophyllite at pH 9 was calculated as one-eighth of the rate of silicon release, i.e. $1 \times 10^{-12} \text{ mol/m}^2/\text{s}$. This is comparable with the dissolution rate of $2 \times 10^{-12} \text{ mol/m}^2/\text{s}$ for chrysotile at pH 8 (Bales and Morgan, 1985) and $1 \times 10^{-12} \text{ mol/m}^2/\text{s}$ for talc at pH 5 (Lin and Clemency, 1981b), but faster than that of most aluminous sheet silicate minerals at 25°C (Nagy, 1995).

Figure 5.12 compares the solute concentrations in the batch test with the mineral stoichiometry of Kopoasfontein apophyllite. The comparison of total solute concentrations is, however, not always appropriate for estimating dissolution stoichiometry, since an initial non-stoichiometric phase may mask a subsequent stoichiometric phase when the data are plotted in this manner. When normalised to the mineral stoichiometry, the Ca dissolution rate of 5×10^{-12} mol/m²/s is five times faster than the Si dissolution rate, showing that the nett dissolution of apophyllite under these conditions is non-stoichiometric.

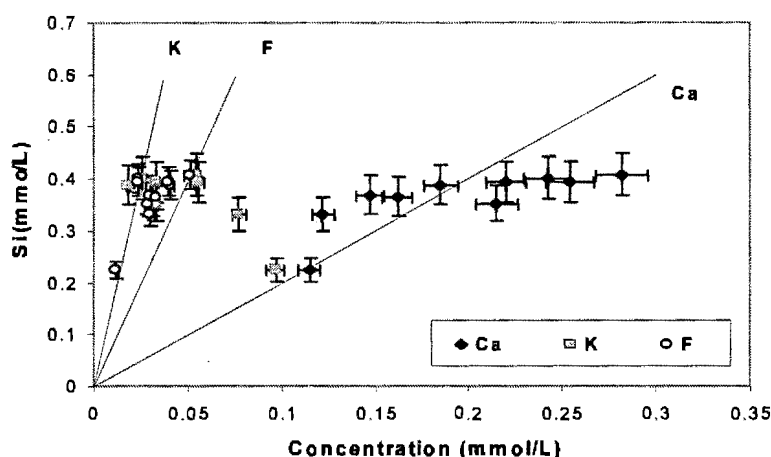


Figure 5.12. Silicon concentration versus Ca²⁺, K⁺ and F⁻ in batch test solutions. The narrow lines show ideal solute ratios if all of the solute is derived from congruent dissolution of Kopoasfontein apophyllite. Error bars indicate estimated maximum analytical errors of 10% for Si, 20% for Ca and K and 14% for fluoride.

5.7.4 Batch dissolution experiment 2

Amrhein and Suarez (1992) used “sequential rinses” in their batch experiments as a means of overcoming the problem of solute build-up in solution during long-term dissolution experiments. This involved removing almost the entire reacting solution at intervals and adding fresh solution to the dissolving mineral solid. This sequential rinse method was adopted for the second apophyllite dissolution test. Dissolution rates were investigated for four different apophyllites with a range of F and NH₄ contents to investigate the effect of chemical substitution on mineral dissolution rate.

5.7.4.1 Method

Four pretreated apophyllite samples (50 -100 μm) from Kopoasfontein (KF/LC13), Guanajuato (GJ/LC6), Paterson (PT/LC7) and Jalgaon (JL/LC8) were used for the experiment. Specific surface area was determined for KF and JL by multi-point nitrogen BET analysis using 1 to 1.5 g samples (D. Rutherford, analyst: US Geological Survey, Denver). These were found to be 0.28 m^2/g for KF and 0.34 m^2/g for JL. Insufficient material was available for surface area measurements of GJ and PT and the area used in the calculations was estimated as 0.3 m^2/g , from the average for the other two samples prepared by the same method. This estimate represents a major source of uncertainty in the results, which are normalised to mineral surface area.

Apophyllite samples were weighed out accurately in 0.13 g portions into sixteen 50 mL polypropylene centrifuge tubes (four per sample). Stock solutions of pH 2, 4, 7 and 10 were prepared from double distilled water by dropwise addition of reagent grade HCl or NaOH. Forty millilitre aliquots of these solutions were added to the reaction tubes so that each apophyllite sample had four different initial pH conditions imposed on the mineral. The samples were mounted vertically on a submerged reciprocating shaker in a water bath that was thermostatted at $25 \pm 1^\circ\text{C}$. The shaker agitated the samples at 60 cycles per minute for the duration of the test.

At one week intervals, the samples were removed from the shaker and the apophyllite allowed to settle to the bottom of the centrifuge tubes. Thirty-five millilitres of the supernatant liquid was carefully withdrawn by pipette for chemical analysis and replaced with fresh solutions, adjusted to the initial pH values of 2, 4, 7 and 10. Samples were returned to the shaker and the dissolution batch test continued for a total of four rinses, lasting 737 hours in total.

Five millilitres of each reacted solution was used to determine the pH after removal from the shaker and the remaining 30 mL was filtered (0.2 μm) before being stored in a refrigerator at 4°C in plastic bottles. Sulphuric acid was used to acidify five millilitres of each sample to preserve NH_4^+ for analysis. Fluoride was analysed on filtered solutions by ion selective electrode within 3 days of removal from the shaker, but the other analyses were all performed after the batch test had ended. Potassium, silicon and calcium analyses were conducted by ICP-AES (B. McCleskey, analyst: USGS, Boulder) and NH_4^+ analyses by ion chromatography (D. Repert, analyst: USGS, Boulder).

5.7.4.2 Results

Analytical data from the sequential rinses are tabled in Appendix H (Table H.2). The measured concentrations were first converted into an equivalent number of moles of solute released per unit mineral surface area, based on the amount of mineral present at the start of the experiment and then accumulated for the successive rinses. A volume correction was made for the effect of the 5 mL of liquid that remained in the centrifuge tube each time the solution was changed.

Dissolution stoichiometry

All apophyllite samples dissolved non-stoichiometrically in solutions of initial pH 2 (i.e. approximately 0.01M HCl), releasing F^- and base cations in greater quantities than Si from the mineral framework. Calcium was released at four times the stoichiometric quantity relative to silicon in acid solutions, while F^- and K^+ accumulation in solution occurred at up to three times the maximum stoichiometric quantity relative to Si (Figure 5.13). The greater scatter in the data for F^- and K^+ compared to Ca^{2+} in Figure 5.13 is expected to result from variations in the chemical composition of the apophyllite samples, arising from substitutions in the mineral lattice. Where NH_4^+ was present, the dissolved amount was also approximately three times the equivalent amount of Si (using 0.4 NH_4 molecules per formula unit for the Guanajuato sample and 0.7 NH_4 per formula unit for Kopoasfontein apophyllite).

This non-stoichiometric dissolution behaviour suggests that the layers between the silicate sheets of apophyllite are preferentially leached out in acid solutions or that silicon is lost by precipitation of solid amorphous silica. The former case is consistent with the observations of Frondel (1979) and Sogo *et al.* (1998) when producing crystalline silica structures from apophyllite by reaction with HCl. Leached surface layers have been postulated from solution compositions and observed directly using surface analytical techniques during the acid dissolution of several silicate minerals including sheet silicates and feldspars (See Section 2.7).

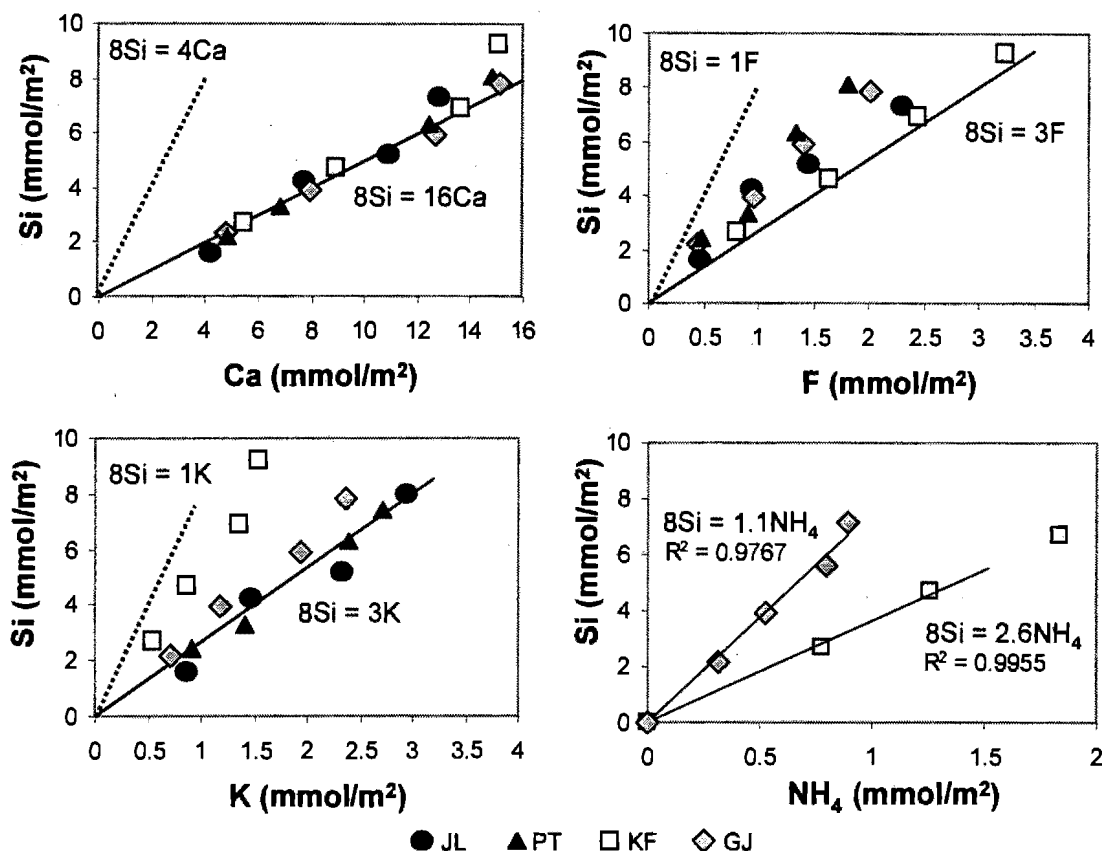


Figure 5.13. Relative amounts of Ca^{2+} , F^- , K^+ and NH_4^+ leached in proportion to Si from apophyllite samples using a batch test with four sequential rinses of 0.01M HCl. The dashed lines show stoichiometric proportions for pure fluorapophyllite and solid lines indicate four times the ideal stoichiometric amount of Ca and three times that of F and K.

The excess dissolved Ca^{2+} over Si was used to estimate the thickness of the leached layer that would form at the mineral surface in 0.01M HCl, assuming that Ca is uniformly leached out. The calculations used the unit cell volumes from Table 5.6 for samples LC6, LC7, LC8 and LC13. The approximate layer thickness ranges from 650 nm after one week of reaction to over 2 μm at the end of the batch test (Figure 5.14). In practice, preferential leaching along the crystal planes parallel to the silicate sheets, rather than uniform three dimensional leaching, means that the actual depth of leaching would be greater than the calculated values.

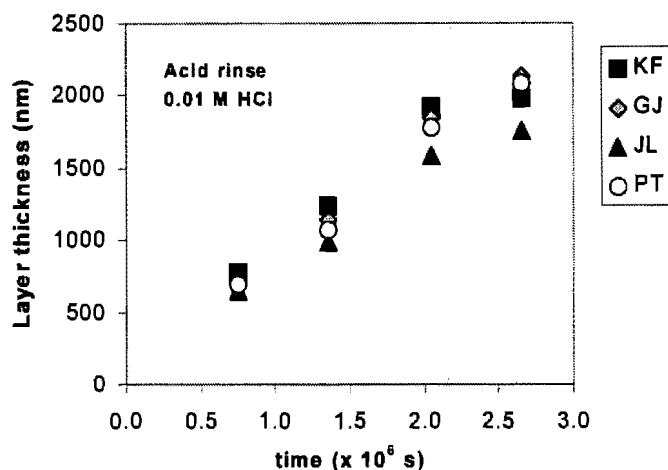


Figure 5.14. Estimated depth of leaching of the apophyllite surface in batch tests reacted with four successive rinses of HCl solution at pH 2. Layer thickness is calculated from the excess Ca over Si dissolved from the mineral structure.

Dissolution of Ca and F relative to Si approaches mineral stoichiometry at neutral to alkaline pH and no leached layer is expected to form (Figure 5.15). Two data groupings were noticed on the graph of Si vs. F. These correspond to approximately 1 and 0.5 moles of F per 8 moles of Si, irrespective of the solution pH. Replotting the data using different symbols for the four apophyllite samples (Figure 5.16) shows that the relative release of F is related to the apophyllite mineral sample used in the batch tests. Samples from Kopoasfontein and Jalgaon release approximately twice as much F relative to Si as those from Guanajuato and Paterson in neutral to alkaline solutions.

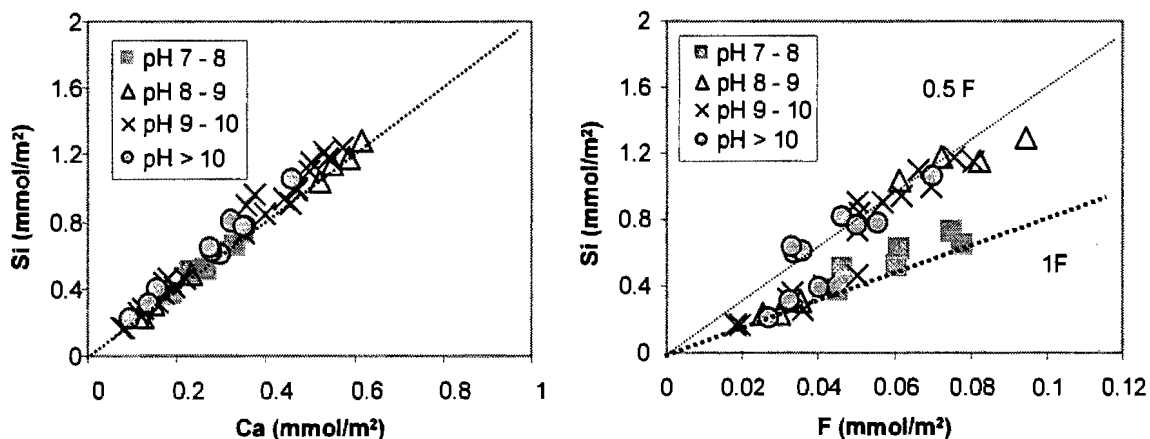


Figure 5.15. Stoichiometric release of Ca^{2+} and F^- relative to Si in sequential rinse batch test solutions. Dashed lines show ratios of 4 Ca and either 1 or 0.5 F atoms relative to 8 Si per formula unit of apophyllite. Symbols illustrate the final pH of each solution.

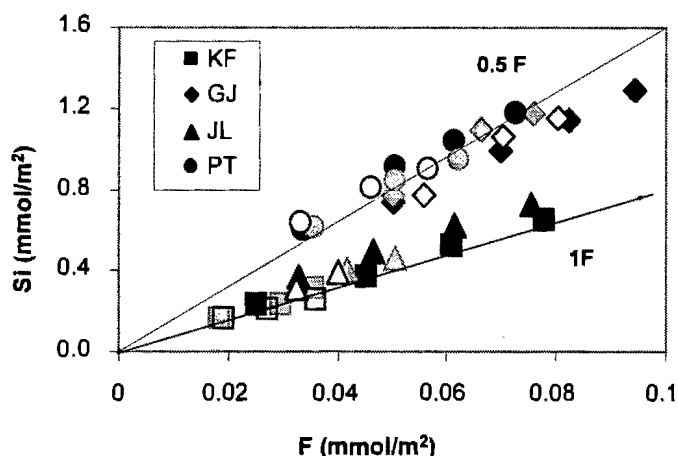


Figure 5.16. Release of Si and F^- from four apophyllite samples in solutions of initial pH 4 (solid symbols), pH 7 (shaded symbols) and pH 10 (open symbols). The lines show stoichiometric release for fluorapophyllite (1F) and a 50% hydroxide-substituted variety (0.5F).

Figure 5.16 shows that the Guanajuato (GJ/LC6) and Paterson (PT/LC7) apophyllites do not behave like high-fluorine samples, as would be expected from the chemical and thermal analyses of the minerals in Sections 5.5.2 and 5.5.3. The dissolution data suggest that these samples have significant substitution of OH in the mineral lattice and that the earlier F concentrations may have been overestimated.

Release of K^+ from the apophyllites under neutral to alkaline conditions shows no obvious trends, other than an excess of K^+ relative to the stoichiometric amount of Si (Figure 5.17). Data are widely scattered and seem to have no relation to pH, except that samples above pH 10 have low K concentrations. Poor data quality could have resulted from poor analytical precision (some data were only reported to one significant figure) and possible contamination of the samples by KCl (from the filling solution of the electrode used to measure pH when adjusting the initial solutions). The reader is therefore cautioned not to make too much of the K^+ results.

Rapid exchange reactions involving H^+ exchange for K^+ at the mineral surface could also lead to changes in dissolved K^+ that are unrelated to mineral dissolution. This could cause high initial K^+ concentrations relative to Si, especially for solutions of initial pH 4. Exchange equilibria may shift as the pH drifts upwards during the batch tests causing K^+ to be later taken up by the surface again in exchange for H^+ .

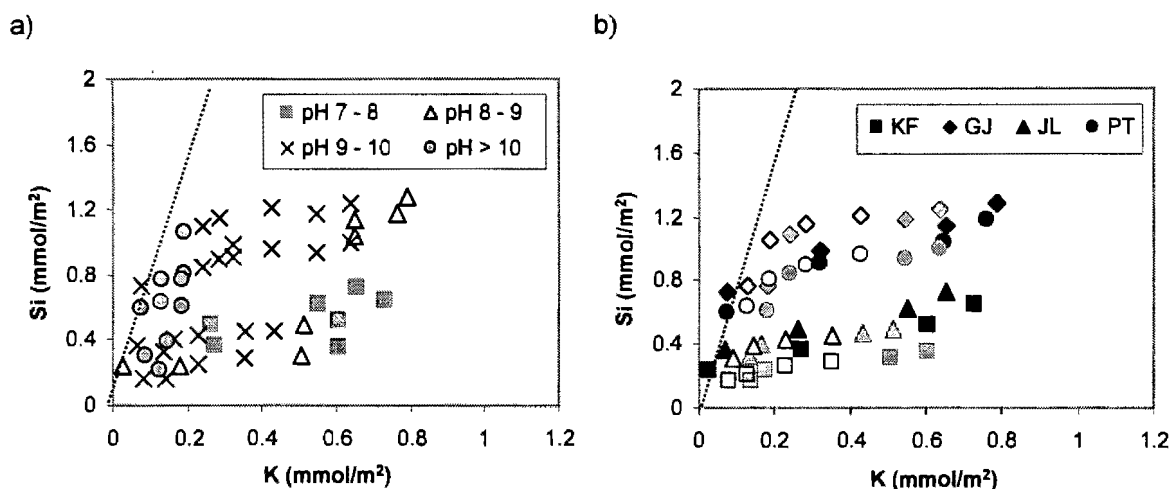


Figure 5.17. Relative release of Si and K^+ from apophyllite samples in batch test experiments at neutral to alkaline pH. Data symbols are plotted to show a) final pH and b) mineral identity using the same key for symbols as in Figures 5.15 and 5.16. The dashed line in both graphs shows the stoichiometric ratio of Si to K in pure fluorapophyllite.

Dissolution rates in acid solution

The accumulation of solutes with time displayed linear behaviour in acid solutions of initial pH 2 for all four apophyllite samples over the first three weeks of the sequential rinse batch test (Figure 5.18). In the final week, however, concentrations of Ca^{2+} , K^+ and NH_4^+ were lower than anticipated by a zero-order rate law with respect to the reaction products in some of the samples.

This result could indicate that the leached surface layer had become so thick that diffusion of species into and out of the leached layer, rather than surface reactions, had become the rate limiting step. The surface silica layer formed during acid dissolution of feldspars, however, is highly porous and is not anticipated to lead to diffusion-limited kinetics (Casey *et al.*, 1988). Instead, a depletion of the source material is responsible for the observed slowing of the dissolution-, or rather leaching rates. Calculating the cumulative amount of Ca removed at each step of the sequential rinse showed that 90 to 92% of the original Ca in the mineral samples was removed by the start of week four. The rate of silica dissolution is unaffected by the surface leaching and linear dissolution is maintained throughout the experiment.

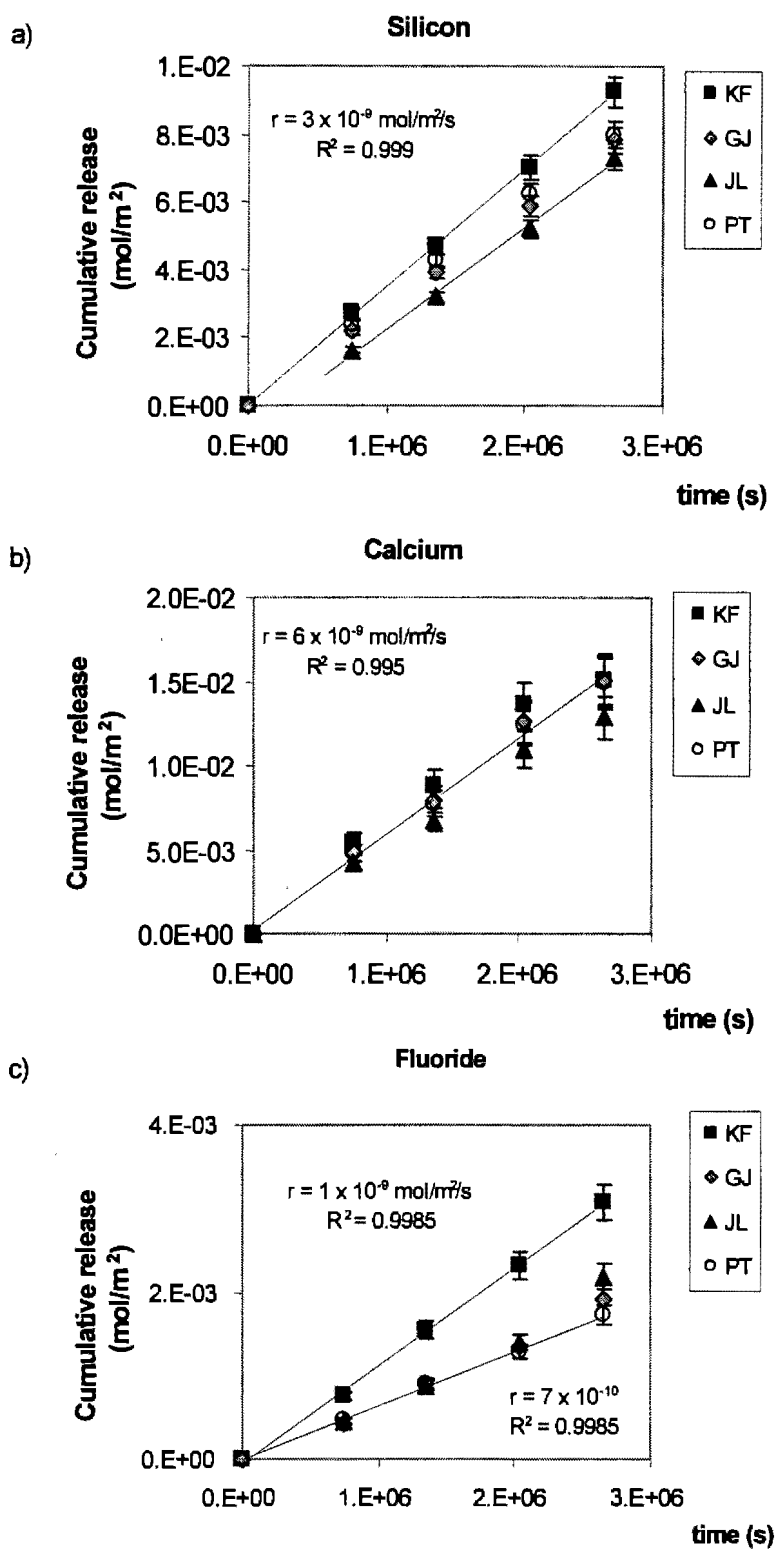


Figure 5.18 a - c). Calculated accumulation of Si, Ca²⁺ and F⁻ in solution with time during dissolution of Kopoasfontein (KF), Guanajuato (GJ), Jalgaon (JL) and Paterson (PT) apophyllite from sequential rinse experiments with HCl solutions of initial pH 2 (0.01M).

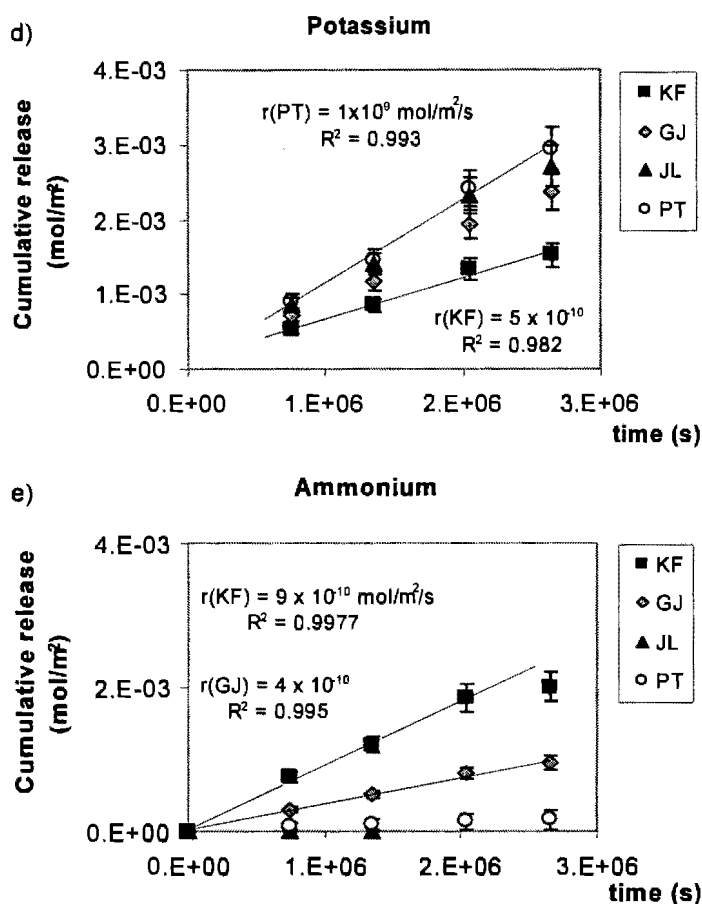


Figure 5.18 d - e). Calculated accumulation of NH_4^+ and K^+ in solution with time during dissolution of Kopoasfontein (KF), Guanajuato (GJ), Jalgaon (JL) and Paterson (PT) apophyllite from sequential rinse experiments with HCl solutions of initial pH 2 (0.01M).

Linear regression through the data points in Figure 5.18 has been used to calculate the rate of release of solutes from apophyllite reported in Table 5.16. The rates are reported as initial rates, using the origin as the first data point in the regression, unless otherwise noted. The final data point for Ca^{2+} , NH_4^+ and K^+ has been omitted due to expected depletion of starting material. No change in the dissolution rate of Si was noted with time and the steady state dissolution rate is assumed to be equal to the initial dissolution rate. Interstitial ions are released from apophyllite at an average rate of $1.3 \times 10^{-9} \text{ mol/m}^2/\text{s}$, which is 3.3 times faster than the rate of decomposition of the silica sheets ($3.9 \times 10^{-10} \text{ mol/m}^2/\text{s}$) in 0.01M HCl acid solution. Of the four apophyllite samples studied, the ammonian variety from Kopoasfontein has the fastest rate of both interstitial ion and framework silica dissolution in acid solutions.

Table 5.16. Zero-order (linear) initial rates of solute accumulation from apophyllite samples during four sequential rinses with 0.01M HCl in a 736 hour batch dissolution test.

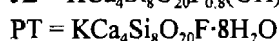
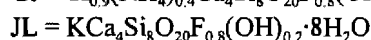
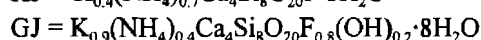
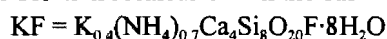
Mineral		Rate (mol/m ² /s)					Average for interlayer
sample		K ⁺	F	NH ₄	Ca	Si	
KF	abs ^a	6.28×10 ⁻¹⁰	1.20×10 ⁻⁹	9.49×10 ⁻¹⁰	6.65×10 ⁻⁹	3.48×10 ⁻⁹	
	stoich ^b	1.6×10 ⁻⁹	1.2×10 ⁻⁹	1.4×10 ⁻⁹	1.7×10 ⁻⁹	4.4×10 ⁻¹⁰	1.5×10 ⁻⁹
GJ	abs ^a	9.49×10 ⁻¹⁰	8.02×10 ⁻¹⁰ *	4.05×10 ⁻¹⁰	6.12×10 ⁻⁹	2.93×10 ⁻⁹	
	stoich ^b	1.1×10 ⁻⁹	1.0×10 ⁻⁹	1.0×10 ⁻⁹	1.5×10 ⁻⁹	3.7×10 ⁻¹⁰	1.2×10 ⁻⁹
JL	abs ^a	1.13×10 ⁻⁹	9.32×10 ⁻¹⁰ *	n.d. [#]	5.27×10 ⁻⁹	3.00×10 ⁻⁹ *	
	stoich ^b	1.1×10 ⁻⁹	1.2×10 ⁻⁹		1.3×10 ⁻⁹	3.8×10 ⁻¹⁰	1.2×10 ⁻⁹
PT	abs ^a	1.16×10 ⁻⁹	6.78×10 ⁻¹⁰	n.d.	6.02×10 ⁻⁹	3.05×10 ⁻⁹	
	stoich ^b	1.2×10 ⁻⁹	6.8×10 ⁻¹⁰		1.5×10 ⁻⁹	3.8×10 ⁻⁹	1.1×10 ⁻⁹

* Not regressed through the origin, some contamination may have been present in starting solutions.

n.d. = could not be determined since most samples were below the analytical detection limit.

^a abs = absolute rate for individual solutes

^b stoich = overall rate of dissolution recalculated on the basis of mineral stoichiometry:



The initial release rates of Si (3×10^{-9} mol/m²/s) and Ca (6×10^{-9} mol/m²/s) in acid solution are very fast. At these rates, much of the original starting material (24% of the Si and 94% of the Ca) is removed by dissolution during the batch test and the assumption of a constant reacting surface area is not valid. Adjusting the rates at each step to account for the expected loss of surface area, would give faster reaction rates as the experiment progresses. Such an increase in rate could be explained by the decrease in pH with time that occurs as a result of the decreased rate of H⁺ consumption as the amount of reacting mineral is depleted.

Dissolution rates in neutral to alkaline solution

Dissolution data for the higher pH solutions initially appeared to show parabolic trends in the change of concentration with time as illustrated by the example of fluoride accumulation in solutions of starting pH 7 in Figure 5.19. This behaviour was originally interpreted in the silicate dissolution literature as being indicative of diffusion-controlled reaction kinetics. However, diffusion effects in solution have been avoided by agitating the samples on a shaker and there is no appreciable leached surface layer through which reactants and products must diffuse. The

periodic introduction of fresh rinses of reactant solution should also prevent the build-up of solutes to levels of saturation where back-reactions or secondary product precipitation could lower solute concentrations. The mineral starting material is not significantly depleted during the reactions and surface area effects are expected to be negligible.

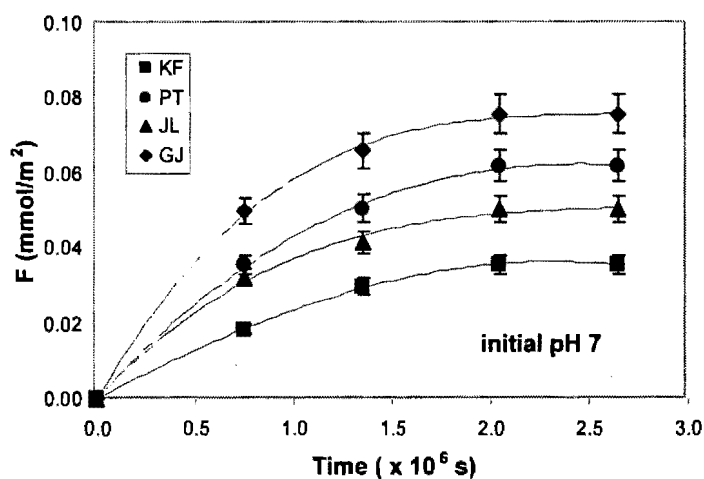


Figure 5.19. Apparent parabolic trend in the cumulative concentration of F^- with time in batch test using sequential rinses of pH 7 NaOH solutions.

Silicate mineral dissolution is now widely accepted to be a surface-controlled process (Wieland *et al.*, 1988), obeying a linear rate law with respect to the solute products. The problem of parabolic increases in concentrations in the sequential rinse batch test was overcome by recognising that the reaction rate slows from a fast initial rate to a slower steady-state dissolution rate with time and by considering the effects of the drift in pH during the reaction.

The concentration versus time data was, therefore, replotted without the zero points at the start of the experiment and the rates of accumulation of the various solutes determined by linear regression through points of similar final pH, rather than initial pH of the reactant solutions. In some cases, data from the initial week of the experiment were also excluded where the reaction was considered to have not yet reached steady state with respect to a particular component so that the data point did not fit the linear trend of the later points. The rates of accumulation of Si, Ca^{2+} , K^+ and F^- from the four apophyllite samples are shown in Figure 5.20 and summarised in Table 5.17.

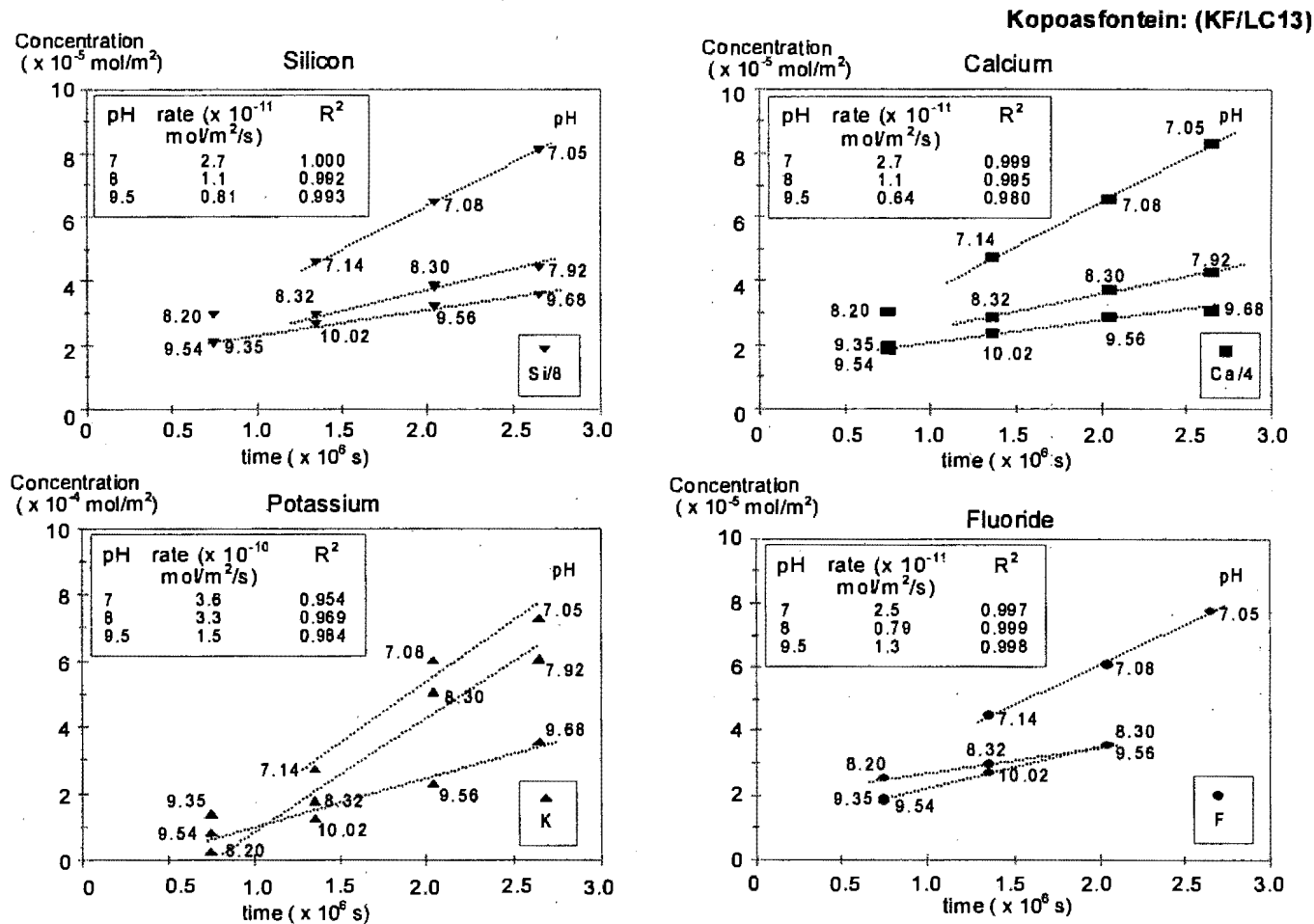


Figure 5.20a). Rates of release of Si, K⁺, Ca²⁺ and F⁻ as a function of pH from dissolution of Kopoasfontein apophyllite in neutral to alkaline solutions over 737 hours.

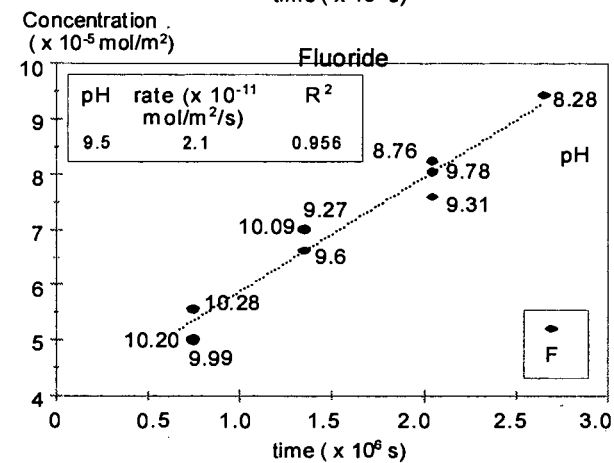
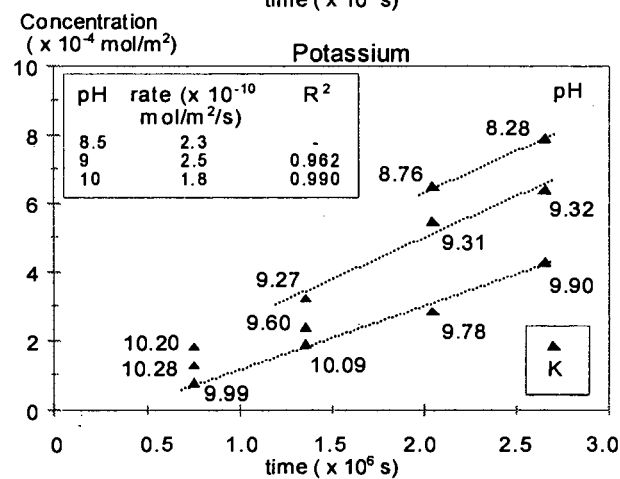
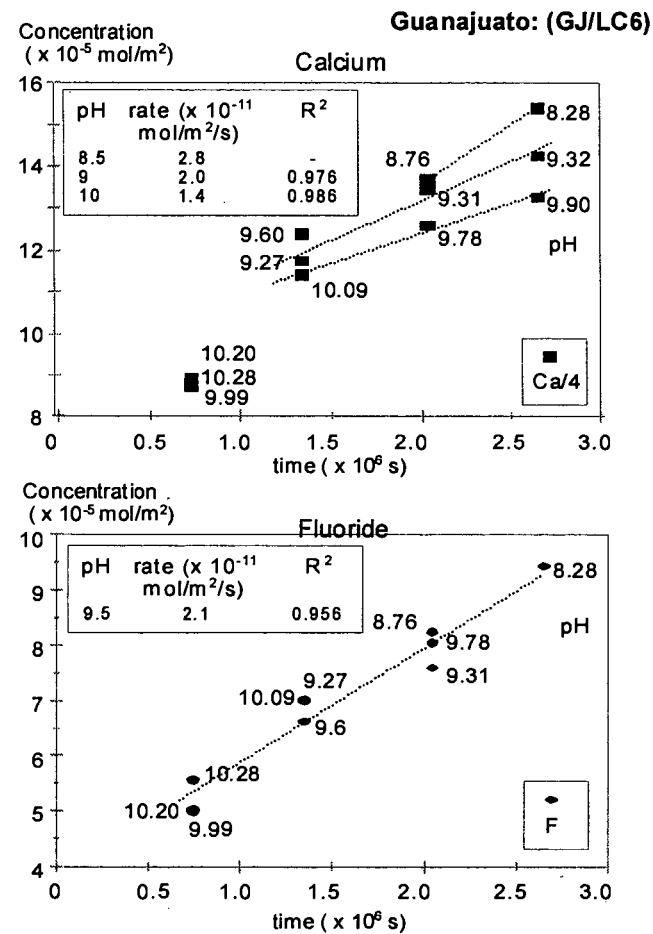
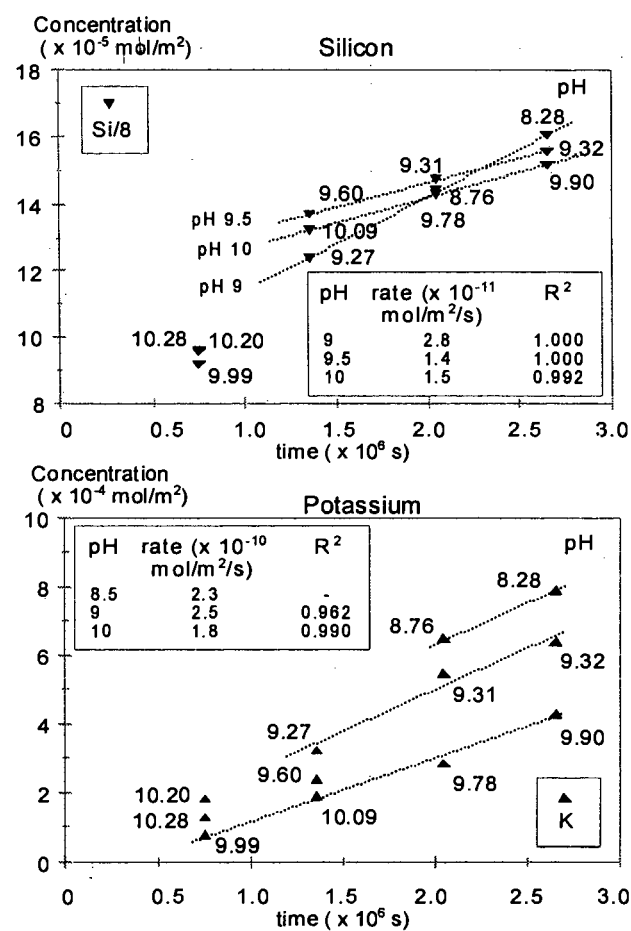


Figure 5.20b). Rates of release of Si, K⁺, Ca²⁺ and F⁻ as a function of pH from dissolution of Guanajuato apophyllite in neutral to alkaline solutions over 737 hours.

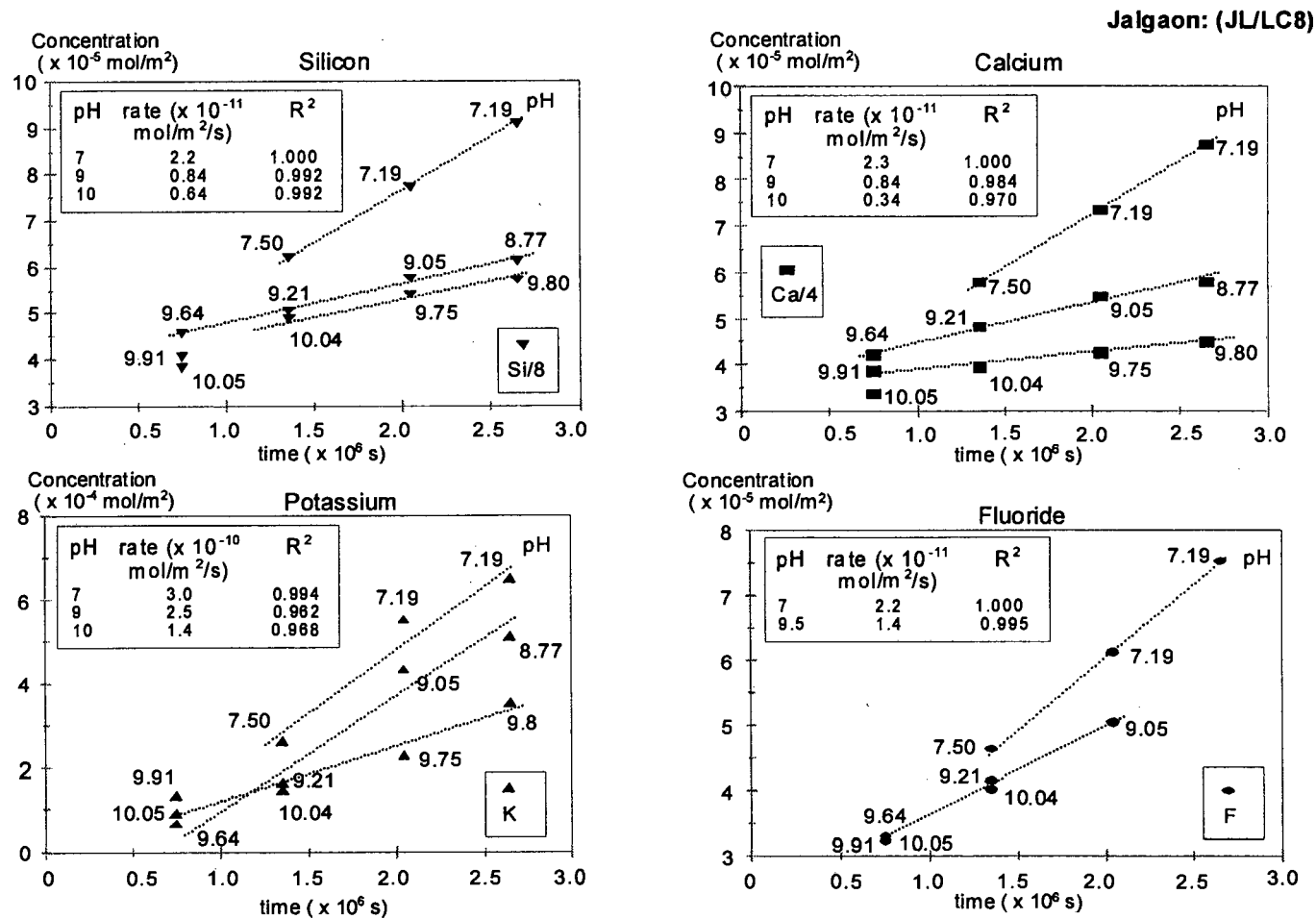


Figure 5.20c). Rates of release of Si, K⁺, Ca²⁺ and F⁻ as a function of pH from dissolution of Jalgaon apophyllite in neutral to alkaline solutions over 737 hours.

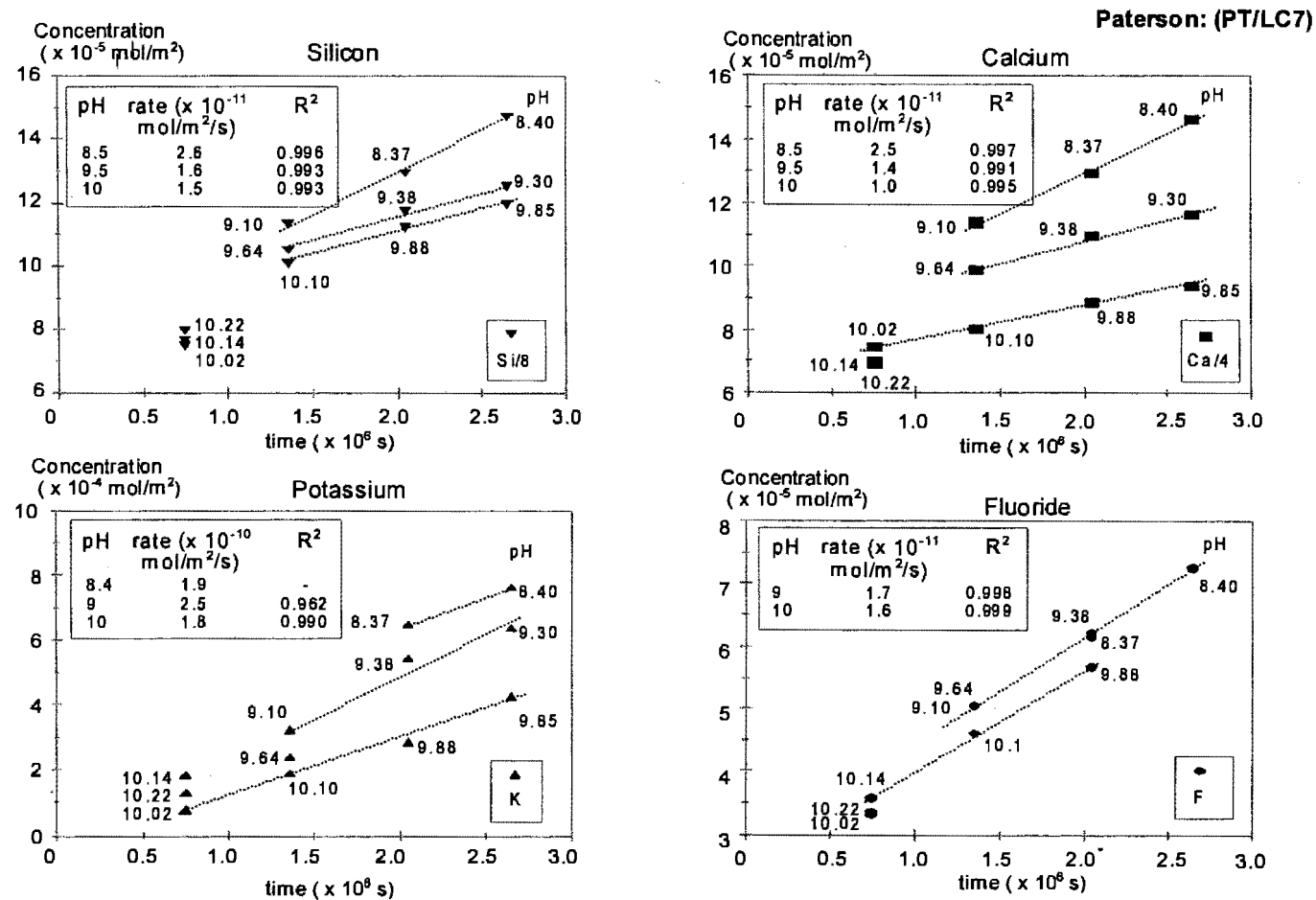


Figure 5.20d). Rates of release of Si, K⁺, Ca²⁺ and F⁻ as a function of pH from dissolution of Paterson apophyllite in neutral to alkaline solutions over 737 hours.

Table 5.17. Zero-order (linear) steady state rates of solute accumulation and mineral dissolution for apophyllite samples over four sequential rinses with solutions adjusted to pH 4, 7 and 10.

Mineral sample	Final pH (approx.)	Rate (mol/m ² /s)				
		Si/8	Ca/4	F	K	Mineral [#]
KF	7	2.70×10 ⁻¹¹	2.74×10 ⁻¹¹	2.51×10 ⁻¹¹	3.55×10 ⁻¹⁰	2.7×10 ⁻¹¹
	8	1.13×10 ⁻¹¹	1.10×10 ⁻¹¹	7.85×10 ⁻¹²	3.25×10 ⁻¹⁰	1.1×10 ⁻¹¹
	9.5	8.13×10 ⁻¹²	6.36×10 ⁻¹²	1.33×10 ⁻¹¹	1.45×10 ⁻¹⁰	7.2×10 ⁻¹²
GJ	8.5	n.d.	2.80×10 ⁻¹¹	n.d.	2.29×10 ⁻¹⁰	2.8×10 ⁻¹¹
	9	2.82×10 ⁻¹¹	1.95×10 ⁻¹¹	n.d.	2.45×10 ⁻¹⁰	2.4×10 ⁻¹¹
	9.5	1.43×10 ⁻¹¹	n.d.	2.14×10 ⁻¹¹	n.d.	1.4×10 ⁻¹¹
	10	1.50×10 ⁻¹¹	1.43×10 ⁻¹¹	n.d.	1.79×10 ⁻¹⁰	1.5×10 ⁻¹¹
JL	7	2.21×10 ⁻¹¹	2.29×10 ⁻¹¹	2.24×10 ⁻¹¹	3.04×10 ⁻¹⁰	2.3×10 ⁻¹¹
	9	8.44×10 ⁻¹²	8.38×10 ⁻¹²	n.d.	2.52×10 ⁻¹⁰	8.4×10 ⁻¹²
	9.5	n.d.	n.d.	1.38×10 ⁻¹¹	n.d.	n.d.
	10	6.42×10 ⁻¹²	3.41×10 ⁻¹²	n.d.	1.37×10 ⁻¹⁰	6.4×10 ⁻¹²
PT	8.5	2.58×10 ⁻¹¹	2.50×10 ⁻¹¹	n.d.	1.86×10 ⁻¹⁰	2.5×10 ⁻¹¹
	9	n.d.	n.d.	1.68×10 ⁻¹¹	2.45×10 ⁻¹⁰	n.d.
	9.5	1.55×10 ⁻¹¹	1.39×10 ⁻¹¹	n.d.	n.d.	1.6×10 ⁻¹¹
	10	1.45×10 ⁻¹¹	1.04×10 ⁻¹¹	1.62×10 ⁻¹¹	1.79×10 ⁻¹⁰	1.5×10 ⁻¹¹

[#] Overall rate of apophyllite mineral dissolution calculated from average values for Si and Ca release, assuming zero-order reaction kinetics with respect to Si and Ca. At pH 10 the rate is taken as being equivalent to the rate of Si release only, since Ca may be affected by supersaturation with respect to secondary Ca phases. Fluoride and potassium are not included in the overall rate calculation due to uncertainties in stoichiometry in the mineral samples and possible potassium contamination of solutions.

Dissolution rates are not conventionally presented as a function of final pH, but this method was adopted to overcome the difficulties of calculating rates as a function of initial pH for this data set. The major drawback is the change in pH, and hence the change in rate, during each successive rinse in the batch experiment. The drift in pH is smaller, and hence the change in rate will be lower, for the more alkaline solutions. For starting solutions of pH 4, however, the actual dissolution rate would start off faster and decrease over the week as the pH drifts towards pH 7. When the data is analysed, the linear rate law is fitted through data that represents dissolution under neither the initial nor the final pH, but rather the cumulative effect of a changing dissolution rate, under changing pH conditions, over the week.

The rate of release of K⁺ is an order of magnitude higher than that of the other three components

in Table 5.17, although possible contamination of the samples must call the quality of the K^+ data, and any interpretations based on these, into question. There is also a wider scatter in the K^+ data and the fit of regression lines is not as good as for the other components. The rate of accumulation of NH_4^+ from the Kopoasfontein apophyllite at pH 7 is 8.5×10^{-12} mol/m²/s, or a relative rate of 1.2×10^{-11} mol/m²/s based on 0.7 NH_4 molecules per formula unit. This is less than half the rate for the other solutes. The rate of solute accumulation is, however, not necessarily the rate of release from apophyllite in this case, since NH_4^+ could be lost to oxidation. Unfortunately, NH_4 is a minor component and NH_4^+ data were frequently below the analytical detection limit, so no other rates of NH_4^+ release could be determined for comparison. The stoichiometric rates of Si and Ca^{2+} release are generally in very good agreement for most of the samples, indicating that congruent dissolution of the mineral occurs in neutral to alkaline solutions. Figure 5.21 shows the Ca^{2+} and Si dissolution rates of the four apophyllite samples as a function of final pH.

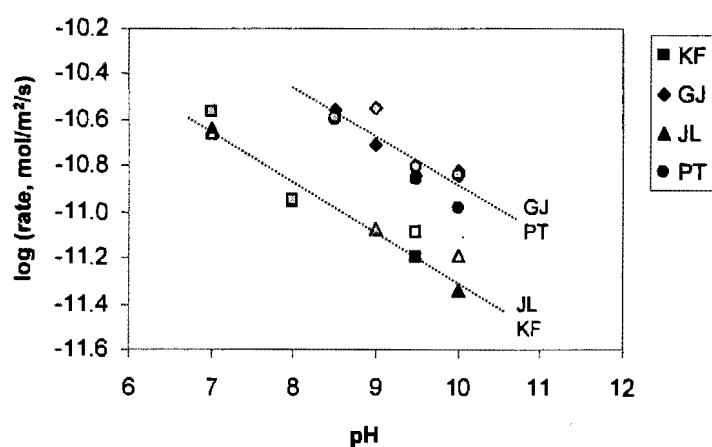


Figure 5.21. Rates of release of Ca/4 (solid symbols) and Si/8 (shaded symbols) from apophyllite mineral samples as a function of final solution pH during sequential rinse batch test.

The dissolution rate shows a decreasing trend with increasing pH in the neutral to alkaline region. The dotted lines in Figure 5.21 show the change in rate with pH is similar for all samples, but that samples from Guanajuato and Paterson dissolve at a faster rate than those from Kopoasfontein and Jalgaon under the same pH conditions. The average of the stoichiometric Si and Ca^{2+} release rates is used as the overall dissolution rate of apophyllite in Figure 5.21, except for pH 10 solutions where Ca^{2+} dissolution rates from GJ and JL are significantly lower than Si, possibly affected by precipitation of secondary phases, so Si rates are favoured.

A sensitivity analysis was conducted to ensure that the rates obtained for the Guanajuato and Paterson samples are really higher than those for Kopoasfontein and Jalgaon and not simply introduced by the use of the estimated surface area in the rate calculations. The y-error bars for GJ and PT in Figure 5.22 show that the influence of varying the mineral surface area from 0.2 m²/g (upper values) to 0.45 m²/g (lower values) is not sufficient to make the data points fall within the range of those for KF and JL. The surface area of the GJ and PT samples would need to be increased to 0.8 to 1 m²/g for the calculated rates to be indistinguishable from those of KF and JL and it is unlikely that the estimated surface area values are incorrect by such an amount. Other error bars in Figure 5.22 show a range of 0.5 pH units, to account for variations in the pH of solutions used to calculate the rates, and 0.2 log units difference in y-values for KF and JL, being the maximum between difference in calcium and silicon rates averaged for the overall dissolution rates.

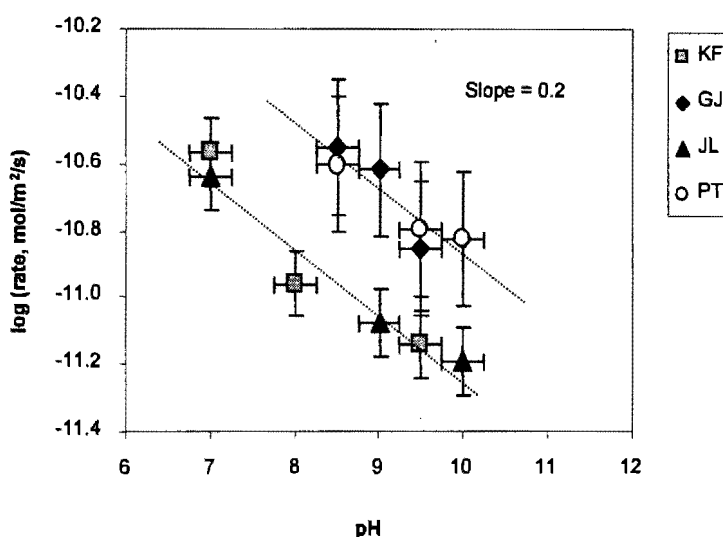


Figure 5.22. Dissolution rates of apophyllite samples from Kopoasfontein (KF), Guanajuato (GJ), Jalgaon (JL) and Paterson (PT) in dilute aqueous solutions of neutral to alkaline pH.

The samples GJ and PT which dissolve fastest are also those which produced lower concentrations of F⁻ relative to Si in solution (Figure 5.16) and were speculated to be of higher OH⁻ content than KF and JL. In neutral to alkaline solutions, it appears that the substitution of OH for F could have a more significant influence in destabilising the apophyllite mineral structure during dissolution than substitution of NH₄ for K. The latter would have increased the rate of dissolution of KF and GJ relative to the other samples.

5.7.5 Batch dissolution experiment 3

The third batch experiment was aimed at testing the reproducibility of the sequential rinse method and exploring the pH dependence of apophyllite dissolution. A four-week sequential rinse experiment (Amrhein and Suarez, 1992) was repeated using the apophyllite sample from Kopoasfontein, this time with a wider range of initial pH conditions from pH 2 to 12. Sodium chloride was used as a background electrolyte in the third batch test to maintain a uniform ionic strength of 0.01M.

5.7.5.1 Method

A stock solution of 0.01M NaCl was prepared by dissolving 0.5588 g sodium chloride (Merck *pro analysi* GR ACS, 99.5% NaCl) in one litre of deionised water in a glass volumetric flask. This was used to prepare a series of initial solutions of pH 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 by addition of 0.01M HCl or 0.01M NaOH (BDH, CVS, 0.1N HCl or 0.1N NaOH ampules), so that all reaction solutions were of approximately equivalent 0.01M ionic strength. Solutions of pH 2 and pH 12 were pure 0.01M HCl and 0.01M NaOH, respectively. The other solutions were prepared by initial addition of an estimated amount of acid or base needed to reach the desired pH and then adjusted to the exact pH by further dropwise addition of HCl or NaOH to a stirred beaker in which a calibrated combination glass electrode was immersed.

Kopoasfontein apophyllite (50-100 μ m, BET surface area = 0.449 m²/g) was accurately weighed out in 0.10 g portions into eleven 50 mL Greiner plastic centrifuge tubes. Thirty millilitre aliquots of the pH-adjusted solutions were then added to the reaction tubes and the screw-top lids sealed. The tubes were mounted horizontally on a flat-bed reciprocating shaker and agitated at approximately 60 cycles per minute for one week.

The samples were removed from the shaker and the solid allowed to settle to the bottom. The pH of each solution was measured before carefully siphoning off the top 25 mL of solution for analysis. The centrifuge tubes were refilled to the 30 mL mark with 0.01M NaCl stock solution and the pH in each tube adjusted back to the initial value by addition of NaOH or HCl. Pure 0.01M HCl or 0.01M NaOH was used to refill the pH 2 and pH 12 samples and the volume of NaCl added for the pH 3 and pH 11 samples was decreased so that the final volume did not

exceed 30 mL once the acid or base was added. Samples were then returned to the shaker for a second week of agitation at approximately 90 cycles/minute.

At the end of the second rinse, samples were once again removed, the pH measured and the reacted solutions removed for analysis before refilling, adjusting to the original pH and returning to the shaker for a third rinse. Two additional rinses were completed following the above procedure to give a total of four rinses over a reaction time of 650 hours.

The decanted solutions were filtered under gentle suction through porosity 4 sintered glass crucibles which were dried and weighed before and after filtering. The mass of solid in the crucible after the second rinse was found to be negligible (maximum 0.00013 g), allaying the concern that some solid material could be lost as suspended particles when decanting the solutions and lead to overestimation of dissolution. After the fourth and final rinse, the entire sample was filtered through the sintered glass crucibles and the remaining mineral solid recovered and weighed to determine the total mass loss.

The reacted solutions were analysed in the laboratories of the Geology Department, UCT within one week of being recovered from the mineral solid. Dissolved monomeric silica was determined by colorimetry using the yellow molybdosilicate method (see Appendix C) on undiluted 10 mL samples, except for the pH 2, pH 3 and pH 12 solutions which were diluted two to five times to decrease their concentrations to within the working range of the method. Major cations and anions, including Ca^{2+} , K^+ , and F^- were determined by IC. Ammonium was detected in the pH 2 samples (i.e. pure 0.01M HCl), but poor separation of the NH_4^+ peak and the large Na^+ peak originating from the added NaCl electrolyte or NaOH, precluded analysis of NH_4^+ in the other samples by the IC method. Titration to end point pH 4.5 with 0.01M HCl was used to determine the alkalinity of undiluted 5 mL samples, where sufficient sample volume remained after the other analyses. Mineral saturation indices for a variety of possible solid phases after speciation, were calculated using the PHREEQC-1.5 software program (Parkhurst, 1995) and the WATEQ4F thermodynamic database (Ball and Nordström, 1991).

Solute release rates were calculated as the number of moles released per unit surface area, based on the mass of solid present at the start of the experiment and the original BET surface area. These were then accumulated for the successive rinses involving the same mineral sample, making a correction for the 5 mL of the previous solution which remained at the start of rinses 2, 3 and 4. The cumulative concentrations were used to calculate linear (zero-order) dissolution rates with respect to the dissolved products. The use of the original surface area was considered reasonable for the samples above initial pH 4, where less than 10% of the original mass was removed over the 4 weeks of the batch test. Insufficient material was available for surface area measurement after reaction under each different starting pH condition.

The recovered apophyllite mineral samples after reaction and a sample of unreacted mineral starting material were mounted on sample stubs and carbon coated for examination under scanning electron microscope coupled to energy dispersive X-ray analysis (SEM-EDX) (D. Gerneke, operator: Physics Department, UCT).

5.7.5.2 Results

Raw analytical data from the third batch experiment and the calculated quantities of solutes released from the Kopoasfontein sample under initial pH conditions from pH 2 to pH 12 are given in Table H.3 in Appendix H.

Dissolution stoichiometry and leached layers

The stoichiometry of apophyllite dissolution was found to be dependent on the pH conditions of the reactant solutions. Dissolution was non-stoichiometric when initial solutions were at pH 2, with release of F^- and Ca^{2+} occurring at approximately four times the anticipated rate based on Si release. Increasing the starting pH to 3 and above produces roughly congruent dissolution behaviour until pH 12, when the amount of Si dissolved is in excess of the other solutes (Figure 5.23).

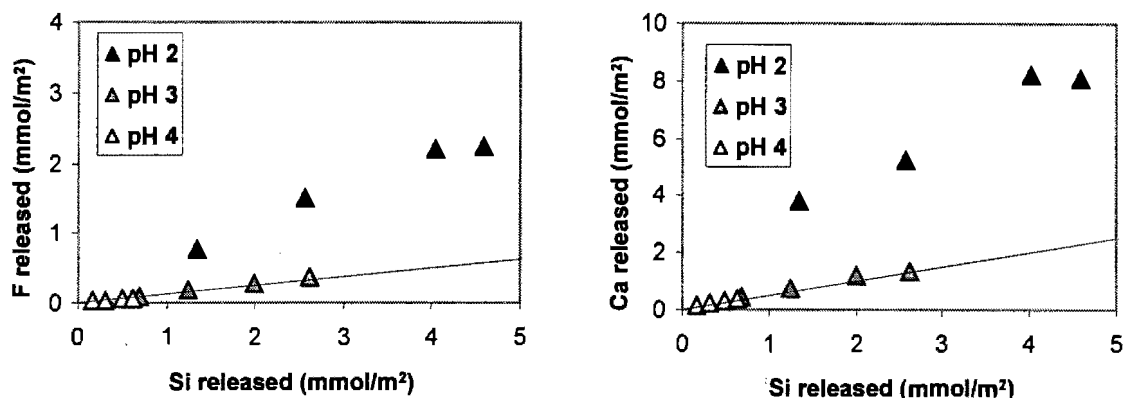


Figure 5.23a). Release of F^- and Ca^{2+} relative to Si from apophyllite samples in acid solutions of initial pH 2, 3 and 4 during sequential rinse dissolution test. The lines show stoichiometric ratios of 1 F : 8 Si and 4 Ca : 8 Si.

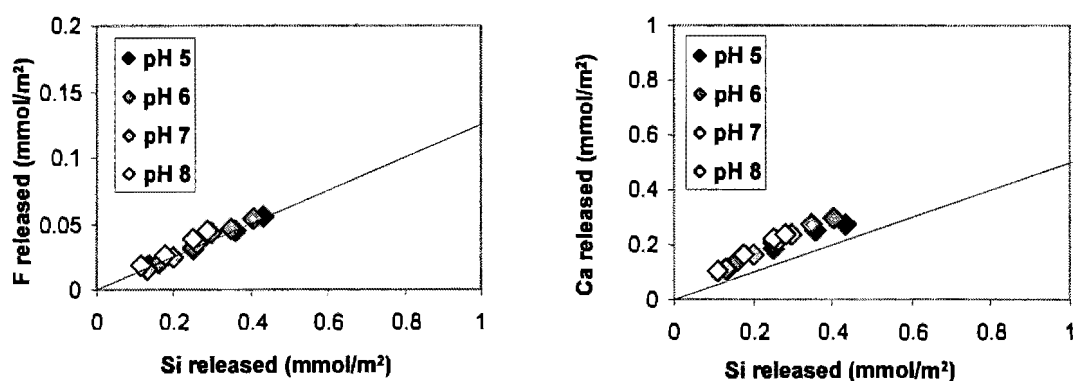


Figure 5.23b). Release of F^- and Ca^{2+} relative to Si from apophyllite samples in near-neutral solutions of initial pH 5 to 8 during sequential rinse dissolution test. The lines show stoichiometric ratios of 1 F : 8 Si and 4 Ca : 8 Si.

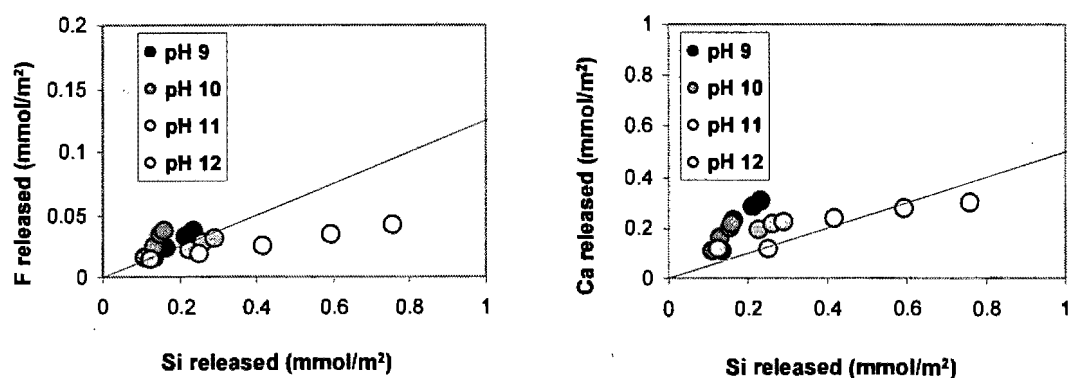


Figure 5.23c). Release of F^- and Ca^{2+} relative to Si from apophyllite samples in basic solutions of initial pH 9 to 12 during sequential rinse dissolution test. The lines show stoichiometric ratios of 1 F : 8 Si and 4 Ca : 8 Si.

The position and bonding of Ca and F atoms in the apophyllite structure suggests that these two species will be released together in quantities related by the mineral stoichiometry. The slight excess of Ca^{2+} , compared with F^- in the graphs in Figures 5.23 b) and c), is possibly related to overestimation of Ca^{2+} at low concentrations by the IC analytical method. The Ca^{2+} concentration in a Dionex certified cation standard was found to be overestimated by up to 30% during the analytical runs in which the sequential rinse data was collected (see Appendix C).

Under the scanning electron microscope, apophyllite reacted in solutions of pH 2 showed signs of intense leaching after 4 sequential rinses. The platy sheets of the mineral were deformed and buckled and the grain porosity greatly increased in comparison to the original material (Figure 5.24). The cumulative molar quantities of Ca and F removed over the first three weeks of the experiment (see Table H.3) are equivalent to 85 (Ca) to 90 % (F) of the amount present in the original mineral sample at the start. In comparison, only 20% of the original Si dissolved over the first three weeks of the batch test.

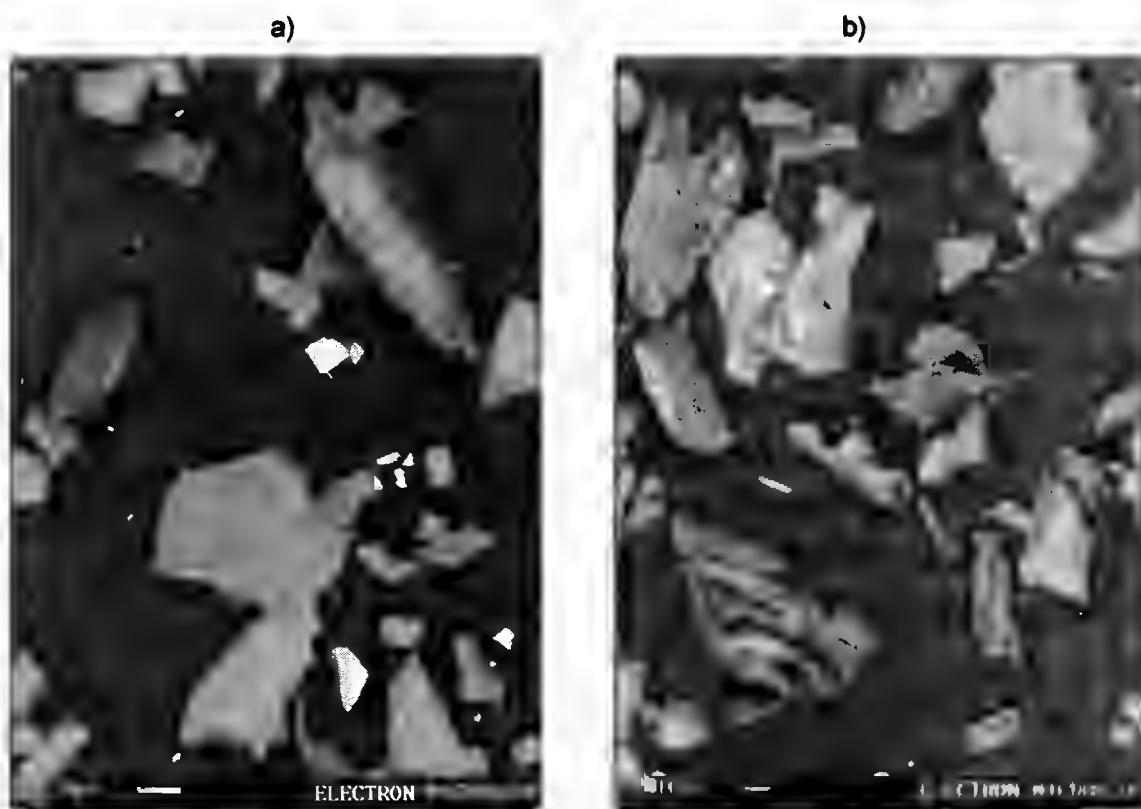


Figure 5.24. Backscattered electron images from SEM examination of a) unreacted Kopoasfontein apophyllite (50 - 100 μm) before dissolution experiments and b) Kopoasfontein apophyllite after four weeks' dissolution at pH 2.

These images show that the final surface area is likely to be vastly different from that at the start of the experiment and use of the original surface area in dissolution rate calculations will affect the accuracy of the results. An energy-dispersive X-ray spectrum for a single grain of acid-leached apophyllite confirmed that only Si and O are present in the outer layers of the mineral residue penetrated by the X-ray beam, with none of the Ca, F and K, detectable in the unreacted sample, remaining (Figure 5.25).

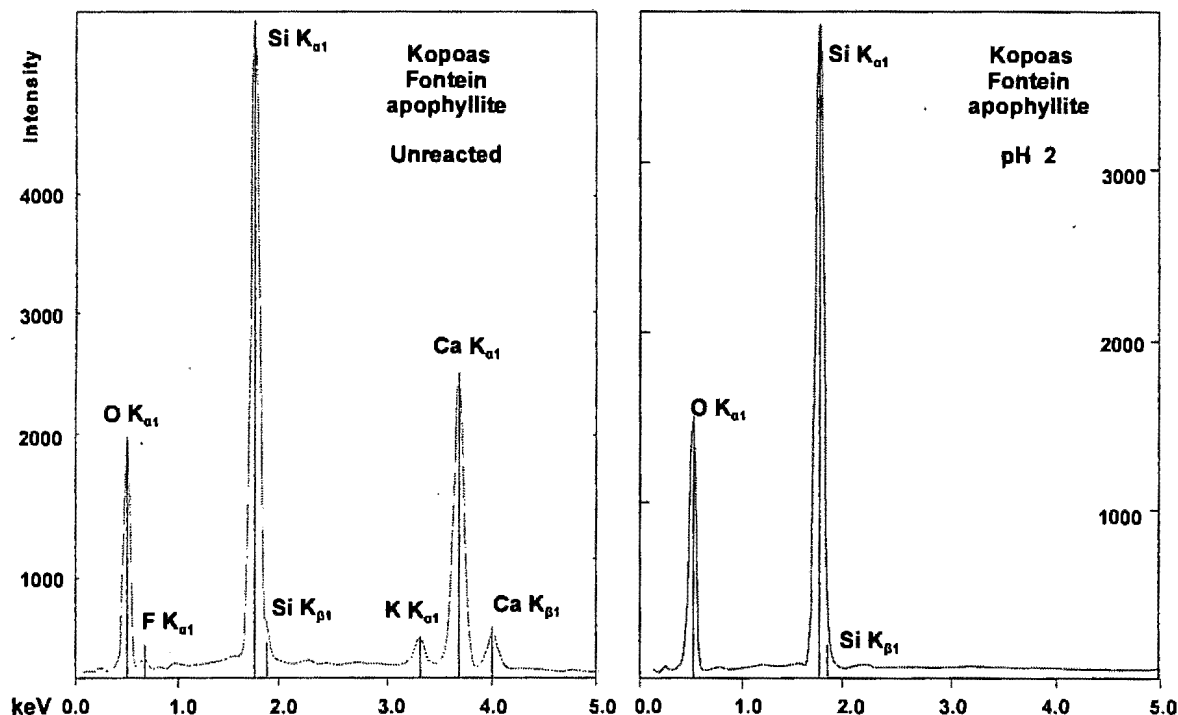


Figure 5.25. Energy-dispersive X-ray fluorescence spectra for single apophyllite grains before and after 1 month dissolution in 0.01 M HCl, showing complete leaching of all detectable K, F and Ca after reaction at pH 2.

After four rinses of one week each in HCl/NaCl solutions of pH 3, the relative amount of Si removed from the Kopoasfontein apophyllite was approximately equivalent to that of Ca and F. Of the original amounts, 13.3% of Si, 13.9% of Ca and 14.5% of the F were calculated to have dissolved. Stoichiometric dissolution in pH 3 solutions is also supported by examination of the reacted mineral under SEM. The secondary electron images show pitting of the mineral surfaces, rather than separation along the basal planes as found for pH 2 (Figure 5.26).



Figure 5.26. Secondary electron images of mineral surface etching on Kopoasfontein apophyllite reacted for four weeks in HCl/NaCl solution of pH 3.

No significant preferential dissolution of the interstitial ions or silica sheets was found at any pH condition between pH 3 and pH 11. SEM examination of samples reacted at pH 7 (Figure 5.27) showed no distinct evidence of leaching.

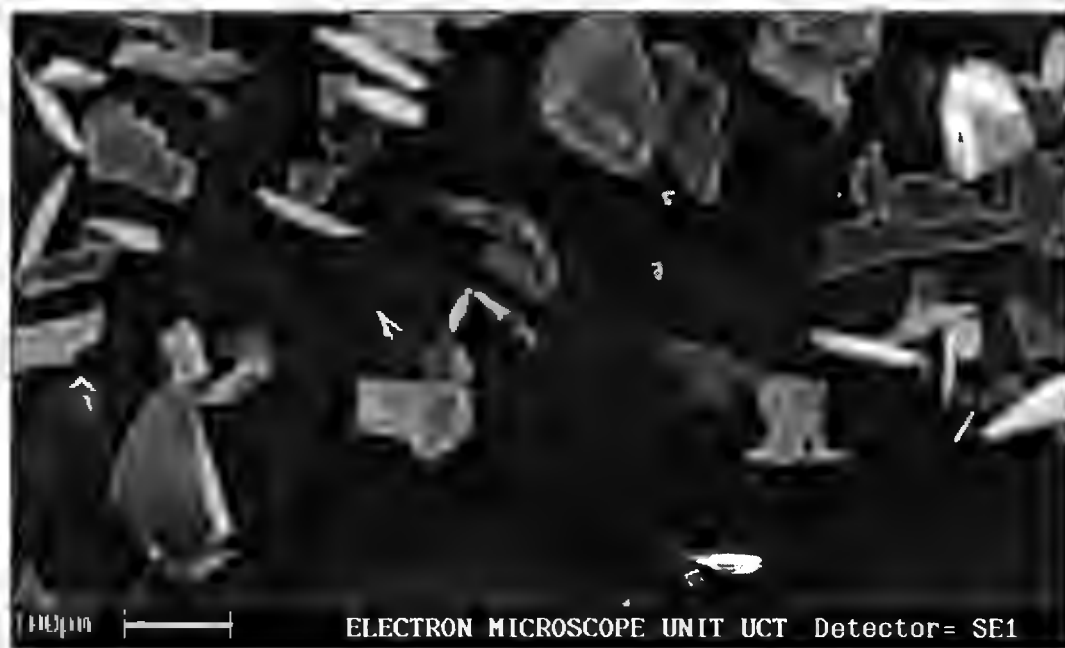


Figure 5.27. Secondary electron SEM image showing the morphology of Kopoasfontein apophyllite after 4 weeks' dissolution in a solution of pH 7 (0.01M NaCl).

The dissolution data in Table H.3 suggest that Si is removed in excess of Ca and F at pH 12, but the amounts are small in comparison to the Ca and F leaching at pH 2. SEM images also do not show significant deformation of the mineral grains reacted for 4 weeks at pH 12 (Figure 5.28) and the EDX spectrum for apophyllite reacted at pH 12 is very similar to that of the unreacted sample in Figure 5.25. Based on a pure apophyllite starting material, only 4% of the original Si was removed after reaction at pH 12, in comparison with 3% Ca and 1.7% of the F. It was suspected that the dissolved Si might be in excess at pH 12 due to precipitation of insoluble secondary phases such as CaCO_3 or CaF_2 , but no obvious surface coatings of secondary material could be found on the mineral grains under the SEM, even at 2000 times magnification.

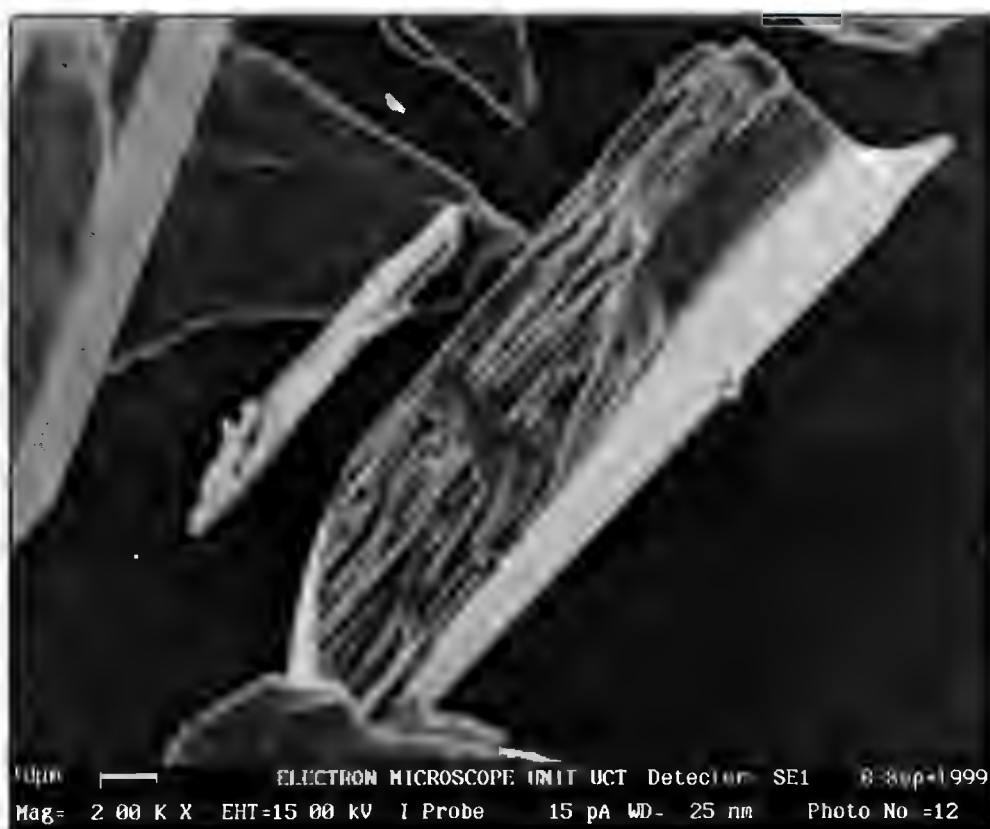


Figure 5.28. Secondary electron image of Kopoasfontein apophyllite after 4 weeks' reaction with a solution of pH 12 (0.01M NaOH).

Saturation indices for sparingly soluble mineral phases containing Ca, F and Si were calculated from the composition of all 44 solutions collected during the four week batch test. These were used to assess the possibility of solute concentrations being influenced by equilibria with new secondary phases. If mineral precipitation occurs, then the measured solute concentrations will

be controlled by reactions other than that of the dissolving apophyllite. The results for calcite, fluorite, quartz, amorphous silica and wollastonite are shown in Figure 5.29.

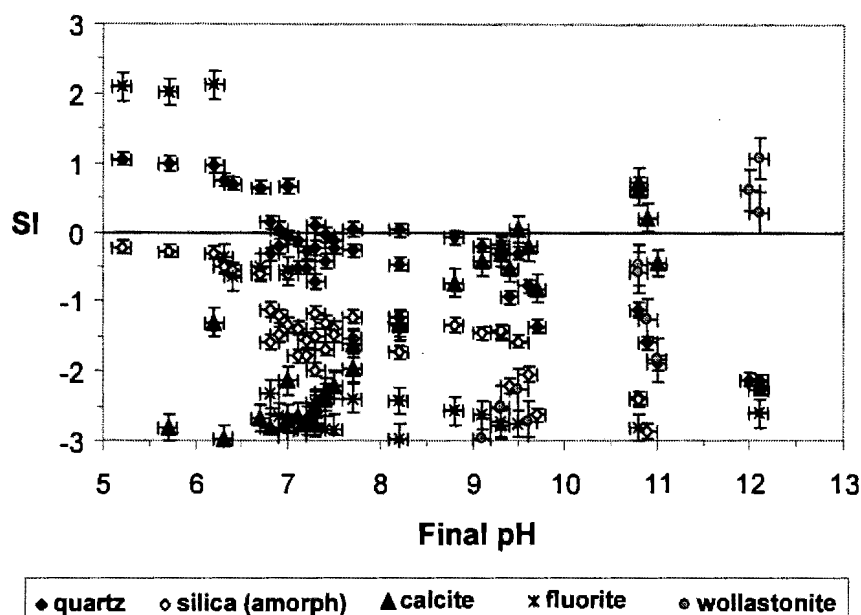


Figure 5.29. Saturation indices for selected Ca, F and Si-bearing phases that could influence solute concentrations in the batch test solutions.

All of the solutions were calculated to be undersaturated with respect to amorphous silica (SiO_2), while only those near pH 10 and above were found to be supersaturated with respect to calcite. It is possible that Ca release from apophyllite is underestimated because of CaCO_3 precipitation at high pH. This is unlikely however, since ratios of Ca to F at high pH show excess Ca based on apophyllite stoichiometry (rather than a deficit of dissolved Ca as would be expected if Ca precipitates) and no evidence of surface coatings was found by SEM on the pH 12 sample. The degree of supersaturation for calcite is also very slight ($\text{SI} < 1$) and precipitation should not occur.

Very high pH solutions are also supersaturated with respect to wollastonite (CaSiO_3), but rapid precipitation from low temperature aqueous solutions is not a realistic expectation. Neither is the precipitation of ordered quartz likely to occur from the solutions with pH between 5 to 7. Rapid leaching of Ca and F from apophyllite in 0.01M HCl results in solutions which become supersaturated with respect to fluorite (CaF_2) as the pH rises during each of the first three rinses. This could have some influence on the calculated rate of Ca and F leaching in acid solutions.

With rare exceptions in the first or second week of reaction, K^+ concentrations are in excess of that anticipated by the release of either 0.4 or 1 K^+ ion per formula unit of apophyllite (Figure 5.30). Calculations of K^+ removal range from a minimum of 18% of the original K^+ dissolved after 4 rinses at pH 12 to a maximum 100% of the available K^+ dissolved after only three rinses at pH 2 (using 0.4 K^+ per formula unit).

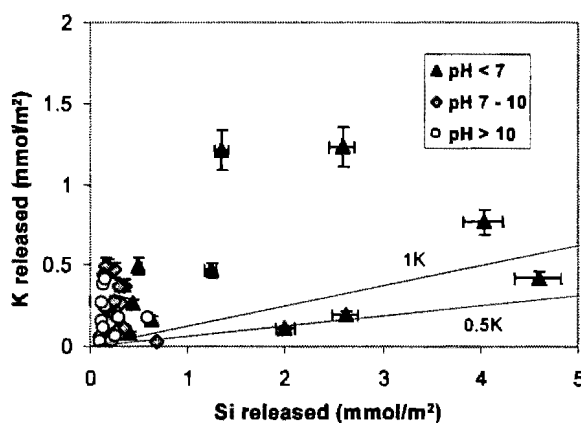


Figure 5.30. Release of K^+ relative to Si from apophyllite samples as a function of final solution pH during sequential rinse dissolution test. The lines show stoichiometric ratios of 1 K : 8 Si and 0.4 K : 8 Si. Error bars show an estimated maximum 10% error in Si and 20% error in K data.

As with the previous experiments, ion exchange could be a contributing factor but trends in much of the K^+ data are inconsistent with that of the other components and contamination of the solutions is feared to have occurred. Since the KCl filling solution from the pH electrode is the suspected source of the K^+ contamination, the pH 2 (0.01M HCl) and pH 12 (0.01M NaOH) solutions are the least likely to be affected. (These were not pH-adjusted and so did not come into regular contact with the electrode).

Ammonium in acid solutions of starting pH 2 is present at three times the concentration expected from a mineral stoichiometry of 0.7 NH_4 molecules per formula unit, based on the dissolved Si concentrations. The release of K^+ and NH_4^+ relative to Si at pH 2 is higher than that of Ca^{2+} and F^- . This could be related to the position which the atoms occupy in the mineral lattice. The Ca atoms share covalent bonds with the F and with apical O atoms from SiO_4 tetrahedra, whereas NH_4 or K are coordinated in a weaker bonding arrangement with 8 H_2O molecules.

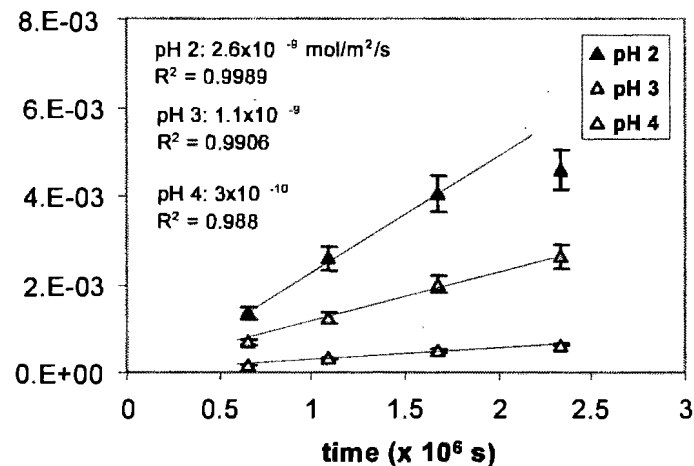
Dissolution rates in acid solutions

The data in Table H.3 indicate that dissolution of apophyllite is relatively rapid in solutions of initial pH 2, but rates decrease markedly with an increase in pH of the rinse solutions. Plots of the concentrations of Si, F, Ca and K release from the mineral against time were prepared for solutions of initial pH 2, 3 and 4 and the dissolution rates with respect to the various components calculated by fitting a regression line through the linear portion of the data (Figure 5.31).

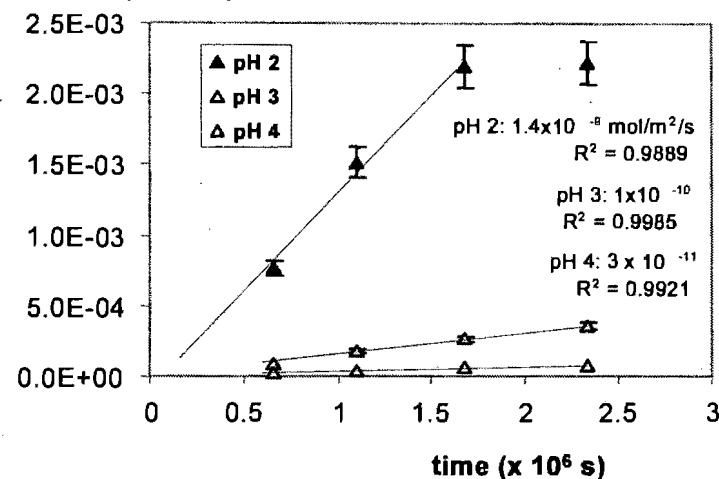
For solutions of initial pH 2, and K^+ and Ca^{2+} release in solutions of pH 3, solute concentrations decreased significantly during the fourth rinse and the final data point was excluded from the linear regression. Molar volume calculations show that a thick leached layer is likely to have formed on the mineral surface over the first three weeks and diffusion through this layer could explain the decreased rate of Ca^{2+} , F^- , K^+ and NH_4^+ dissolution. Leaching, however, does not provide a suitable explanation for a decline in the rate of Si release. The most probable cause of the decreased reaction rate during the fourth rinse in 0.01M HCl is depletion of the apophyllite starting material. The solution reacted under lower pH conditions in the final week than the previous three rinses, giving a final pH close to the initial pH of 2. The pH would remain low if the starting material was depleted because of the decreased consumption of protons by the dissolution reaction. By the last week of the experiment, there was calculated to be very little Ca and F and no K left to dissolve.

In most cases in Figure 5.31, data from the first rinse was excluded from the regression calculation because of the artificially rapid initial dissolution from fresh, unreacted surfaces. This was not possible for pH 2 reactions and Ca and K release at pH 3, as it would have necessitated fitting a line through only two data points.

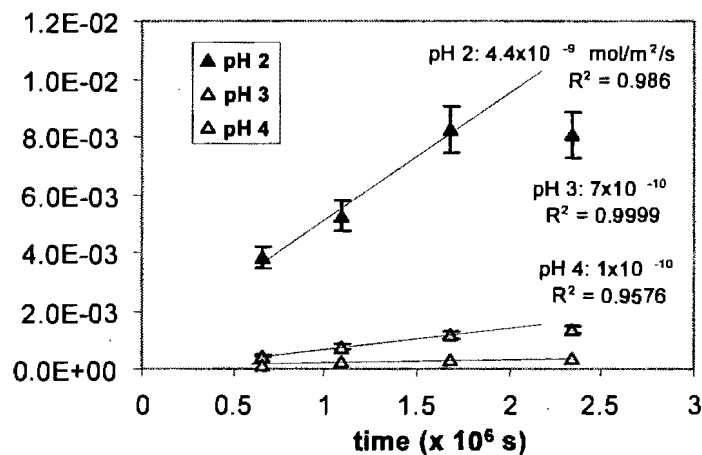
Si released (mol/m²)



F released (mol/m²)



Ca released (mol/m²)



K or NH₄ released (mol/m²)

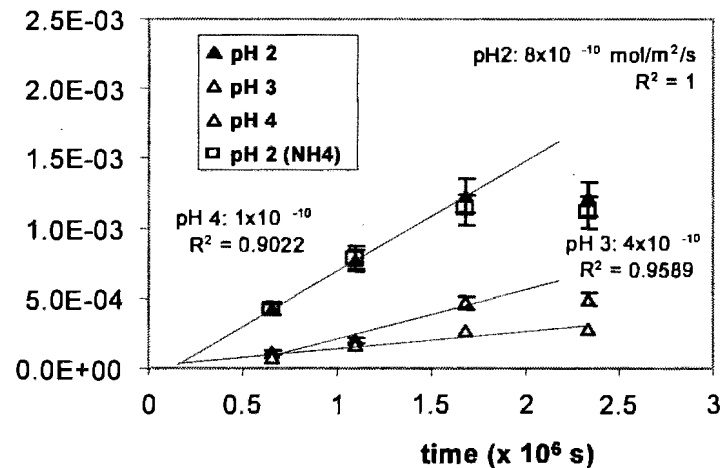


Figure 5.31. Release of Si, Ca²⁺, F⁻, K⁺ and NH₄⁺ from Kopoasfontein apophyllite during four sequential rinses with HCl/NaCl solutions of pH 2, 3 and 4.

The overall dissolution rates of the apophyllite mineral and its components in 0.01M HCl/NaCl solutions of initial pH 2, 3 and 4 are reported in Table 5.18. Where dissolution was found to be non-stoichiometric (pH 2), the rate of release of 8 moles of Si was taken as the rate of apophyllite dissolution. For the other pH conditions (pH 3 and 4), regression lines were fitted through the mean values of Si/8 and F data to obtain the overall rate. Ca and K data were not included because of the greater uncertainty about the quality of these data, discussed earlier in this chapter. The final pH values in Table 5.18 are the mean values for the first three rinses at pH 2 and the second to fourth rinses at pH 3 and 4.

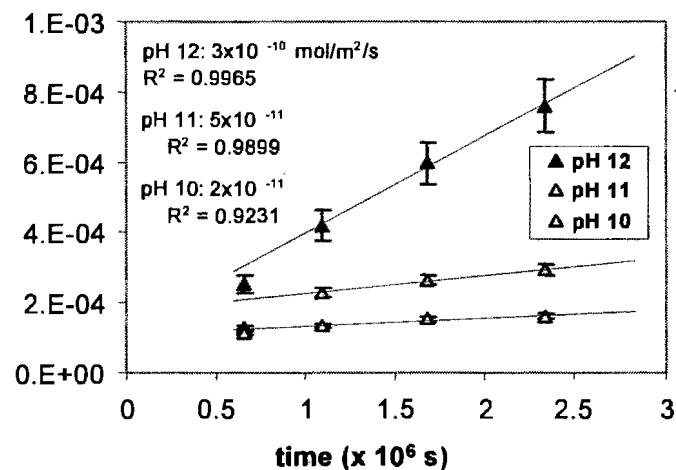
Table 5.18. Rates of dissolution of apophyllite and its components in acid solutions of initial pH 2, 3 and 4.

Initial pH	pH 2	pH 3	pH 4
Final pH (mean $\pm$ s.d.)	5.66 $\pm$ 0.49	6.47 $\pm$ 0.24	6.99 $\pm$ 0.30
Rates (mol/m²/s)			
Si	2.6 $\pm$ 0.3 $\times 10^{-9}$	1.1 $\pm$ 0.1 $\times 10^{-9}$	2.5 $\pm$ 0.2 $\times 10^{-10}$
Ca	4.4 $\pm$ 1.2 $\times 10^{-9}$	7.2 $\pm$ 1.6 $\times 10^{-10}$	1.3 $\pm$ 0.3 $\times 10^{-10}$
F	1.4 $\pm$ 0.2 $\times 10^{-9}$	1.5 $\pm$ 0.2 $\times 10^{-10}$	3.0 $\pm$ 0.4 $\times 10^{-11}$
K	7.9 $\pm$ 1.6 $\times 10^{-10}$	3.6 $\pm$ 0.6 $\times 10^{-10}$	9.3 $\pm$ 2.2 $\times 10^{-11}$
NH ₄	6.9 $\pm$ 1.5 $\times 10^{-10}$	n.d.	n.d.
Apophyllite	3.3 $\pm$ 0.4 $\times 10^{-10}$	1.4 $\pm$ 0.3 $\times 10^{-10}$	3.0 $\pm$ 0.4 $\times 10^{-11}$
log (Rate)	-9.48 $\pm$ 0.05	-9.85 $\pm$ 0.09	-10.51 $\pm$ 0.08

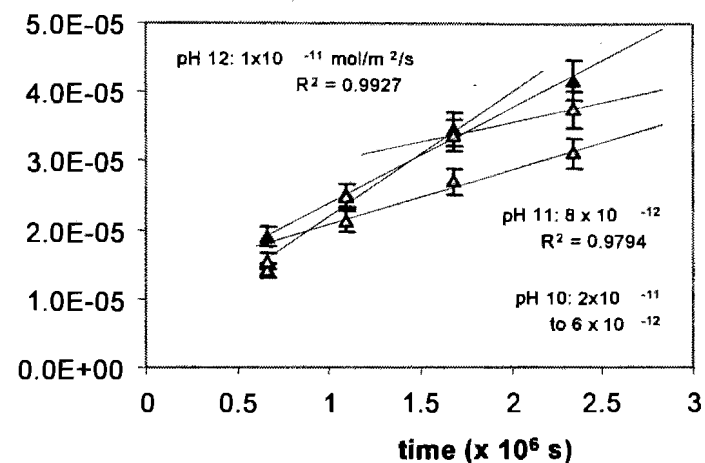
Dissolution rates in basic solutions

Dissolution of apophyllite possibly increases with increasing pH in the region above pH 10, but the dissolution rates are generally an order of magnitude lower than those measured for acid solutions and the errors in measurement are large because of the low solute concentrations. Regression through data points from the second to fourth rinses was once again used to determine the reaction rates, but the correlation coefficients (R^2) show that the data fit is not good. Data for Si release from apophyllite is considered the most reliable indicator of the mineral dissolution, since the high Si content of the mineral generates dissolved concentrations which are high enough to be measured accurately with the available analytical techniques. Potassium data shows a very poor fit to the linear trends superimposed on the last three data points. Excluding the third point (shown with circular symbols) and including the first, as indicated in Figure 5.32 gives a very good linear fit and the K⁺ data from week 3 has been rejected due to suspected calibration errors.

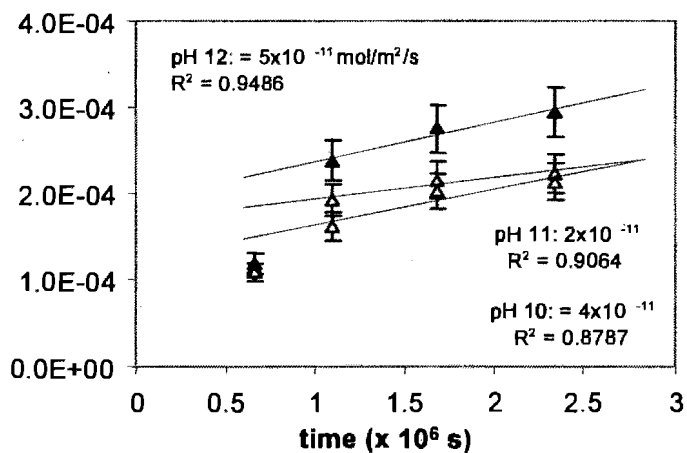
Si released (mol/m²)



F⁻ released (mol/m²)



Ca released (mol/m²)



K released (mol/m²)

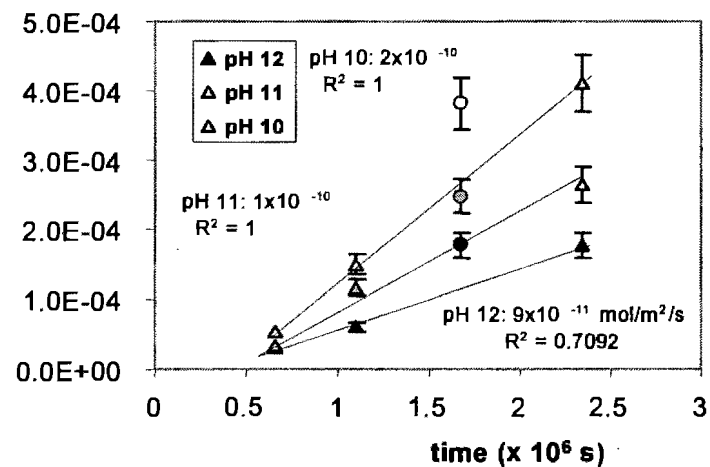


Figure 5.32. Release of Si, Ca²⁺, F⁻ and K⁺ from Kopoasfontein apophyllite during four sequential rinses with NaOH/NaCl solutions of pH 10, 11 and 12.

Rates of F^- release at pH 10 are the most relevant for the fluoride contamination risk in the artificial recharge trials at Kopoasfontein, but the data plotted in Figure 5.32 gives a very poor linear fit through the last three data points. Instead the fluoride release rate was calculated as ranging from the fast initial rate (1.8×10^{-11}) to a slower longer-term rate (5.6×10^{-12} mol/m²/s). The calculated dissolution rates are summarised in Table 5.19.

Table 5.19. Rates of dissolution of apophyllite and its components in basic solutions of pH 10, 11 and 12.

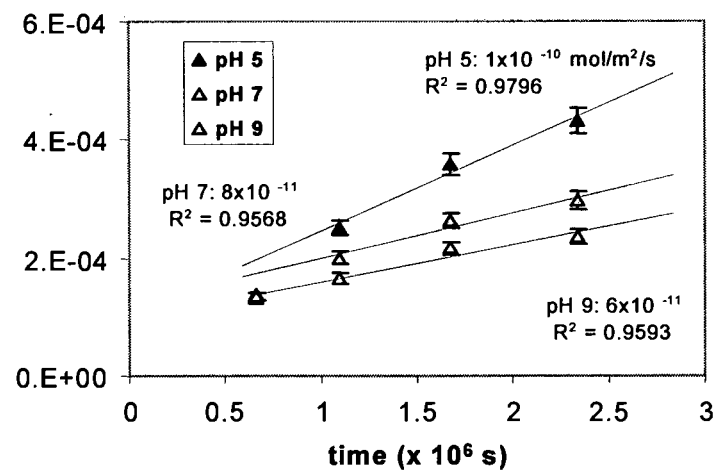
Initial pH	pH 12	pH 11	pH 10
Final pH (mean $\pm$ s.d.)	12.06 $\pm$ 0.03	10.88 $\pm$ 0.08	9.59 $\pm$ 0.06
Rates (mol/m²/s)			
Si	$2.7 \pm 0.5 \times 10^{-10}$	$5.2 \pm 2.1 \times 10^{-11}$	$3.0 \pm 0.8 \times 10^{-11}$
Ca	$4.5 \pm 4.3 \times 10^{-11}$	$2.9 \pm 2.9 \times 10^{-11}$	$4.1 \pm 3.0 \times 10^{-11}$
F	$1.4 \pm 0.3 \times 10^{-11}$	$7.9 \pm 0.3 \times 10^{-12}$	$1.8 \text{ to } 5.6 \times 10^{-11}$
K	$9.0 \pm 1.9 \times 10^{-11}$	$1.2 \pm 0.3 \times 10^{-10}$	$2.1 \pm 0.4 \times 10^{-10}$
Apophyllite*	$3.4 \pm 0.6 \times 10^{-11}$	$6.5 \pm 2.6 \times 10^{-12}$	$3.8 \pm 1.0 \times 10^{-12}$
log (Rate)	-10.48 $\pm$ 0.07	-11.22 $\pm$ 0.18	-11.44 $\pm$ 0.11

* Mean value of rates for Si/8

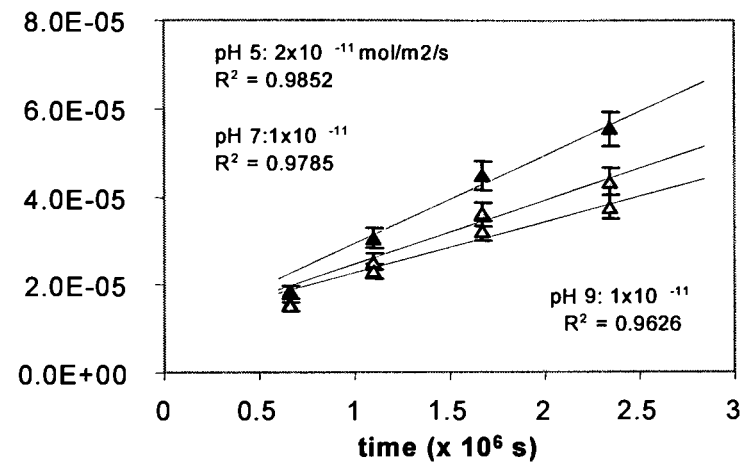
Dissolution rates near neutral pH

Dissolution of apophyllite in solutions near neutral pH is stoichiometric and very slow in comparison to the pH 2 and pH 12 dissolution rates. The resulting solute concentrations in the dissolution batch test were, therefore, very low and relatively large uncertainties are associated with the collection of analytical data and fitting of regression lines. Plots of the data for solutions of initial pH 5, 7 and 9 are shown in Figure 5.33 and the dissolution rates summarised in Table 5.20. Rates of Ca^{2+} and K^+ release, in particular, appear to be almost constant over this pH range.

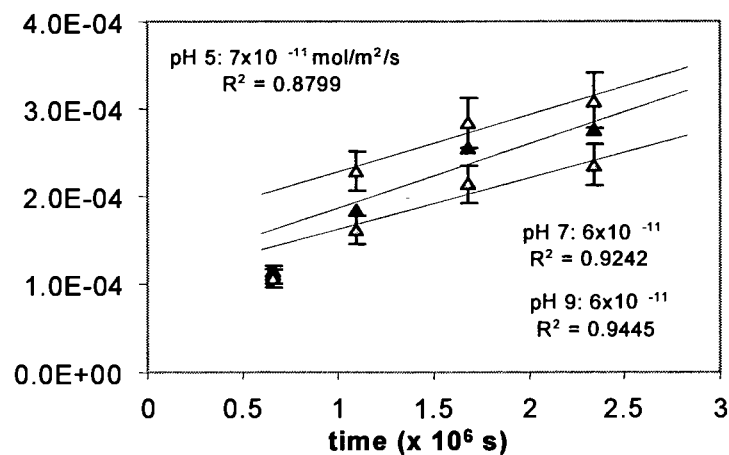
Si released (mol/m²)



F released (mol/m²)



Ca released (mol/m²)



K released (mol/m²)

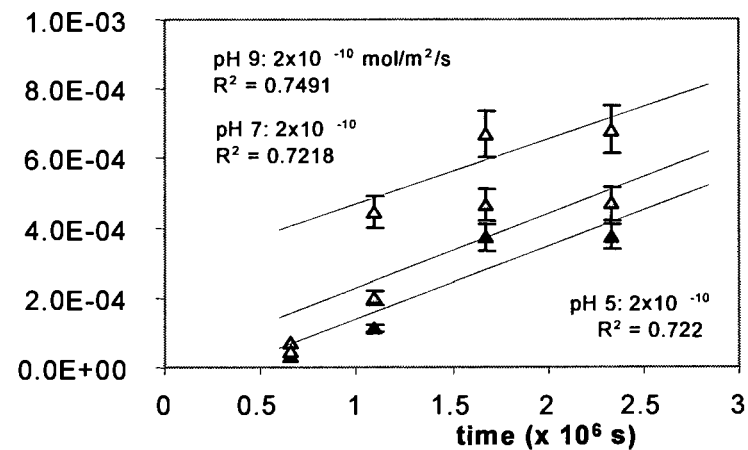


Figure 5.33. Release of Si, Ca²⁺, F⁻ and K⁺ from Kopoasfontein apophyllite during four sequential rinses with HCl or NaOH in 0.01M NaCl at pH 5, 7 and 9.

Table 5.20. Rates of dissolution of apophyllite and its components in near-neutral solutions of initial pH 5 to pH 9.

Initial pH	pH 5	pH 6	pH 7	pH 8	pH 9
Final pH (mean $\pm$ s.d.)	7.08 $\pm$ 0.23	7.13 $\pm$ 0.33	7.25 $\pm$ 0.19	7.42 $\pm$ 0.29	7.67 $\pm$ 0.44
Rates (mol/m²/s)					
Si	1.5 $\pm$ 0.3 $\times$ 10 ⁻¹⁰	1.2 $\pm$ 0.3 $\times$ 10 ⁻¹⁰	7.8 $\pm$ 2.0 $\times$ 10 ⁻¹¹	8.9 $\pm$ 1.9 $\times$ 10 ⁻¹¹	6.0 $\pm$ 1.1 $\times$ 10 ⁻¹¹
Ca	7.4 $\pm$ 3.7 $\times$ 10 ⁻¹¹	7.5 $\pm$ 4.0 $\times$ 10 ⁻¹¹	5.9 $\pm$ 3.2 $\times$ 10 ⁻¹¹	5.6 $\pm$ 3.2 $\times$ 10 ⁻¹¹	6.4 $\pm$ 4.3 $\times$ 10 ⁻¹¹
F	2.0 $\pm$ 0.5 $\times$ 10 ⁻¹¹	1.7 $\pm$ 0.5 $\times$ 10 ⁻¹¹	1.4 $\pm$ 0.4 $\times$ 10 ⁻¹¹	1.5 $\pm$ 0.4 $\times$ 10 ⁻¹¹	1.1 $\pm$ 0.3 $\times$ 10 ⁻¹¹
K	2.0 $\pm$ 0.2 $\times$ 10 ⁻¹⁰	1.1 $\pm$ 0.2 $\times$ 10 ⁻¹⁰	2.1 $\pm$ 0.5 $\times$ 10 ⁻¹⁰	2.1 $\pm$ 0.6 $\times$ 10 ⁻¹⁰	1.9 $\pm$ 0.9 $\times$ 10 ⁻¹⁰
Apophyllite*	1.9 $\pm$ 0.4 $\times$ 10 ⁻¹¹	1.5 $\pm$ 0.4 $\times$ 10 ⁻¹¹	9.8 $\pm$ 3.0 $\times$ 10 ⁻¹²	1.1 $\pm$ 0.2 $\times$ 10 ⁻¹¹	7.5 $\pm$ 1.4 $\times$ 10 ⁻¹²
log (Rate)	-10.74 $\pm$ 0.09	-10.84 $\pm$ 0.11	-11.02 $\pm$ 0.11	-10.96 $\pm$ 0.08	-11.13 $\pm$ 0.08

* Mean value of rates for Si/8.

5.7.5.3 Discussion: Final versus initial pH

As with the second batch test experiment, an attempt was made to fit regression lines to the dissolution data from the third batch test on the basis of the final pH of the solutions, taking this as the pH under which the dissolution reaction occurred. The success of this approach, however, was hampered by a lack of data points in the low pH region. There was a wide scatter of the data points for solutions with final pH between 6.7 and 9.3, which also hampered the identification of suitable points for linear regression calculations. As a result, the rates reported in the previous sections were calculated on the basis of the initial pH of the solutions added to the mineral samples. Above pH 10, no significant drift in the pH was observed during the batch test and the dissolution rates reported are for approximately constant pH conditions (Figure 5.34).

Below pH 7, reactions with apophyllite cause a rapid rise in the solution pH in contact with the mineral, especially during the first rinse of the experiment. The pH during the fourth sequential rinse failed to rise significantly above the initial pH.

Initially, it was suspected that exchange of H⁺ for K⁺ could be a contributing factor in this pH-buffering effect, consuming protons by the reaction:



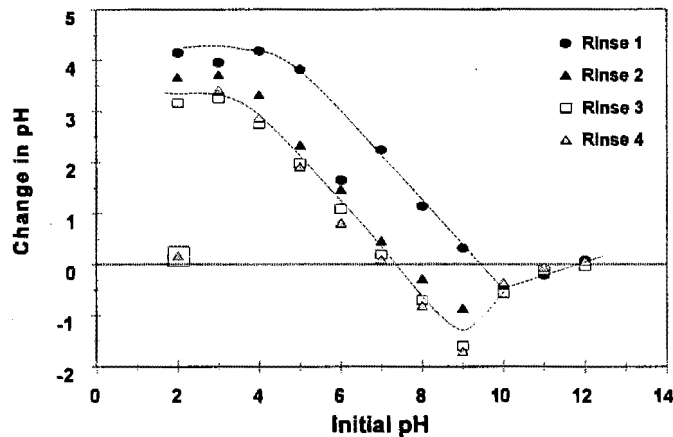


Figure 5.34. Change in pH after each week, during a four-week sequential rinse batch test with Kopoasfontein apophyllite, plotted against the initial pH of the HCl/NaCl or NaOH/NaCl solution added to the mineral.

The ion exchange explanation is, however, not supported by the observations. As an example, the change in pH during the first rinse with 0.01M HCl is from 2 to 6.15 pH units, i.e. a decrease in H^+ concentration of 1×10^{-2} mol/L. The increase in K^+ concentration over this same period was 25 mg/L, i.e. 6.4×10^{-4} mol/L, which is 15 times lower than the amount of H^+ consumed. Even if all the K^+ in solution is derived by proton exchange, the contribution to the rise in pH by this mechanism is negligible.

Using the same sample, the increase in Ca concentration during the first rinse is 5.7×10^{-3} mol/L. If this concentration of Ca^{2+} is derived from stoichiometric dissolution of apophyllite, then 1.4×10^{-3} mol apophyllite/L were dissolved during this rinse. The amount of K^+ released by apophyllite dissolution alone would be expected to be 5.7×10^{-4} mol/L or 22.4 mg/L. The measured concentration of K^+ is close enough to this value that all K^+ in solution can be explained by apophyllite dissolution once all errors are taken into account.

All the pH drift, within error, can also be explained by the dissolution of apophyllite. According to equation 5.12, two mol H^+ are consumed for each mol Ca^{2+} released. Therefore, a 5.7×10^{-3} mol/L increase in Ca^{2+} , would be accompanied by a decrease of 1.1×10^{-2} mol/L H^+ . Since most of the mineral was dissolved during the first three weeks, there was almost no dissolution during the fourth sequential rinse and, as a result, very little change in pH, Ca^{2+} or K^+ in the final week.

The change in pH (or consumption of H^+) could not be used as an accurate measure of apophyllite reaction rate (based on reaction 5.12), nor of surface exchange equilibria (reaction 5.14), because it is likely to be affected by several simultaneous reactions in solution that were not quantified. These include carbonate equilibria (since CO_2 was not excluded) and nitrification of NH_4^+ .

5.7.6 Limitations of the batch test method and analyses

Dissolution behaviour is controlled by several variables which operate in conjunction and it is difficult to separate the effects of all relevant parameters. Many variables which affect the rate of silicate dissolution, most notably pH and solution saturation state, could not be effectively controlled in batch experiments of this nature.

Although closed system conditions with no external pH control provides a closer approximation of the natural situation than a pH-stat experiment or flow through reactor, the change in rate with changing pH complicates the fitting of data to rate law expressions. Solution pH rose from pH 2 to pH 5 - 6 over the week-long rinses of the sequential rinse experiments until the interstitial species were depleted. The pH rose almost instantly to above pH 9 when neutral pH solutions were introduced to the apophyllite. The mineral itself appears to have buffered the pH near 9.4 for the first 100 hours of batch test 1. After this, however, a steady drift towards lower pH values was observed, most likely from the uncontrolled dissolution of atmospheric CO_2 , which is a factor in many of the test solutions. Only solutions above pH 10 displayed minimal pH drift.

A general criticism of the use of batch tests for dissolution experiments is that the accumulation of solutes in solution prevents the "far-from-equilibrium" reaction conditions conventionally used when measuring reaction kinetics. This is less of a concern for apophyllite, than for aluminosilicate minerals where sparingly-soluble aluminous phases tend to precipitate in side reactions and interfere with the determination of the dissolution rate. Supersaturation with respect to calcium carbonate in the alkaline solutions could have affected the calcium concentrations in some of the batch test samples. Unfortunately this could not be quantified in all cases, as alkalinity was not always measured.

The use of small sample volumes was necessitated by the small amount of natural apophyllite

available for the dissolution experiments. This placed a restriction on the number of parameters that could be analysed using the available methods and the accuracy of these analyses. Multiple determinations of solute concentrations were not possible and only a few sample runs were repeated.

Although the analytical detection limit for K^+ and Ca^{2+} by FAAS and ICP-AES is low (0.05 to 0.1 mg/L), the dilution of the samples introduces an additional source of error to these data. Where cations were analysed by IC, the errors are considerably larger. Potassium contamination from the pH electrode is also a concern in many of the samples, because of the low concentrations involved. Ammonium and fluoride data lie close to the analytical detection limit of 0.1 mg/L for the IC technique and errors are likely to be large. The ISE used in batch test 2 gives more reliable F^- data than IC. It is also possible that deterioration of the samples occurred during storage before analysis, especially where samples were accumulated until the end of a test, or that a small loss of volume occurred by evaporation through the plastic reaction containers while on the shaker.

Finally, the surface area measurements introduce an additional source of error when reaction rates are normalised to the initial BET surface area of the mineral. This is problematic where surface areas change significantly during mineral dissolution or where small sample volumes have affected the accuracy of the BET measurement or required surface areas to be estimated.

5.7.7 pH-dependence of apophyllite dissolution

The control of pH on the rate of silicate mineral dissolution was discussed in Section 2.6.2. Dependence on pH for feldspar- and phyllosilicate dissolution rates generally follows a pattern similar to that of Figure 2.3, where the rate is divided into three domains: an acid region, typically below pH 4 or 5, where the rate of dissolution increases exponentially with increasing H^+ activity (decreasing pH); a neutral region, where the dissolution rate is independent of pH and an alkaline region, typically above pH 8, where dissolution rate increases with increasing pH (Drever, 1997; p. 229).

The relationship between initial pH and the rate of dissolution of apophyllite appears to display these characteristic pH zones (Figure 5.35), but the basic transition point may occur at pH 10 to

11, a higher pH of than that for feldspars. There may also be a slight pH-dependence in the “neutral” region.

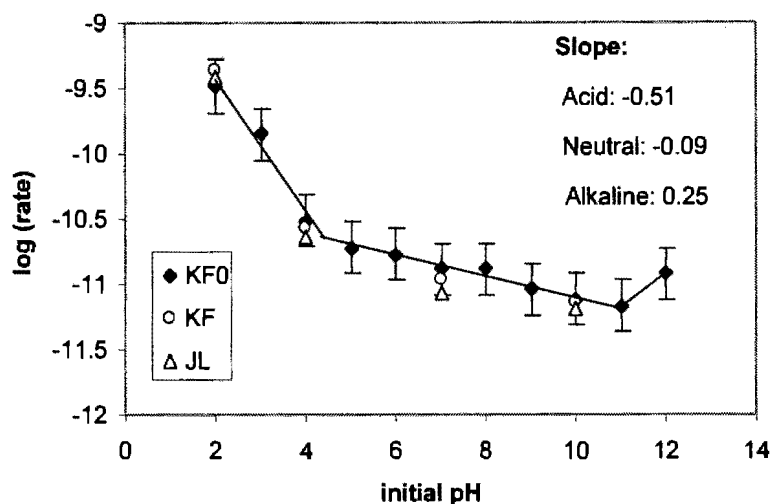


Figure 5.35. Control of initial solution pH on dissolution rate of fluorapophyllite measured in sequential rinse batch experiments. KF0 is Kopoasfontein apophyllite in batch test 3 and KF and JL are Kopoasfontein and Jalgaon apophyllite results from batch test 2. Error bars indicate a range of ± 0.2 log units, being the maximum difference between the rates of release of the individual solutes (Si/8; Ca/4 or F) used to calculate the overall dissolution rate for the mineral.

In the acid range, between pH 2 and 4, the pH-rate relationship is described by equation 2.18, with $k_H = 4 \times 10^{-9}$ mol/m²/s and $n = 0.51$. This is consistent with other studies of silicate hydrolysis which often give n values near 0.5 in the acid range. Nagy (1995) has compiled literature values of n for kaolinite and chlorite which range from 0 to 0.5 depending on experimental conditions. A reaction order of 0.5 is generally interpreted by transition state theory as a proton-promoted surface reaction involving one H^+ and two molecules of the dissolving mineral in the activated surface complex.

Reaction rates for fluorapophyllite dissolution increased slightly with increasing pH above pH 11, but the scarcity of data points in this region gives poor confidence in the calculated reaction order of $m = -0.25$. The uncertainty in the data for the neutral to alkaline region is also large enough that the rate might instead be considered independent of pH. Values of m for phyllosilicates, range from -0.1 for muscovite, illite and montmorillonite (Nagy, 1995) to -0.25 for kaolinite (Carroll and Walther, 1990). Reactions in this region of the pH range are dominated by

deprotonation of surface silica tetrahedra.

Since the experiments were not performed under buffered pH conditions, the data from these experiments can also be plotted based on the final pH of each solution. In this case, the rate-dependence on pH increases in the acid region, shifting the acid transition point to near pH 8, but the alkaline region is not significantly affected (Figure 5.36).

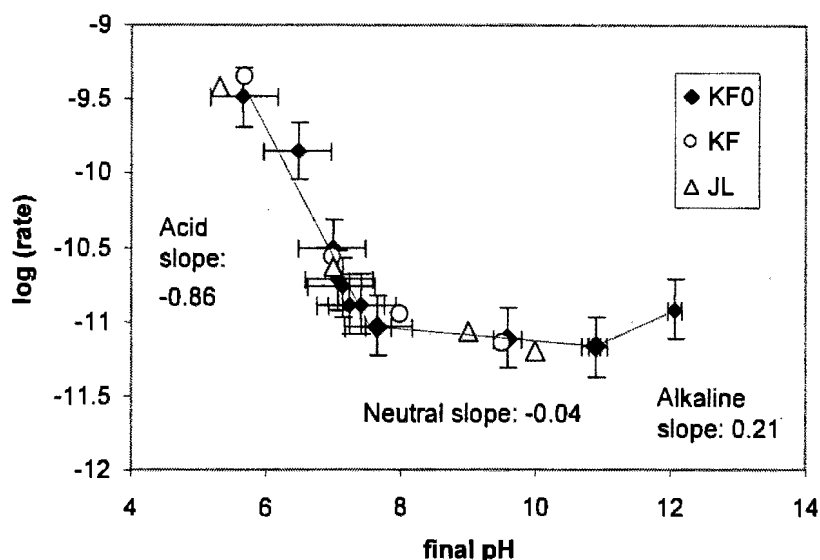


Figure 5.36. Control of final solution pH on dissolution rates of fluorapophyllite measured in sequential rinse batch experiments. KF0 is Kopoasfontein apophyllite in batch test 3 and KF and JL are Kopoasfontein and Jalgaoon apophyllite results from batch test 2. Error bars indicate a range of ± 0.2 log units in the dissolution rate for the mineral and 0.5 pH to 0.1 pH units, based on the standard deviation of pH readings for successive rinses.

Figures 5.35 and 5.36 show that the measured dissolution rates for fluorapophyllites from the second and third batch tests are very similar, indicating good reproducibility for the sequential rinse test method.

This data set is, however, problematic in terms of developing kinetic models of apophyllite dissolution, because the pH was not held constant during the batch tests. Any reaction orders calculated as a function of initial, final or even intermediate pH will, therefore, not be accurate enough to draw conclusions on the mechanistic aspects of the dissolution reaction.

5.7.8 Summary of dissolution test results

Simple laboratory batch tests all using 50-100 μm pretreated mineral samples and typically lasting up to one month have been used to determine the dissolution rate of apophyllite under various reaction conditions. The observed trends conform to expectations, based on dissolution tests for other silicate minerals.

Dissolution rates are slow and show a strong dependence on pH, with increasing rates found for concentrated acid and alkali solutions. Measured rates range from the long-term steady-state rate of 1×10^{-12} mol apophyllite/ m^2/s at pH 9 to the relatively rapid release of interstitial species (Ca^{2+} , K^+ , F^-) at stoichiometric rates of 1.5×10^{-9} mol/ m^2/s over 1 month (4 rinses) in 0.01M HCl. The breakdown of the silicate framework under acid conditions (HCl, pH 2) gives an overall dissolution rate of 3 to 4×10^{-10} mol apophyllite/ m^2/s . In general, the dissolution rate of apophyllites in neutral to alkaline solutions (pH 7 - 10) occurred at rates from 1 to 3×10^{-11} mol apophyllite/ m^2/s in the batch test experiments.

Dissolution reactions are non-stoichiometric at very low and also possibly at very high pH. As other workers have found for many aluminosilicates, the leaching of base cations from the mineral forms a leached layer at the surface after acid reaction. The leached layer in apophyllite reached a maximum thickness of nearly 2 μm after 4 weeks reaction with 0.01M HCl. Under acid attack, NH_4^+ and K^+ are released fastest, followed by Ca^{2+} and F^- , while SEM-EDX analysis confirms that only the Si and O remain in the solid phase in the outer layer of the mineral. Since the amount of Al in these apophyllite samples is small, the accepted aluminosilicate dissolution mechanism of proton attack at Al-O bonds in preference to Si-O, must be replaced by some other pathway, probably attack of Ca-O and Ca-F bonds.

The results of the second batch experiment indicate that compositional variation in the mineral may affect the rate of dissolution. An NH_4 -rich sample dissolved fastest in acid solution, but the dissolution of F-poor apophyllites tended to be accelerated over those with high F content in neutral to alkaline solutions. Ammonium substitution appears to have little effect on the rate at pH greater than 3. This agrees with findings on the thermal stability of apophyllites, where OH substitution causes greater destabilisation of the crystal than NH_4 substitution (Section 5.5.3).

CHAPTER 6

GENERAL DISCUSSION: EVOLUTION OF KOPOASFONTEIN GROUNDWATER, THE ROLE OF APOPHYLLITE AND IMPLICATIONS FOR ARTIFICIAL RECHARGE

6.1 Introduction

Parent geology exerts a strong influence on the composition of groundwater solutes via the availability, relative solubility and rate of dissolution of minerals in the soil zone and aquifer. At Kopoasfontein, groundwater in the breccia pipe displays chemical features that are characteristic of waters from silicate host rocks in igneous or metamorphic terrain. These include elevated dissolved silica (from degradation of silicates); excess Na^+ which is not balanced by Cl^- ions (derived from the weathering of primary silicate minerals, such as feldspars, or cation exchange on aluminosilicates); low total dissolved solids (due to slow dissolution rates of most silicate minerals) and significant alkalinity (generated by proton consumption during silicate hydrolysis reactions). High pH and fluoride concentrations are also characteristic of the Kopoasfontein groundwater, and the role of silicate mineral weathering, and particularly reactions of fluorapophyllite, in creating such conditions are examined.

Sodium and bicarbonate are the dominant ions in solution in many groundwaters from stratified sedimentary sequences (Freeze and Cherry, 1979) and crystalline igneous terrains (Frengstad and Banks, 2000), irrespective of the host rock type. This composition, accompanied by high pH and low Ca^{2+} concentrations, is often explained as the culmination of a sequence of chemical reactions. These begin with the infiltration of CO_2 -charged rainwater and dissolution of carbonate minerals in the recharge zone, to give a Ca-HCO_3 water type, followed by ion exchange of dissolved Ca^{2+} for Na absorbed on the aquifer solids along the groundwater flow path (Appelo and Postma, 1996). In such cases, it is universal thermodynamic equilibria, e.g carbonate system and ion exchange equilibria, rather than the aquifer lithology, which control the groundwater evolution. Frengstad and Banks (2000) have also shown that high pH, Na-HCO_3 water can evolve without cation exchange if primary sodium- and calcium-bearing silicates dissolve in systems closed to CO_2 . In this case Ca^{2+} is removed by the precipitation of secondary calcite, rather than by ion exchange.

This chapter examines the origin of the Kopoasfontein groundwater and lithological influences on its composition. It also attempts to decipher what role, if any, fluorapophyllite plays in the evolution the pH and fluoride in the groundwater. Mass balance calculations and forward modelling of apophyllite dissolution reactions are used to investigate the controls on various parameters in the Kopoasfontein groundwater. While the groundwater environment and mineralogy is complex, and it is not possible to quantify the effects of all possible geochemical reactions in the system, the modelling exercises will have served some purpose if they can be shown to constrain some of these reactions to within readily comprehensible limits.

6.2 High pH groundwaters and carbonate equilibria

Although the Na-HCO₃ water type is common, it is relatively rare to encounter a natural water that has evolved to the pH found in the Kopoasfontein breccia pipe, without it being accompanied by substantial salinity. This is particularly true for a semi-arid region where carbonate equilibria often dominate pH buffering and the landscape contains abundant soluble salts. Natural groundwaters with pH above 10 have, however, been reported in some unusual geological settings. While the Kopoasfontein site does not produce such extremely alkaline groundwaters as some of these examples, it does share with these rare water types a host rock of unusual mineralogy and hydrothermal history.

6.2.1 Examples of high pH groundwater systems

Highly mineralised calcium hydroxide groundwaters in northern Jordan have a pH of up to 12.9, the highest reported pH for natural waters (Linklater *et al.*, 1996). These waters were found to be in equilibrium with portlandite, Ca(OH)₂ (Saines *et al.*, 1980). Thermal metamorphism due to combustion of organic-rich marl and limestone, is the suspected origin of the thick layers of portlandite-rich rock through which infiltration occurs to acquire this rare chemistry.

Groundwaters with pH values greater than 11 have also been found in association with serpentinizing fluids during present-day metamorphism of ultramafic rocks in the western United States (Barnes and O'Niel, 1969; Barnes, 1970). These metamorphic groundwaters are of varied chemistry, including Ca-OH and Na-Cl types.

Highly alkaline waters, of similar composition to those of Kopoasfontein, are reported by Kraynov *et al.* (1969) from the Lovozero massif in the former Soviet Union. Although considerably more mineralised than the Calvinia samples, these waters are characterised by elevated fluoride and silica and have a pH range of 9.5 to 12, with Ca^{2+} often below detection levels. Dissolution of primary silicates, principally nepheline, in the absence of CO_2 causes high dissolved silica and alkalinity, while the F^- in this case is derived from the dissolution of abundant villiaumite (NaF) in the rocks. Nepheline ($\text{Na}_3\text{K}(\text{Al}_4\text{Si}_4\text{O}_{16})$) is also devoid of alkaline earth elements which could buffer the pH through equilibria with sparingly soluble carbonate minerals.

Kopoasfontein groundwaters also share chemical characteristics with leachates from oil shale wastes of the Green River Formation, USA. Heat treatment during retorting of the shales to extract oil has a similar effect to that of hydrothermal alteration of the Kopoasfontein shale. Organic matter is driven off under elevated temperature and the oil shale residue produces highly alkaline leachates (pH 8 to 13) with elevated F^- concentrations. Other anionic trace elements such as As, Mo, Se and B are also mobilised from the oil shales in this alkaline environment (Saether *et al.*, 1981).

6.2.2 pH buffering processes in aquifers

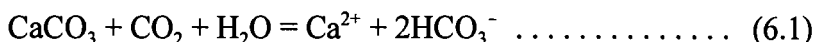
Most groundwater is fed by meteoric water in the form of rain or snowmelt. These are not pure waters, but contain various natural and anthropogenic solutes, influenced by proximity to the oceans and large urban settlements. Carbonate equilibria predict a pH of 5.7 for low ionic strength water in contact with CO_2 at the atmospheric concentration of $10^{-3.5}$ atm at 20°C . Precipitation in rural, continental areas generally has a pH between 5 and 6. Acidic precipitation in the form of dilute sulphuric or nitric acid may occur over industrial areas where sulphur and nitrogen species are emitted to the atmosphere in large volumes. The acidified precipitation may then have pH values closer to 4 or 3.

Reactions in the soil zone also have the ability to generate considerable amounts of acid. Root and microbial respiration affect carbonate equilibria, creating a CO_2 atmosphere in soils which is generally much higher than that of the earth's atmosphere. These conditions lower the pH even

further if there is no buffering system to control H^+ in the soil zone.

Chemical weathering of minerals is essentially the only process by which acidity from the atmosphere can be neutralised over long periods of time (Drever, 1997; p. 299). Neutralisation is also possible by cation exchange, but weathering reactions are still necessary to maintain the supply of exchangeable cations. Mineral dissolution by weak acid/strong base reactions consumes acidity in the unsaturated zone and helps to buffer the soil and groundwater against acidification. These acid-base reactions involve weak acids of the carbonate and silicate systems and strong bases from the dissolution of carbonate, silicate and aluminosilicate minerals. Rocks which contain carbonate minerals are unlikely to develop acid groundwaters, because of the fast dissolution kinetics of carbonates, but carbonate-free silicates, especially acid igneous rocks and quartzites containing slow-dissolving silicate minerals are susceptible to acidification (Appelo and Postma, 1996; p. 226).

The pH of most natural waters is controlled by reactions involving the carbonate system (Drever, 1997; p. 41). When carbonate minerals are present in the aquifer, their dissolution and precipitation are important regulators of pH. These solubility equilibria are, in turn, strongly controlled by the availability of CO_2 by reactions such as:



If CO_2 is available, $CaCO_3$ will tend to dissolve, while removal of CO_2 (e.g. degassing) favours the reverse reaction, causing $CaCO_3$ precipitation. Even in silicate aquifers that do not contain primary carbonates, carbonate buffering can control pH by the reverse of reactions such as 6.1, which cause carbonate deposition when Ca^{2+} (or Mg^{2+}) and HCO_3^- are present (from CO_2 weathering of silicate minerals). Anaerobic decay with sulphate reduction also causes an increase in bicarbonate alkalinity and thus tends to cause precipitation of calcite (Drever, 1997; p. 55).

Carbon dioxide loss from groundwater in the unsaturated zone close to the surface is responsible for the deposition of calcretes (Talma, 1981). Where deep groundwaters are close to equilibrium with calcite or dolomite, exsolution of CO_2 in fissures or caves will cause precipitation of carbonate, changing the water composition towards higher pH and lower bicarbonate

concentrations. Carbon dioxide production in the aquifer, by oxidation of organic matter, for example, will have the opposite effect, causing additional carbonate dissolution and lowering of the pH (Appelo and Postma, 1996; p. 109).

The amount of CaCO_3 that dissolves is dependent on the initial CO_2 concentration and the extent to which it can be replenished by exchanging with a gas phase during the reaction. *Open system* dissolution occurs when a constant partial pressure of CO_2 is maintained e.g. by exchange with the atmosphere or soil gas, while *closed system* conditions occur when the initially available CO_2 is consumed by dissolution reactions such as 6.1 or 2.4 to 2.8 and not replenished (Drever, 1997; p. 60; Appelo and Postma, 1996; p. 105). Since open system dissolution is not limited by CO_2 availability, more CaCO_3 can dissolve under open system- than closed system conditions. The effect of open and closed system calcite dissolution on pH, HCO_3^- and Ca^{2+} concentrations is illustrated in Figure 6.1, which shows the chemical evolution of waters that react with calcite under varying conditions of CO_2 availability (Langmuir, 1971).

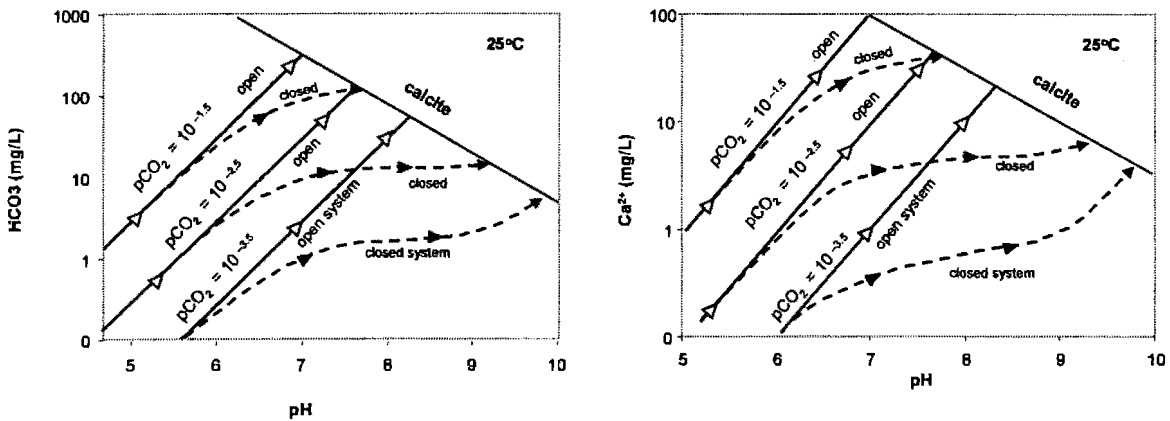


Figure 6.1. Theoretical variations in bicarbonate and calcium concentrations and pH calculated using PHREEQC-2 (Parkhurst and Appelo, 1999) for the evolution of waters towards equilibrium with calcite at 25°C. Closed and open system dissolution with initial CO_2 partial pressures of $10^{-1.5}$, $10^{-2.5}$ and $10^{-3.5}$ atm were modelled (After Langmuir, 1971).

The diagram illustrates how calcite saturation can impose an upper limit on the pH of groundwaters in carbonate-bearing aquifers. Groundwaters in equilibrium with calcite can only evolve above pH 8.3 (at 25°C) in systems which are closed to CO_2 , where pCO_2 may fall below atmospheric concentrations. The difference between closed and open system evolutionary paths

has been used to diagnose the type of environment where Ca^{2+} has entered the groundwater and hence, the location of the infiltration area (e.g. Langmuir, 1971).

Although silicate mineral dissolution is slow, silicate hydrolysis reactions consume protons and are an important long-term buffering mechanism against soil- groundwater acidification. Silicate dissolution can also lead to extremely alkaline pH in low CO_2 environments. This is especially true where primary silicates release alkali cations which form soluble carbonate phases, such as Na^+ and K^+ . Dissolution of feldspars, for example, in systems closed to CO_2 produce alkaline solutions of pH greater than 9 for K-feldspar and close to 10 for albite (McBride, 1994; p. 210). In this case neither Ca^{2+} nor HCO_3^- is available for regulation of the solution pH by carbonate equilibria.

6.3 Forward modelling of apophyllite dissolution

Dissolution of fluorapophyllite has been simulated using the geochemical code PHREEQC-2 (Parkhurst and Appelo 1999), to investigate the influence on pH, Ca^{2+} and F^- concentrations when apophyllite dissolves under various environmental conditions. The aim of the modelling exercise was to test the feasibility and reaction conditions for evolving high-fluoride waters with fluorapophyllite as the only source of F^- . Calcite and silica are known to be weathering products of apophyllite and these secondary phases have been included in the simulations.

6.3.1 Model input parameters

The input file stipulated that 1×10^{-3} mol of pure fluorapophyllite, $\text{KCa}_4\text{Si}_8\text{O}_{20}\text{F} \cdot 8\text{H}_2\text{O}$, be added in 40 equal steps to a solution of specified composition at 25°C . Starting solutions were:

1. *Artificial recharge*:- pure water equilibrated with CO_2 at a pressure of $10^{-3.5}$ atm to approximate the surface water used for subsurface injection.
2. *Natural recharge*:- pure water equilibrated with CO_2 at 10^{-2} atm to approximate soil water after passage through a zone of moderate biological activity. This solution was also allowed to equilibrate with calcite, which was assumed to be in excess in the soil.

For each solution, the reactions were simulated to occur both under open system (i.e. constant

CO₂ pressure of 10^{-3.5} or 10⁻² atm maintained for the duration of reaction) and closed system conditions (i.e. no addition of CO₂ after the initial equilibration). Open system conditions could be expected if dissolution of apophyllite occurs near surface in the unsaturated zone, while closed system conditions are experienced at depth below the water table, if no local source of CO₂, such as degradation of aquifer organic matter, is present. Precipitation of calcite, fluorite and amorphous silica was allowed if these phases became supersaturated. The system of modelled reactions is summarised in Table 6.1.

Fluorapophyllite saturation was not specified as a limitation, because of the slow kinetics of silicate precipitation and the uncertainty of reaching equilibrium under low temperature conditions. Low confidence in the predicted solubility of the mineral was also a factor in excluding fluorapophyllite precipitation. As an indication of the possible implications of fluorapophyllite equilibrium, a saturation index was calculated for this mineral using the estimated log K_{sp} ≈ 20 from Section 5.6. Default thermodynamic values from the PHREEQC database were used for the other constants. The input data files are attached as Appendix I.

Table 6.1. Theoretical reactions of congruent and incongruent dissolution of pure fluorapophyllite, in the presence and absence of dissolved CO₂, as modelled in PHREEQC-2 simulations.

Reaction	
Open system dissolution	
<i>Congruent dissolution:</i>	
$\text{KCa}_4\text{Si}_8\text{O}_{20}\text{F} \cdot 8\text{H}_2\text{O} + 8\text{CO}_2 + 12\text{H}_2\text{O} = \text{K}^+ + 4\text{Ca}^{2+} + 8\text{H}_4\text{SiO}_4 + 8\text{HCO}_3^- + \text{F}^-$	(6.2)
<i>Calcite precipitation:</i>	
$\text{KCa}_4\text{Si}_8\text{O}_{20}\text{F} \cdot 8\text{H}_2\text{O} + 4\text{CO}_2 + 8\text{H}_2\text{O} = \text{K}^+ + 4\text{CaCO}_3 + 8\text{H}_4\text{SiO}_4 + \text{F}^-$	(6.3)
<i>Calcite + silica precipitation:</i>	
$\text{KCa}_4\text{Si}_8\text{O}_{20}\text{F} \cdot 8\text{H}_2\text{O} + 4\text{CO}_2 = \text{K}^+ + 4\text{CaCO}_3 + 8\text{SiO}_2 + \text{F}^- + 8\text{H}_2\text{O}$	(6.4)
<i>Calcite + silica + fluorite precipitation:</i>	
$2\text{KCa}_4\text{Si}_8\text{O}_{20}\text{F} \cdot 8\text{H}_2\text{O} + 7\text{CO}_2 = 2\text{K}^+ + 7\text{CaCO}_3 + 16\text{SiO}_2 + \text{CaF}_2 + 15\text{H}_2\text{O} + \text{OH}^-$	(6.5)
Closed system dissolution, after CO₂ is consumed	
<i>Congruent dissolution:</i>	
$\text{KCa}_4\text{Si}_8\text{O}_{20}\text{F} \cdot 8\text{H}_2\text{O} + 12\text{H}_2\text{O} = \text{K}^+ + 4\text{Ca}^{2+} + 8\text{H}_4\text{SiO}_4 + \text{F}^- + 8\text{OH}^-$	(6.6)
<i>Fluorite precipitation:</i>	
$2\text{KCa}_4\text{Si}_8\text{O}_{20}\text{F} \cdot 8\text{H}_2\text{O} + 24\text{H}_2\text{O} = 2\text{K}^+ + 7\text{Ca}^{2+} + 16\text{H}_4\text{SiO}_4 + \text{CaF}_2 + 16\text{OH}^-$	(6.7)

6.3.2 Modelling results

The results of the modelling simulations are presented graphically in Figures 6.2 to 6.5. The time scale in the figures has been calculated using a dissolution rate of 1×10^{-11} mol/m²/s, the minimum dissolution rate measured in neutral to alkaline solutions as reported in Section 5.7, and taking an arbitrary surface area of 1 m² fluorapophyllite in contact with 1 kg of solution.

Simulation 1

The simulated artificial recharge water (solution 1, $p\text{CO}_2 = 10^{-3.5}$) is poorly-buffered and pH rises rapidly on contact with fluorapophyllite. Under open system conditions (Figure 6.2), calcite saturation is soon reached and the precipitation reaction, 6.3, prevents further accumulation of HCO_3^- , effectively buffering the pH near pH 8.3.

Precipitation of amorphous silica (reaction 6.4) places an upper limit on the concentration of dissolved Si, which levels off after the addition of 0.25 mmol fluorapophyllite. Finally, fluorite saturation is also reached, becoming an additional sink for Ca^{2+} . The common ion effect increases calcite solubility, allowing HCO_3^- to accumulate again once fluorite precipitation begins, but at a much slower rate than at the beginning of the simulation. The effect of OH^- in reaction 6.5 is to cause a gradual increase in the solution pH as further fluorapophyllite dissolves. Alkalinity and F^- continue to increase, while Ca^{2+} added by the apophyllite is steadily depleted.

Rough solubility estimates indicated that fluorapophyllite saturation would be reached after the dissolution of 0.125 mmol apophyllite under open system conditions at $p\text{CO}_2 = 10^{-3.5}$. Fluoride concentrations by this stage are already at 2.4 mg/L, above health guidelines for drinking water.

Simulation 2

For closed system dissolution of fluorapophyllite (Figure 6.3), the small amount of HCO_3^- added in the artificial recharge water is rapidly depleted and log $p\text{CO}_2$ drops below -7, while the pH rises to pH 10 and above as a result of OH^- produced in reaction 6.6. The low initial HCO_3^- limits calcite precipitation, allowing high Ca^{2+} to develop as fluorapophyllite dissolves, since fluorite is the only sink for Ca^{2+} in reaction 6.7.

Simulated artificial recharge: $\log(p\text{CO}_2) = -3.5$, open system.

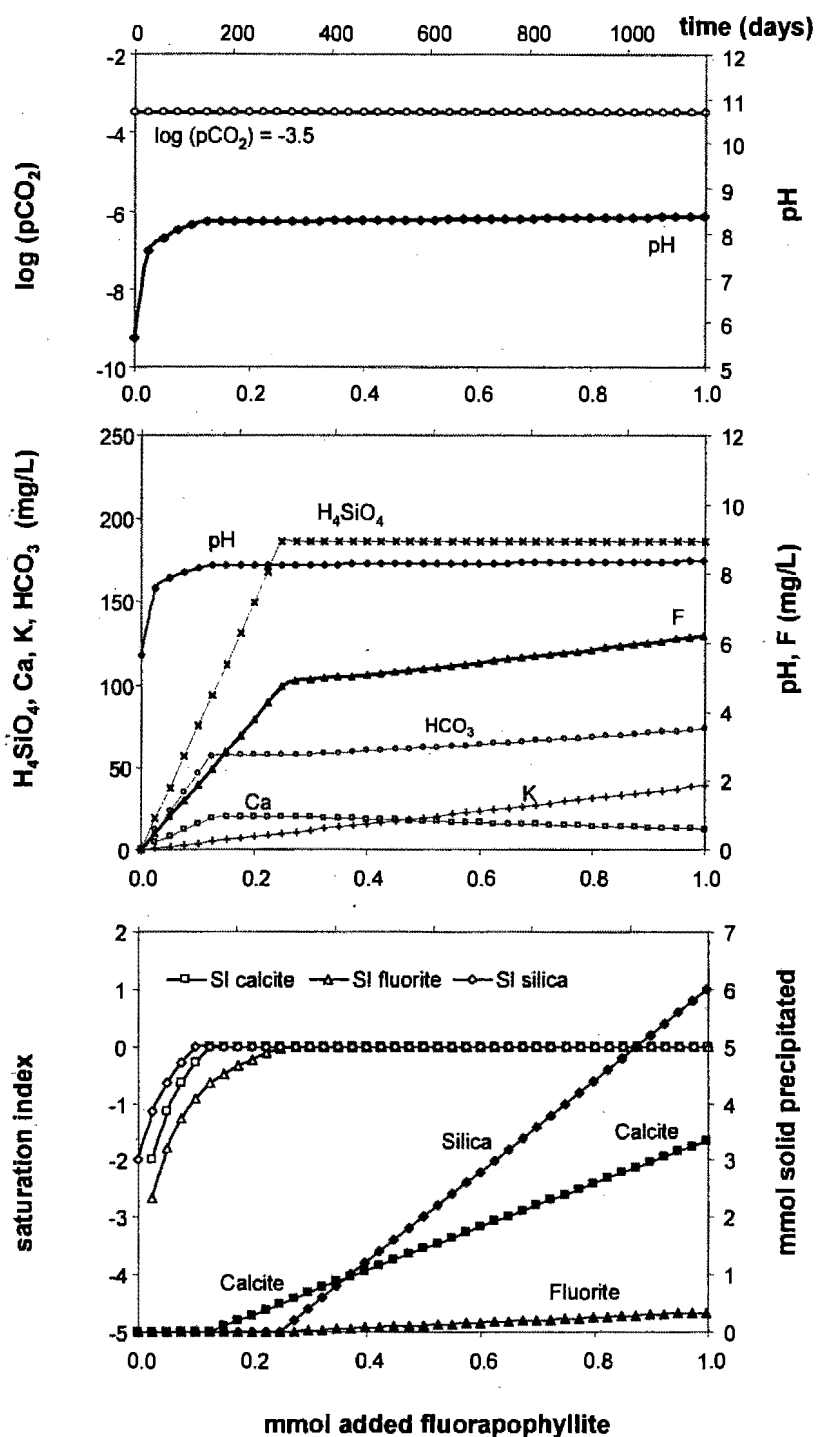


Figure 6.2. Modelled pH, solute composition, saturation indices and precipitated secondary phases during simulation 1. The simulation involved dissolution of 1×10^{-3} mol fluorapophyllite per kg H₂O under open system conditions in equilibrium with CO₂ at atmospheric pressure ($p\text{CO}_2 = 10^{-3.5}$ atm). Supersaturated calcite, amorphous silica and fluorite were allowed to precipitate, as shown in the final graph.

Simulated artificial recharge: $\log(p\text{CO}_2)_{\text{initial}} = -3.5$, closed system.

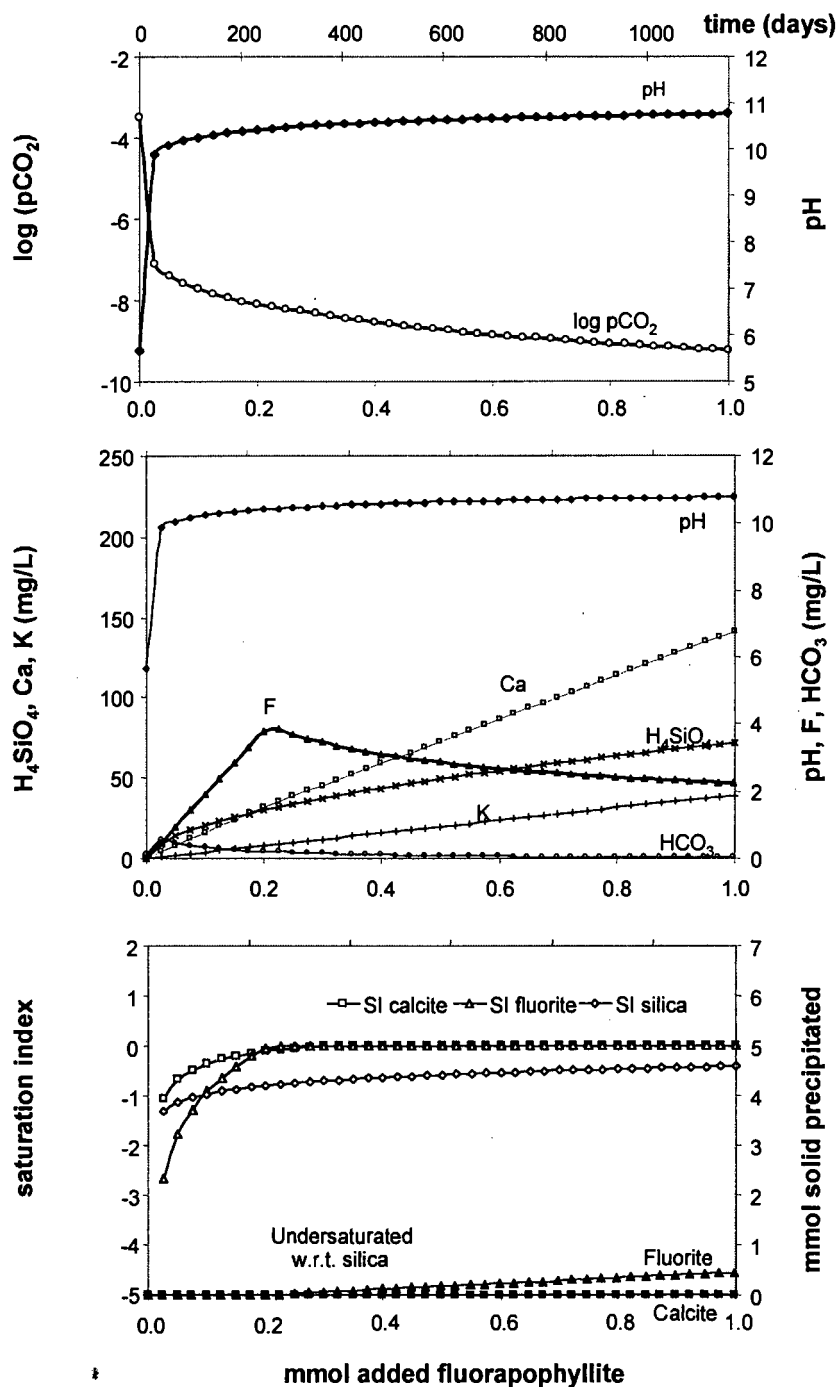


Figure 6.3. Modelled pH, solute composition, saturation indices and precipitated secondary phases during simulation 2. This involved dissolution of 1×10^{-3} mol fluorapophyllite per kg H₂O under closed system conditions. The initial solution was equilibrated with CO₂ at atmospheric pressure ($p\text{CO}_2 = 10^{-3.5}$ atm) and then allowed to react with fluorapophyllite without further addition of CO₂. Calcite, amorphous silica and fluorite were allowed to precipitate if saturation was reached.

Fluorite is the main secondary phase in this instance and its deposition places a limit on dissolved F^- concentrations, which reach a maximum of 3.8 mg/L. Without calcite precipitation, incongruent dissolution of fluorapophyllite and precipitation of fluorite also produces large amounts of OH^- , leading to very alkaline conditions (reaction 6.7). Silica is soluble under the pH conditions of this simulation and the solution remains below saturation with respect to amorphous silica. The low H_4SiO_4 concentration is a reflection of the dissociation of this species at high pH, rather than low total dissolved silicon concentrations. Some restriction on these reactions may be imposed by the fact that fluorapophyllite is estimated to be supersaturated after the addition of the first 0.025 mmol in this alkaline solution, but this has not been included in the simulation.

Simulation 3

Simulated natural recharge (solution 2, $pCO_2 = 10^{-2}$) provides a better approximation of the conditions for dissolution in natural subsurface environments. In this case the initial solution has dissolved CO_2 under higher pressure conditions than atmospheric and equilibrated with calcite, producing relatively high concentrations of Ca^{2+} and HCO_3^- before it reacts with apophyllite.

On-going CO_2 dissolution and calcite precipitation maintain the pH near 7.3 under open system conditions. Any Ca^{2+} added by apophyllite dissolution is lost to both calcite and fluorite precipitation, so the overall Ca^{2+} concentration gradually decreases. The graphs in Figure 6.4 show similar patterns to those of simulation 1, but give higher Ca^{2+} and HCO_3^- and lower pH and F^- for the same amount of apophyllite dissolved. It is not feasible to evolve a water of pH 10 under these reaction conditions, since vast quantities of fluorapophyllite (over 2 kg per kg water) must be dissolved, accompanied by the precipitation of unreasonably large amounts of calcite, fluorite and silica.

Estimated fluorapophyllite solubility is higher under the neutral pH conditions of this simulation and allows up to 17.5 mmol to dissolve, producing a concentration of 15.4 mg/L F^- before supersaturated conditions are reached at pH 8.

Simulated natural recharge: $\log(p\text{CO}_2) = -2.0$, open system.

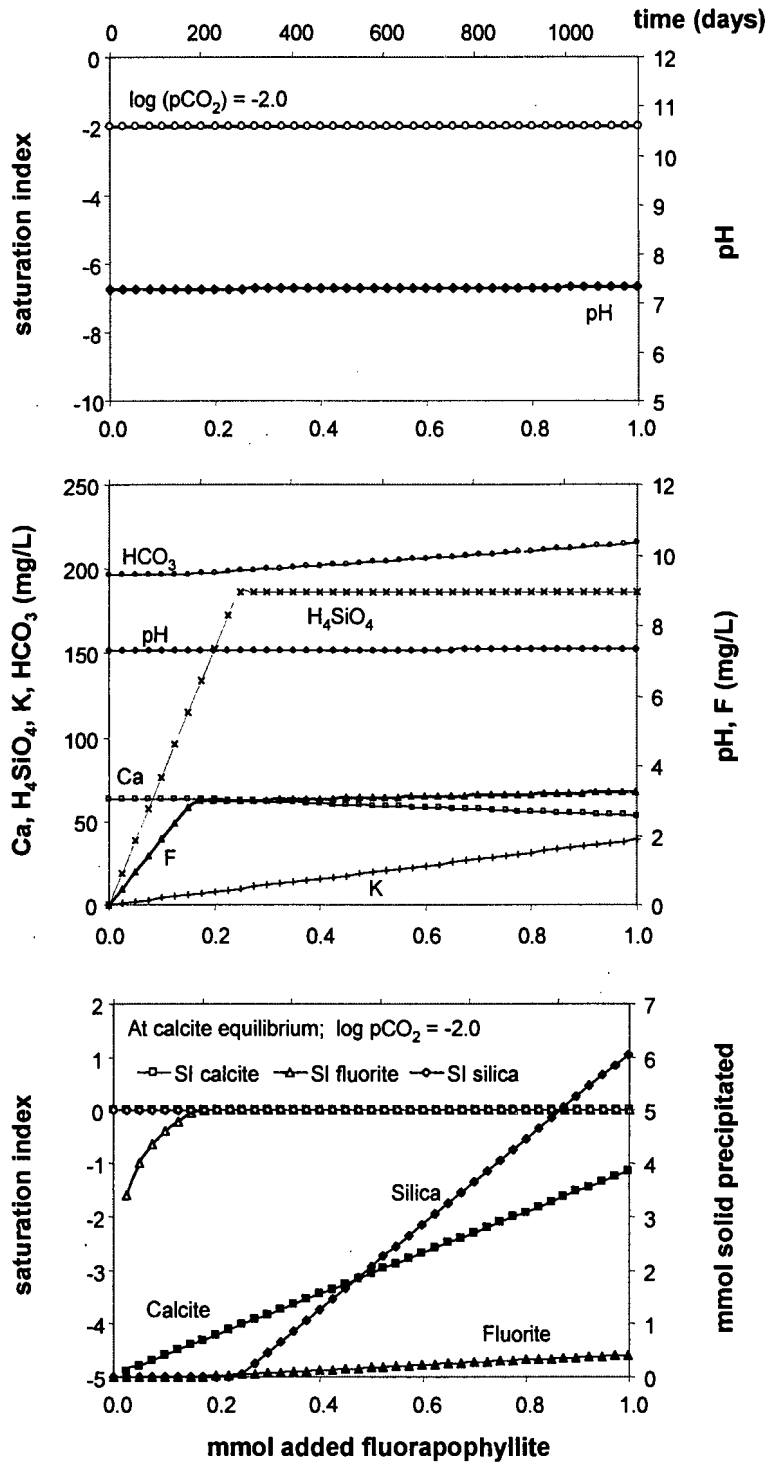


Figure 6.4. Modelled pH, solute composition, saturation indices and precipitated secondary phases during simulation 3. In this case, 1×10^{-3} mol of fluorapophyllite per kg H_2O is allowed to dissolve under open system conditions in equilibrium with calcite and CO_2 at a partial pressure of 10^{-2} atm. Supersaturated calcite, amorphous silica and fluorite were allowed to precipitate.

Simulation 4

Natural groundwater conditions in the Karoo should be most closely approximated by the final simulation. The initial recharge solution is in equilibrium with calcite at a moderate soil $p\text{CO}_2$ and then evolves under closed system conditions, reacting with silicate minerals below the water table. Typical values for the partial pressure of CO_2 in soils are 10^{-3} to 10^{-1} atm (Freeze and Cherry, 1979; p. 241).

Closed system conditions produce a maximum F^- concentration, $\text{F}^-_{\text{max}} = 6.6 \text{ mg/L}$, and minimum Ca^{2+} concentration, $\text{Ca}^{2+}_{\text{min}} = 10.5 \text{ mg/L}$, after dissolution of 0.5 mmol of fluorapophyllite (Figure 6.5). The maximum and minimum points correspond to a steep increase in pH and levelling off of the amount of calcite and silica precipitation as HCO_3^- becomes depleted. Fluorite precipitation continues to remove some of the dissolved Ca^{2+} , but not in the same proportion as that added by the apophyllite.

The pH in simulation 4 rises to 10.1 after dissolution of the specified 1×10^{-3} mol of fluorapophyllite under closed system conditions. The estimated saturation index for fluorapophyllite, however, reaches zero after dissolution of only 0.25 mmol of the mineral, and reactions beyond this point may be limited by apophyllite solubility.

A sensitivity analysis was conducted to determine the effect on F^-_{max} and $\text{Ca}^{2+}_{\text{min}}$ of changing the initial CO_2 partial pressure in the soil environment. Increasing $p\text{CO}_2$ increases the maximum amount of F^- that can be solubilised and decreases the minimum Ca^{2+} value as shown in Table 6.2. The maxima and minima are also shifted to higher pH values after dissolution of greater amounts of fluorapophyllite with increasing initial $p\text{CO}_2$.

Simulated natural recharge: $\log(p\text{CO}_2)_{\text{initial}} = -2.0$, closed system.

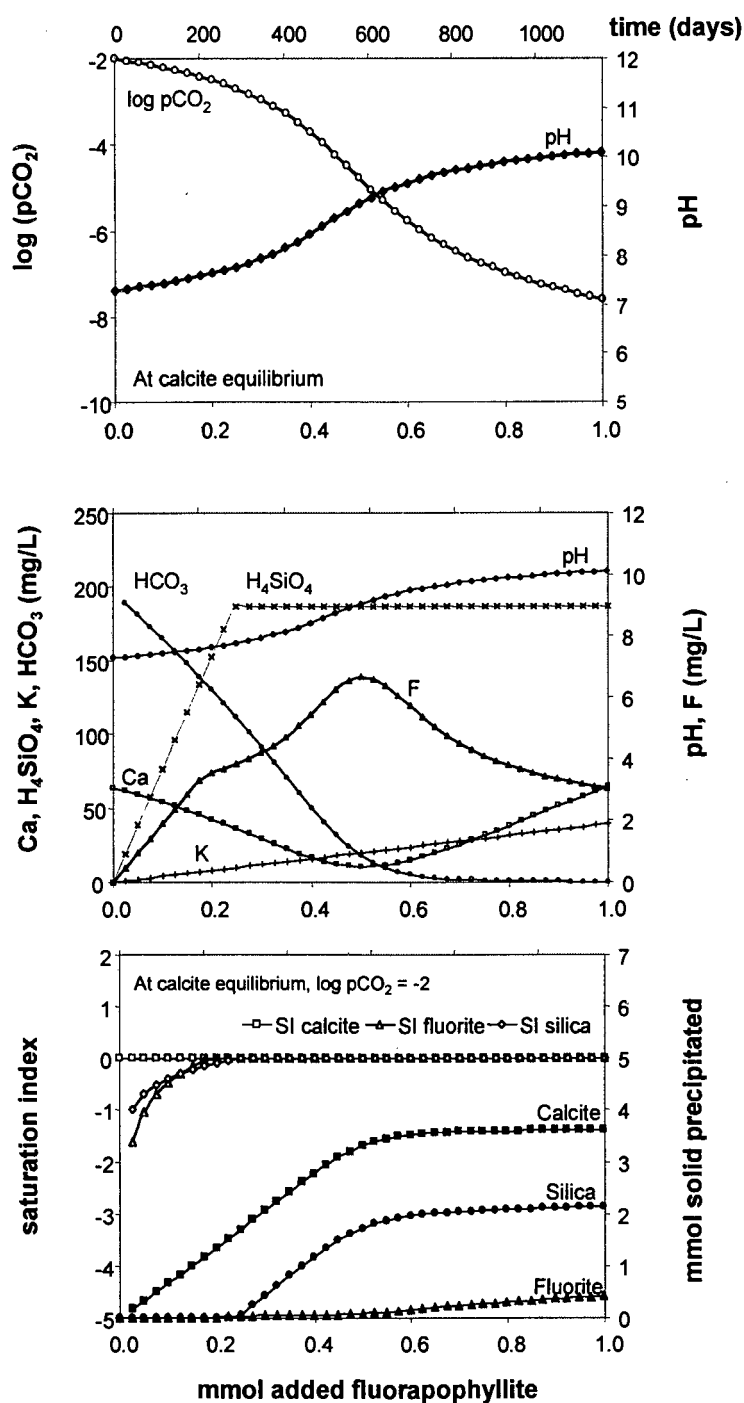


Figure 6.5. Modelled pH, solute composition, saturation indices and precipitated secondary phases during dissolution of 1×10^{-3} mol fluorapophyllite per kg H₂O under closed system conditions in simulation 4. The initial solution was equilibrated with calcite and CO₂ at a partial pressure of 10^{-2} atm before reacting with fluorapophyllite without further addition of CO₂. Supersaturated calcite, amorphous silica and fluorite were allowed to precipitate.

Table 6.2. Calculated maximum fluoride concentrations and minimum calcium concentrations from PHREEQC-2 simulations dissolving fluorapophyllite under closed system conditions of differing initial CO₂ partial pressure in equilibrium with calcite. Supersaturated fluorite, silica and calcite were allowed to precipitate.

log (pCO ₂ initial)	-2.0	-1.8	-1.5	-1.2	-1.0
F ⁻ _{max} (mg/L)	6.6	7.1	8.1	10.1	12.4
Ca ²⁺ _{min} (mg/L)	10.5	9.3	7.2	4.7	3.2
pH	9.05	9.08	9.14	9.22	9.40
log (pCO ₂) at F ⁻ _{max}	-4.78	-4.78	-4.78	-4.77	-4.96
Amount fluorapophyllite dissolved (mmol)	0.5	0.625	0.9	1.35	1.85

6.3.3 Discussion

The use of modelling calculations to investigate the possibility of apophyllite dissolution under natural and artificial recharge conditions at Kopoasfontein is limited in its approach. The stoichiometric dissolution of a monomineralic assemblage of pure fluorapophyllite is an oversimplification that fails to take into account the effects of other minerals in the breccia pipe. These include the clay minerals and metal sulphides which also play a role in regulating pH and solute concentrations in the groundwater. A simplified approximation has also been used for the recharge water chemistry, which excludes any addition of atmospheric and pedogenic salts. The substitution of NH₄ for K in the Kopoasfontein fluorapophyllite has also been neglected in the simulations. Potassium is a spectator ion in most of the simulated reactions and simply accumulates in stoichiometric proportions as apophyllite dissolves, but ammonium may be involved in biological oxidation reactions which could affect the solution pH. Potassium and ammonium are also likely candidates for ion exchange in the natural system. The modelling exercise is, nevertheless, useful in predicting trends that may be anticipated from apophyllite dissolution reactions and their role in Kopoasfontein hydrochemistry.

No one model has been found that simultaneously reproduces the pH, F⁻ and Ca²⁺ conditions in the groundwater of the Kopoasfontein breccia pipe (Figure 6.6) and it is easily concluded that apophyllite dissolution, accompanied by calcite, fluorite and silica precipitation, cannot be the only control on these constituents in the breccia pipe.

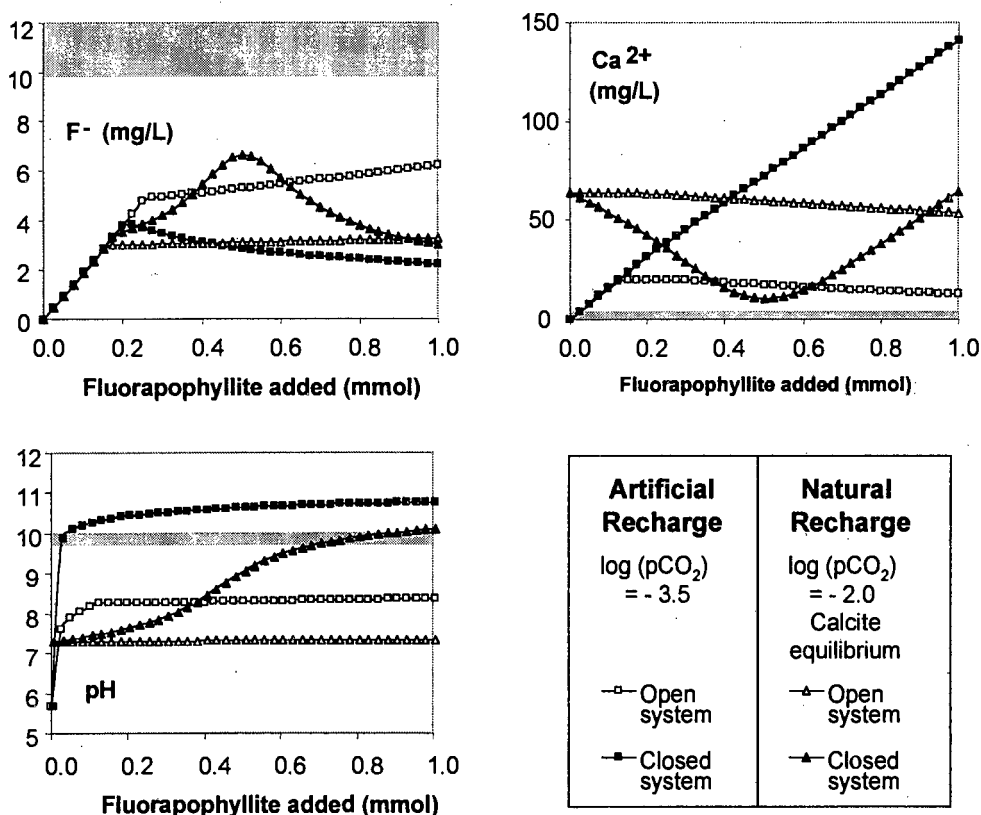


Figure 6.6. Modelled fluoride, calcium and pH in solutions reacted with fluorapophyllite under simulated natural and artificial recharge conditions. Solid symbols indicate closed system dissolution and open symbols, systems open to CO_2 . The gray band marks the observed conditions for groundwater from the Kopoasfontein breccia pipe.

Natural groundwater in the Kopoasfontein breccia pipe is expected to have evolved by silicate dissolution reactions in a low $p\text{CO}_2$ groundwater environment, i.e. under closed system conditions, which allow the high pH conditions to develop. Carbonate equilibria buffer the solution pH in open systems and it seems unlikely that deep groundwater in the Kopoasfontein breccia could have evolved under such conditions. Open system conditions may be valid for the upper part of the breccia pipe, and might be anticipated during artificial recharge, but are not realistic for the reactions at depth that evolved the natural groundwater composition.

Where open system conditions prevail, a constant supply of carbonate species is maintained which precipitates most of the added Ca^{2+} from fluorapophyllite as calcite, allowing additional F^- to dissolve. This could have caused the calcite-filled fractures in the upper 50 m of the

Kopoasfontein breccia pipe. In the absence of excess carbonate, however, dissolved Ca^{2+} and F^- from fluorapophyllite are likely to combine to produce fluorite¹.

The insolubility of fluorite imposes an upper limit on the amount of dissolved F^- that can be derived from fluorapophyllite alone in a system closed to CO_2 . Only at a very high initial pCO_2 of $10^{-1.2}$ and above were the models found to generate F^- in the concentrations seen at Kopoasfontein, by closed system fluorapophyllite dissolution. These CO_2 pressures do not seem reasonable for the Karoo environment, which is semi-arid and should have relatively low soil biological activity.

The low stoichiometric quantity of fluorine in fluorapophyllite requires large quantities of mineral dissolution to be able to generate high dissolved fluoride. The required amount of dissolution will be even higher for mixed hydroxyapophyllite species, in which the fluoride content is lower. In the modelling simulations, each of the solutions could theoretically be evolved to a fluoride concentration of 10 mg/L and above under open system conditions. This was only possible, however, by the addition of fluorapophyllite far in excess of the amount which would be reasonably expected to dissolve, based on typical silicate mineral behaviour and the estimated solubility of apophyllite.

Fluoride concentrations above the recommended South African guideline level of 0.7 mg/L (Muller *et al.*, 1998), however, appear to be easily obtained by fluorapophyllite dissolution under all simulated recharge conditions, since this is below the fluorite solubility limit. Fluoride could pose a health risk for the storage of drinking water in this environment and may require treatment after recovery.

The results of the modelling exercise anticipate that it is not feasible for the the entire fluoride content of the natural Kopoasfontein groundwater to have been derived by stoichiometric

¹ Calcite is not the only possible Ca^{2+} sink in the breccia pipe environment, although it is the main reaction competing with fluorite precipitation in these simulations. Other possibilities for removing Ca^{2+} from solution include gypsum precipitation if sulphate is added by metal sulphide oxidation or cation exchange of Ca^{2+} with Na^+ on the clay mineral exchange complex. The former is unlikely since Kopoasfontein waters are undersaturated with respect to gypsum. The latter will be discussed further in the following section on mass balance modelling.

dissolution of fluorapophyllite. This implies that at least part of the fluoride in solution must be brought in with the inflow to the breccia pipe, leached non-stoichiometrically from fluorapophyllite, added by ion exchange with OH^- from the alkaline groundwater or derived from other mineral sources which contribute relatively less calcium than apophyllite.

6.4 Inverse modelling of Kopoasfontein groundwaters

Another approach to treating mineral weathering reactions is to use mass balance calculations. These relate changes in water chemistry to the dissolution or precipitation of specific minerals on a quantitative basis, disregarding thermodynamic and kinetic constraints on the reactions. Mass balance budgets provide a useful way of identifying the likely sources of solutes and possible reactions which may explain the difference in water chemistry between two points on a flow path. In some cases it is possible to reconstruct the contributions of several weathering reactions to the final water composition. This has been attempted for the groundwater from the Kopoasfontein breccia pipe.

Mass balance calculations essentially consist of solving a matrix of simultaneous linear equations to account for the concentrations of the various species in solution. There are generally several sets of equations, however, that may explain an observed composition, since the possible reacting minerals and the composition of the minerals is not usually unique (Drever, 1997; p. 244).

Limitations of mass balance modelling need to be considered when applying the approach to mineral weathering problems. These include (Appelo and Postma, 1996; p. 219):

- ▶ Non-unique solutions. Different choices of phases may lead to equally consistent reaction schemes i.e. balanced calculations do not prove that the reactions take place.
- ▶ Thermodynamic stability of precipitating and dissolving phases is not considered.
- ▶ Kinetics of mineral weathering are not considered.
- ▶ Steady state conditions are assumed and no account is taken of temporal variations in the input composition.
- ▶ Calculations assume a homogeneous reaction between the initial and final compositions.

The geochemical modelling code PHREEQC-2 (Parkhurst and Appelo, 1999) has been used to perform mass balance calculations that might help to decipher the origin of the Kopoasfontein groundwater. The code has an inverse modelling (mass balance) routine which allows the user to specify initial and final water compositions and mineral or gas phases that may react or solutions that may mix to produce the observed changes. Conservation of electrons is also specified in the calculations to ensure that oxidative and reductive reactions balance each other. The inclusion of analytical uncertainties in mass balance calculations is a major advantage of the PHREEQC-2 software over previous versions of the code.

6.4.1 Input parameters

The groundwater sample from borehole G39973 collected on 7/7/1999 was selected as the final water composition for inverse modelling calculations. Chemical data for this sample from Table 3.3 was used in the modelling exercise. This is the most current sample that was collected and analysed for a full range of water quality variables by the author and a duplicate analysis by the CSIR laboratory gives increased confidence in the accuracy of the results.

Difficulties were experienced in selecting an appropriate initial water for the mass balance calculations. No boreholes are located directly upgradient from the site and the location of the recharge zone for the deep water in the pipe is not precisely known. The breccia pipe water does not appear to evolve from the shallow groundwater on the farm, which was sampled from a perched water table above the dolerite sill (e.g. sample KF1). The shallow water has a higher salinity than the breccia pipe groundwater and the higher solute content requires either large dilutions or the precipitation of unreasonable quantities of soluble salts to obtain a mass balance.

Two alternatives have been used to contend with this problem. The first is to use a simulated recharge water, being pure water equilibrated with calcite in a 10^{-2} atm CO_2 gas atmosphere, as was used in simulation 4 of the forward modelling. Most of the groundwaters in the area are slightly supersaturated with respect to calcite, so it seems reasonable to expect that recharge to the pipe will contain Ca^{2+} and HCO_3^- . The other approach is to use a low salinity sample from a higher altitude in the Akkerendam part of the Calvinia catchment, which is likely to be on a different flowpath from the water that recharges the breccia pipe, but possibly has a similar

composition to the true recharge water. The sample PS27 (08/01/1980) has been chosen for this purpose, due to its low salinity and low charge imbalance in the major cation data.

Table 6.3 contains saturation indices calculated using PHREEQC-2 for the initial and final waters in the mass balance modelling. These give some indication of whether the reactions proposed in the models will be thermodynamically feasible.

Table 6.3 Saturation indices from PHREEQC-2 for solutions used in mass balance calculations at 25°C.

Sample (Date)	Sim. Recharge	PS27 (8/1/80)	73 (7/7/99)	KF1 (8/7/99)
Description	Initial water pCO ₂ = 10 ⁻² + calcite	Initial water Akkerendam area	Final water breccia pipe	Final water perched water
pH	7.30 (calculated)	7.5	9.83 (field)	7.26 (field)
Ionic strength	4.83 × 10 ⁻³	7.87 × 10 ⁻³	8.49 × 10 ⁻³	1.64 × 10 ⁻²
Albite	-	-	-0.65	-0.87
Anorthite	-	-	-3.16	-2.66
Calcite	0.00	0.02	0.65	0.16
Chalcedony	-	0.17	-0.05	0.21
Chlorite(14Å)	-	-	10.5	-2.6
CO ₂ (gas)	-2.00	-2.14	-4.94	-1.79
Dolomite	-	0.12	1.23	0.39
Fe(OH) ₃ (amorphous)	-	-	0.93	2.07
Fluorapophyllite*	-	-8.03	4.17	-9.06
Fluorite	-	-1.22	-0.39	-0.75
Gypsum	-	-2.35	-3.17	-1.74
Illite	-	-	-1.12	1.67
K-mica	-	-	3.13	6.99
Kaolinite	-	-	-0.24	3.9
Quartz	-	0.58	0.36	0.61
SiO ₂ (amorphous)	-	-0.67	-0.89	-0.63

* Fluorapophyllite SI calculated using estimated log K_{sp} from Section 5.6.

Input files for the mass balance calculations are included in Appendix I.

6.4.2 Mass balance calculations and modelling results

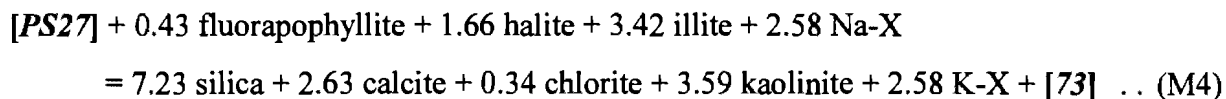
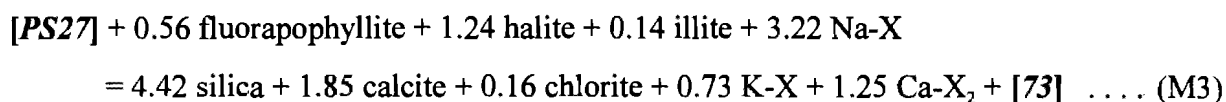
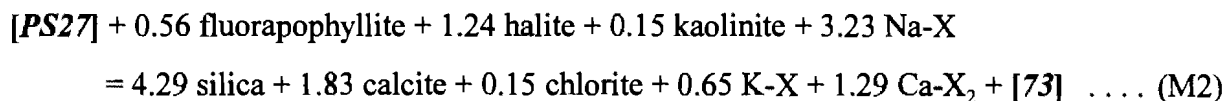
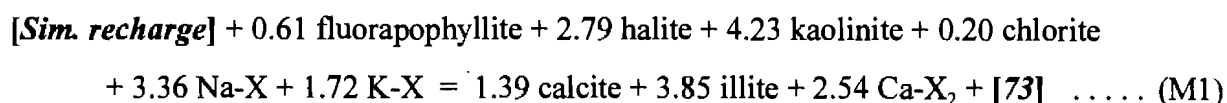
Mass balance run 1: Observed mineral phases and ion exchange

All redox-sensitive parameters were excluded from initial mass balance calculations to simplify the set of parameters needed to explain the water chemistry at Kopoasfontein. Sulphate,

ammonium and iron were not included in the input files and the analytical uncertainty was set at 10% to compensate for the resultant charge imbalance. Mineral phases known to be present in the Kopoasfontein breccia were specified as the reacting solids. These included:

▶ fluorapophyllite: $\text{KCa}_4\text{Si}_8\text{O}_{20}\text{F}\cdot 8\text{H}_2\text{O}$, specified as a dissolving phase only	▶ illite
▶ silica	▶ kaolinite
▶ calcite	▶ chlorite
	▶ halite

Attempts to account for solution compositions using the specified mineral phases were unsuccessful without recourse to ion exchange reactions. Exchangeable Ca, K and Na were, therefore, included in the mass balance. Magnesium is included in the chlorite and illite phases and will be addressed in more detail later. The following models were found to account for the composition changes between the initial and final waters (with reaction amounts specified in mmol/kg H_2O):



Halite is included, even though not reported in the breccia pipe, as a source for the relatively high Na and Cl concentrations in the groundwater. Some of the Na^+ and Cl^- ions are likely to be brought in by the recharge to the pipe (for calculations using simulated recharge) and not necessarily dissolved along the flowpath. Sodium is in excess of chloride in final water 73 and halite is the only mineral source of Na in the mass balance, so additional Na must be added by ion exchange for the reaction to balance.

Fluorapophyllite is the only source of fluoride among the mineral phases, but its dissolution creates an excess of dissolved calcium and silica which must be removed by the precipitation of calcite and silica (for PS27) or calcite and illite (for simulated recharge). Kaolinite supplies the additional Al needed to balance the illite in model M1, but it seems unlikely that such large quantities of clay minerals will react. For this reason, models M1 and M4 are treated with circumspection. Models M2 and M3 involve essentially the same reactions, except for the conversion of kaolinite to chlorite in M2 or illite to chlorite in M3.

The Kopoasfontein groundwater is near to equilibrium with kaolinite, slightly undersaturated with respect to illite and greatly supersaturated with respect to chlorite. While this makes chlorite dissolution unlikely, although there is a large degree of uncertainty in the saturation index calculations for these phases. The exact composition of the chlorite and illite is unknown and the effect of their complex stoichiometry on the calculation of the ion activity product leads to a greater cumulative error in the SI than for simpler mineral phases.

Precipitation of silica and calcite is required by most of the mass balance models. Saturation indices show chalcedony as the silica phase most likely to precipitate, since it is slightly supersaturated in PS27 and very close to equilibrium in final water 73. The waters are all supersaturated with respect to quartz and slightly undersaturated with respect to amorphous silica. Initial water PS27 is in equilibrium with calcite and final water 73 slightly supersaturated with respect to calcite.

In the mass balance calculations, chlorite has been used as a source of Mg for the reaction using simulated recharge and a sink for Mg in the PS27 reactions. Although dolomite has not been reported in the rocks, it is possible that the Mg in the groundwater is controlled by carbonates, rather than aluminosilicate phases. The calculations have been repeated using dolomite as a substitute for chlorite, which has much slower reaction kinetics than the carbonates. The balanced models are:

[*Sim. recharge*] + 0.50 fluorapophyllite + 2.97 halite + 2.51 dolomite + 0.93 kaolinite
+ 3.18 Na-X = 2.31 calcite + 0.81 illite + 2.56 silica + 1.59 Ca-X₂ + [73] M5

$$\begin{aligned}
&[PS27] + 0.46 \text{ fluorapophyllite} + 1.54 \text{ halite} + 2.70 \text{ Na-X} \\
&= 3.64 \text{ silica} + 0.78 \text{ calcite} + 0.86 \text{ dolomite} + 0.55 \text{ K-X} + 1.07 \text{ Ca-X}_2 + [73] \quad \dots \text{ M6}
\end{aligned}$$

$$\begin{aligned}
&[PS27] + 0.58 \text{ fluorapophyllite} + 1.35 \text{ halite} + 1.24 \text{ kaolinite} + 3.00 \text{ Na-X} \\
&= 3.10 \text{ silica} + 1.09 \text{ calcite} + 0.50 \text{ dolomite} + 1.08 \text{ illite} + 1.50 \text{ Ca-X}_2 + [73] \quad \dots \text{ M7}
\end{aligned}$$

Model M6 is preferred over M7 since it does not involve transformations of any of the slowly-reacting clay minerals. In this scheme, illite, chlorite and kaolinite are not actively involved in the addition or removal of solutes, but only act as charged surfaces for ion exchange reactions. The separate precipitation of calcite and dolomite in these models could also be interpreted as precipitation of a single magnesian calcite phase.

Similar results are obtained using the “phase” Mg-X_2 instead of dolomite to control Mg by ion exchange. Even using ion exchange to remove or supply the necessary major cations in solution, however, no mass balance reaction was found for the evolution of final water 73 from simulated recharge water using this set of minerals, without including illite and kaolinite as reacting phases.

Mass balance run 2: feldspar dissolution replaces ion exchange

The use of ion exchange reactions is a convenient tactic for supplying or withdrawing excess cations when mass transfers will not balance. Although ion exchange is commonly used to explain shifts in major ion dominance along a groundwater flow path, and particularly the natural softening reaction that replaces Ca^{2+} in solution with Na^+ from the exchange complex, such explanations are not always justified. Ion exchange reactions are limited by the sorption or exchange capacity of the solids in the aquifer. They also require the inflow of a solution with a cation composition that differs from that which occupies the exchange sites in the soil or aquifer.

At Calvinia, the recharge of dilute rainwater solutions and their slow passage through geological material with a high content of clay minerals, satisfies both these requirements for ion exchange. Nevertheless, mass balance calculations for Kopoasfontein were attempted without the use of Na-X, K-X or Ca-X_2 exchange complexes, to see whether balanced models could be found.

The first step was to introduce a mineral source of Na in addition to halite to remove the need for adding Na-X. Since the Karoo rocks are dominated by silicates, feldspars were chosen as a likely Na source. Plagioclase dissolution and calcite precipitation in systems closed to CO₂ can produce similar changes in major ion chemistry to those produced by cation exchange of calcium for sodium (Frengstad and Banks, 2000). The same initial and final water compositions were used as for the previous runs, with the mineral phases specified as:

▶ fluorapophyllite	▶ illite
▶ halite	▶ kaolinite
▶ silica	▶ either albite or andesine plagioclase,
▶ calcite	with 33% Na replaced by Ca
▶ dolomite	▶ CO ₂ gas

The following balanced mass transfers were found to account for the composition of Kopoasfontein groundwater:

$$[\text{Sim. recharge}] + 0.56 \text{ fluorapophyllite} + 2.92 \text{ halite} + 0.27 \text{ dolomite} + 3.23 \text{ albite} + 1.88 \text{ CO}_{2(g)} \\ = 9.35 \text{ silica} + 4.07 \text{ calcite} + 0.90 \text{ illite} + 0.58 \text{ kaolinite} + [73] \dots\dots\dots \text{M8}$$

$$[\text{Sim. recharge}] + 0.56 \text{ fluorapophyllite} + 2.92 \text{ halite} + 0.27 \text{ dolomite} + 5.21 \text{ plagioclase} \\ + 3.86 \text{ CO}_{2(g)} = 9.35 \text{ silica} + 6.04 \text{ calcite} + 0.90 \text{ illite} + 2.55 \text{ kaolinite} + [73] \dots\dots\dots \text{M9}$$

$$[\text{PS27}] + 0.56 \text{ fluorapophyllite} + 1.59 \text{ halite} + 2.48 \text{ albite} + 0.99 \text{ CO}_{2(g)} \\ = 8.08 \text{ silica} + 2.60 \text{ calcite} + 0.50 \text{ dolomite} + 1.08 \text{ illite} + [73] \dots\dots\dots \text{M10}$$

$$[\text{PS27}] + 0.50 \text{ fluorapophyllite} + 1.51 \text{ halite} + 4.58 \text{ plagioclase} + 2.83 \text{ CO}_{2(g)} \\ = 8.45 \text{ silica} + 4.00 \text{ calcite} + 0.61 \text{ dolomite} + 0.98 \text{ illite} + 2.02 \text{ kaolinite} + [73] \dots\dots\dots \text{M11}$$

Inverse models would not balance without the addition of CO₂ gas as a reactant and greater quantities of CO₂ were required if a mixed plagioclase, rather than the sodium end-member, is used as the source of Na. Plagioclase mass balance also requires greater amounts of calcite and kaolinite precipitation than when albite is used as a reactant.

It is possible to derive balanced expressions for the evolution of the Kopoasfontein groundwater composition from the conversion of fluorapophyllite and primary feldspars to silica, calcite and clay mineral phases, within the uncertainty limits of the data. These reaction schemes, however, produce large amounts of precipitated material, especially silica, and would require long reaction times, making them thermodynamically and kinetically less favourable than the ion exchange reaction schemes.

Mass balance run 3: alternative sources of fluoride

The forward modelling exercise in Section 6.3 suggested that an additional source of F^- is needed to generate the high concentrations in Kopoasfontein groundwater, which may not be attributable to fluorapophyllite alone. Mass balance calculations have been performed using alternative mineral sources of fluoride.

Fluorite dissolution was used as one option for a fluoride source, but a more likely origin for the F^- is the illite in the breccia pipe (see Section 6.6), which may have F substituted for OH in the mineral structure. The illite species in the PHREEQC-2 database was altered to illite-F, by replacing one OH group with F and balancing the dissolution reaction. Mass balance relationships were then found for several combinations of mineral sources for fluoride, using the phases:

▶ silica	▶ halite
▶ calcite	▶ fluorite
▶ dolomite	▶ illite-F, $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)F$
▶ kaolinite	▶ fluorapophyllite

and the ion exchange “phases” Na-X, Ca-X and K-X.

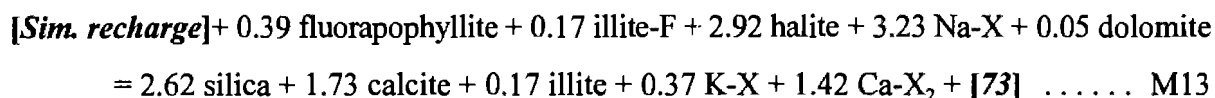
The single possible model found with only Ca exchange for Na, involved dissolution of silica and fluorite and uptake of F by illite, without the involvement of fluorapophyllite:

[Sim. recharge] + 0.45 silica + 2.94 illite + 2.92 halite + 1.73 fluorite + 3.23 Na-X
 (+ 0.04 dolomite) = 1.72 calcite + 2.91 illite-F + 1.61 Ca-X₂ (+ 0.03 kaolinite) + [73] . . M12

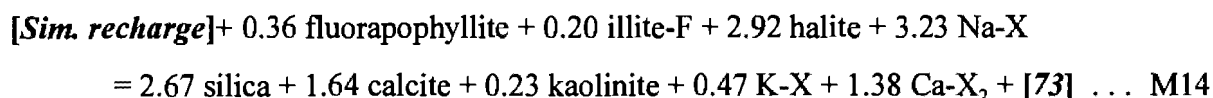
Including K-X in the mass balance runs produced approximately 20 alternative sets of reactions for each initial water that would meet the mass balance requirements within an analytical uncertainty of 10% using PHREEQC-2. Eliminating those models which involve large mass transfers of silicate minerals, the best choice for evolving initial water PS27 to final water 73 appears to be a model similar to M6, which involves dissolution of fluorapophyllite and a negligible amount of illite-F (0.001 mmol/kg H₂O), but no fluorite. Models that dissolve fluorite as the only source of F⁻ for the evolution of initial water PS27 to final water 73, require either the dissolution of calcite or the precipitation of illite-F to meet mass balance requirements. No models were found for these two waters when illite-F was set as the only available fluoride source.

Three possible mass balance reactions to evolve final water 73 from the simulated recharge solution, making use of ion exchange reactions and alternative sources of fluoride ions are:

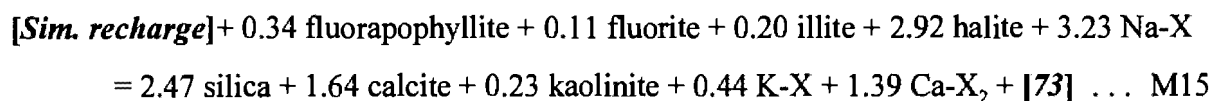
Fluorapophyllite + leaching of illite-F:



Fluorapophyllite + illite-F:



Fluorapophyllite + fluorite:



These three models all involve very similar mass transfers. All the models without fluorapophyllite were eliminated on the grounds of high aluminosilicate mass transfers or using precipitation of illite-F as a sink for removing excess fluoride.

Mass balance run 4: Ammonian fluorapophyllite

The measured composition of the Kopoasfontein apophyllite was included in the inverse modelling simulations as a constraint on ammonium concentrations. Initial attempts to find balanced sets of reactions were not possible without another ammonium-bearing phase to remove excess ammonium from solution, since redox conversions were not included. The ion exchange “phase”, $\text{NH}_4\text{-X}$ was added to the phase constraints to overcome this problem. The effect is to reduce the amount of K-X exchanged and replace this with $\text{NH}_4\text{-X}$. Other phases were chosen from two of the most plausible models found in earlier simulations.

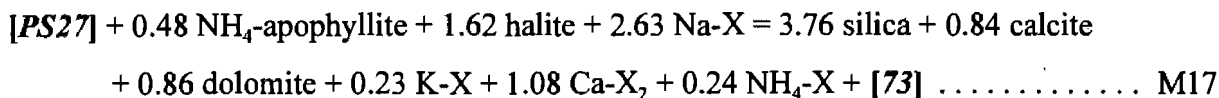
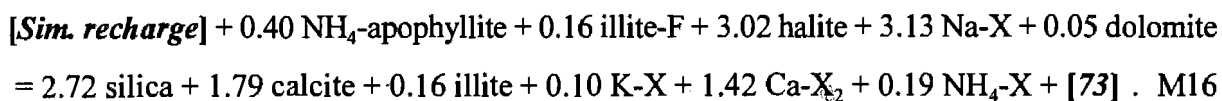
Simulated recharge $\rightarrow$ 73 from M13:

- ▶ ammonian apophyllite,
 $(\text{NH}_4)_{0.7}\text{K}_{0.3}\text{Ca}_4\text{Si}_8\text{O}_{20}\text{F}\cdot 8\text{H}_2\text{O}$
- ▶ silica
- ▶ calcite
- ▶ dolomite
- ▶ illite and illite-F
- ▶ halite
- ▶ NaX , KX and CaX_2
- ▶ $\text{NH}_4\text{-X}$

PS27 $\rightarrow$ 73 from M6:

- ▶ ammonian apophyllite,
 $(\text{NH}_4)_{0.7}\text{K}_{0.3}\text{Ca}_4\text{Si}_8\text{O}_{20}\text{F}\cdot 8\text{H}_2\text{O}$
- ▶ silica
- ▶ calcite
- ▶ dolomite
- ▶ halite
- ▶ NaX , KX and CaX_2
- ▶ $\text{NH}_4\text{-X}$

Possible ammonian fluorapophyllite reactions which account for the water chemistry at 73 are:



It is also possible to use ammonia gas evolution to balance the loss of some or all of the NH_4^+ from solution instead of $\text{NH}_4\text{-X}$. A large percentage of the NH_4^+ in solution would be stable as NH_3 gas under high pH conditions.

Mass balance run 5: Redox reactions

The final stage in the mass balance calculations is to include redox reactions to account for the addition of sulphate and iron to the groundwater. Metal sulphides are known to be present in the Karoo sedimentary rocks and oxidation of pyrite by oxygen in the recharge water is the probable mechanism for producing sulphate in the groundwater. The excess iron from pyrite oxidation is removed by precipitation of amorphous iron hydroxide to balance the equations. Using the same set of phases as for the previous simulation, with the addition of:

- ▶ pyrite, only allowed to dissolve
- ▶ $\text{Fe}(\text{OH})_3$, only allowed to precipitate and
- ▶ $\text{O}_2(\text{g})$

mass balance models are produced which can fully account for the evolution of the Kopoasfontein groundwater from simulated recharge solutions or low salinity Calvinia groundwater, using an analytical uncertainty of only 5% for these calculations.

[Sim. recharge] + 0.55 NH_4 -apophyllite + 2.72 halite + 4.46 Na-X + 0.33 pyrite + 1.25 $\text{O}_{2(\text{g})}$
(+ 0.05 dolomite) = 3.91 silica + 1.80 calcite + 0.15 K-X + 2.10 Ca-X_2 + 0.29 $\text{NH}_4\text{-X}$
+ 0.33 $\text{Fe}(\text{OH})_3$ + [73] M18

[PS27] + 0.52 NH_4 -apophyllite + 1.28 halite + 3.91 Na-X + 0.19 pyrite + 0.70 $\text{O}_{2(\text{g})}$
= 4.10 silica + 0.44 calcite + 0.86 dolomite + 0.24 K-X + 1.70 Ca-X_2 + 0.27 $\text{NH}_4\text{-X}$
+ 0.17 $\text{Fe}(\text{OH})_3$ + [73] M19

Mass balance run 6: Shallow Kopoasfontein groundwater

Mass balance calculations may also explain the composition of the shallow groundwater at the Kopoasfontein research site. Using the same initial water compositions, PS27 and simulated recharge, the composition of the water from the KF1 windpump can be arrived at from either water by dissolution of evaporite salts, dedolomitisation (Plummer *et al.*, 1983), illitization of kaolinite and a small amount of pyrite oxidation. An analytical uncertainty of 5% was used in the calculations.

$$\begin{aligned}
& [\text{Sim. recharge}] + 3.90 \text{ halite} + 1.29 \text{ sylvite} + 0.04 \text{ fluorite} + 2.97 \text{ silica} + 0.80 \text{ gypsum} \\
& + 2.46 \text{ dolomite} + 2.42 \text{ kaolinite} + 0.007 \text{ pyrite} + 0.03 \text{ O}_{2(g)} \\
& = 2.79 \text{ calcite} + 2.10 \text{ illite} + [\text{KFI}] \dots\dots\dots \text{M20}
\end{aligned}$$

$$\begin{aligned}
& [\text{PS27}] + 2.19 \text{ halite} + 1.29 \text{ sylvite} + 0.01 \text{ fluorite} + 2.59 \text{ silica} + 0.51 \text{ gypsum} + 1.46 \text{ dolomite} \\
& + 2.45 \text{ kaolinite} + 0.007 \text{ pyrite} + 0.03 \text{ O}_{2(g)} \\
& = 0.90 \text{ calcite} + 2.13 \text{ illite} + [\text{KFI}] \dots\dots\dots \text{M21}
\end{aligned}$$

The shallow water evolves separately from the deeper groundwater at the site and is likely to have a longer period of contact with soluble salts in the unsaturated zone. Fluorite has been used as a source of soluble F^- from this zone, although similar results are obtained by substituting illite-F.

It is also likely that weathering of the primary mafic minerals in the dolerite sill contributes some of the ions and silica in the shallow groundwater. The alteration of olivine probably supplies some of the iron, magnesium and silica in solution, while weathering of plagioclase will produce sodium and calcium in addition to silica. Biotite or amphiboles may also release some fluoride to the groundwater.

6.4.3 Discussion of mass balance modelling results

The groundwater environment at Kopoasfontein is one of complex mineralogy and geochemistry and the solutions to mass balance calculations for the evolution of the groundwater are not unique. In many cases there are several phases present which may control the release or removal of a single parameter from solution and the choice of potential reaction models is usually a subjective one.

Mass balance models have been proposed for the evolution of shallow and deep groundwater at the Kopoasfontein research site. These evolve the final groundwater composition by the reaction of a limited set of minerals and gases with either low salinity groundwater from the area or a simulated recharge solution in equilibrium with calcite and CO_2 . While these are not the only possible solutions to the mass balance equations and also may not describe the true set of

reactions at the site accurately, they do provide plausible origins for the groundwater solutes.

Mass balance calculations have also generated models involving large volumes of mass transfer for minerals which are slow to react. These have allowed some of the constraints on the geochemical system to be identified. Carbon isotope data, low salinity, elevated temperature and low $p\text{CO}_2$ in equilibrium with the Kopoasfontein water, however, all suggest that the groundwater in the pipe is from a deep flow system and has been isolated from the surface for a reasonable length of time. This means that not all models which involve silicate dissolution or precipitation need be rejected on the grounds of too slow kinetics.

Mass balance models can be derived with fluorapophyllite as the sole source of fluoride in the deep Kopoasfontein groundwater. Stoichiometric dissolution of fluorapophyllite requires the removal of calcite and silica to maintain mass balance in most cases. Chalcedony appears to be the most likely silica phase to precipitate. Similar results could be obtained by leaching the fluoride out of solid apophyllite, leaving the silica skeleton behind. Such non-stoichiometric dissolution has been observed in laboratory experiments, but only below pH 3, which is at the opposite end of the pH spectrum to these groundwaters. Under alkaline conditions, it is the silicon which is more likely to leach from apophyllite.

Based on the inverse modelling results, ion exchange appears to be a more reasonable source of the sodium excess in the breccia pipe groundwaters than feldspar dissolution. Albite and plagioclase dissolution produce larger volumes of SiO_2 that must be precipitated to maintain the silica balance than ion exchange simulations. The clay minerals in the Karoo sedimentary rocks provide a suitable surface for ion exchange and it is possible that the exchange complex is dominated by sodium which has not been flushed from the shales. A combination of the two mechanisms could also be involved over long residence times in Karoo aquifers, with feldspar dissolution occurring close to the recharge source, where CO_2 is available, and ion exchange increasing the sodium excess further along the flow path.

Dissolution of fluorite, dissolution of fluoride-bearing illite or leaching of fluoride from illite all provide possible supplementary sources of fluoride in the deep Kopoasfontein groundwater. Mass balance considerations suggest that large quantities of fluorite dissolution will require an additional sink for fluoride or an additional source of calcium. A combination of fluorapophyllite dissolution and fluoride leaching from illite could reasonably produce the high concentrations of fluoride in the Kopoasfontein groundwater. This is the most likely combination, based on the observed mineralogy of the breccia pipe, where fluorite has not been positively identified.

Balanced models for the evolution of the Kopoasfontein groundwater are possible without the active dissolution or precipitation of layer silicate clay minerals (e.g. M6, M17, M18, M19). In this case illite, chlorite and kaolinite control solute concentrations only by acting as charged surfaces for ion exchange reactions.

The system of redox reactions used in the mass balance, where pyrite is oxidised to ferric hydroxide, involves the simplest possible conversions to account for the iron and sulphate concentrations in the groundwater. While these are valid for the post-dewatering situation in July 2000, it is possible that oxygen may not be available in the deeper parts of the aquifer and other oxidising agents would need to be invoked. Sulphate may also be transported from atmospheric sources, dissolution of gypsum or sulphide oxidation during passage through the oxic parts of the fractured rock aquifer and partly removed by sulphate reduction in the deeper zones.

6.5 Calvinia groundwater systems and the origin of groundwater in the breccia pipes

The geochemistry and isotope characteristics of groundwaters from Calvinia were described in Chapter 3. Groundwater in the Calvinia area occurs in two main aquifer systems, namely alluvial and fractured rock aquifers, and the groundwater in each appears to undergo separate pathways of chemical evolution. Local groundwater flow systems follow the surface topography with flow from the mountain areas draining towards the river channel, but the deeper fractured rock system may be part of a larger aquifer system and large scale flow characteristics for the region have not been investigated.

Shallow groundwater occurs in a primary alluvial aquifer system along the drainage course of the Oorlogskloof River and in the upper weathered zone of the shales. The alluvial system is characterised by groundwater of mixed Ca/Mg/Na-Cl water type with variable quantities of SO_4^{2-} . Sulphate concentrations are higher than in the fractured rock aquifer, probably as a result of oxidising conditions in the shallow groundwater system, which either prevent reduction of dissolved SO_4^{2-} derived from gypsum, or promote the oxidation of metal sulphides such as pyrite in the alluvial sediments. The more mineralised alluvial groundwaters have a composition approaching equilibrium with respect to gypsum, while only a few of the lower salinity samples have not yet reached calcite equilibrium (Figure 6.7).

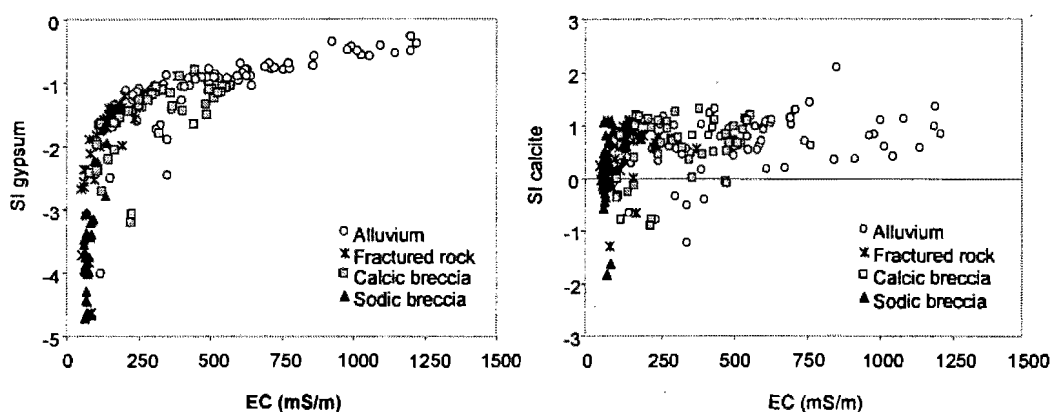


Figure 6.7. Increase in gypsum and calcite saturation indices with increasing salinity for all groundwater samples from the Calvinia area. Saturation indices were calculated using PHREEQC-1.5.

The common ion effect, from Ca^{2+} introduced by gypsum dissolution, may be responsible for the calcite supersaturation observed for most of the alluvial groundwaters. This may also be a result of degassing of CO_2 from the samples before pH measurements were made in the laboratory, since most of the data comes from the NWQDB. The pH measurement used in the saturation index calculations would then be higher than that which would have been measured in the field.

Alluvial groundwaters generally have elevated salinity, which is expected to arise from evapotranspiration and the dissolution of soluble salts that have concentrated in the upper part of the soils and regolith in this semi-arid landscape. Decreasing salinity with depth and the non-marine origin of the Ecce sediments argue against the dissolution of fossil marine salts as a source of salinity in the alluvial groundwaters. Limited stable isotope data presented in Chapter 3

also suggest that mechanism for salinity accumulation is by leaching of solutes from the regolith, rather than infiltration of high salinity recharge waters after concentration by evaporation in open surface water bodies such as farm dams or the Oorlogskloof River.

The deeper groundwater system comprises fractured Karoo sedimentary rocks and may be compartmentalised by dolerite dykes and sills of low permeability. The fractured rock waters have lower salinity than the shallow alluvial groundwaters, indicating more rapid flow conditions or lower availability of soluble salts in the recharge area. The lowest salinity groundwaters are found away from the alluvial deposits in the Akkerendam nature reserve, up against the slopes of the Hantamsberg mountain and salinity increases towards the Oorlogskloof drainage channel. The deeper waters are not recharged by the overlying alluvial system, since considerable salt removal would be required to evolve their composition, but mixing between the two systems is highly probable.

Several low salinity groundwaters from boreholes in fractured rocks show an enrichment in the molar ratio of Na^+ to Cl^- (Figure 6.8) similar to the sodic breccia pipes. This is a characteristic sign that sodium in the groundwater is not all added by atmospheric inputs or dissolution of evaporite or connate salts.

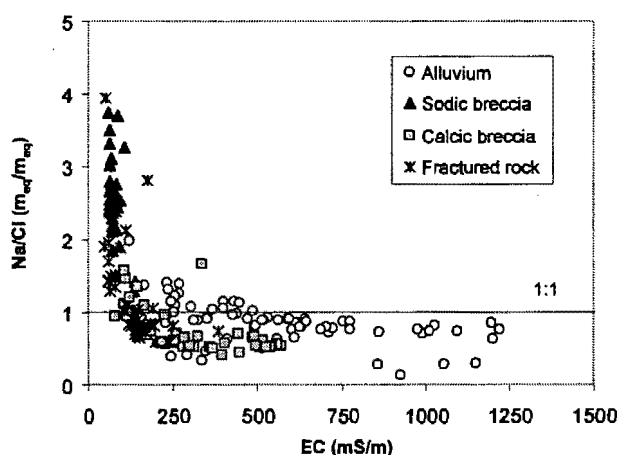


Figure 6.8. Decrease in Na/Cl molar ratio with increasing salinity for groundwater samples from all Calvinia aquifers. The solid line indicates a molar ratio of unity.

The lithogenic Na^+ is probably introduced by cation exchange, with Na^+ being released from sites on clay minerals in exchange for Ca^{2+} or other cations in the recharge water. Another possible

source of excess Na^+ is the dissolution of silicate minerals and particularly weathering of feldspars in the shales and dolerites. Higher salinity alluvial waters and calcic breccia pipes show the reverse trend in Na/Cl ratio, with Cl^- enrichment over Na^+ , suggesting that cation exchange removes Na^+ from solution.

Most groundwater samples from the Calvinia area are saturated or supersaturated with respect to calcite and, with the notable exception of the sodic breccia pipes and rare samples from the other aquifers, carbonate equilibria constrain the groundwater pH between narrow limits from pH 7 to 8.3 (Figure 6.9).

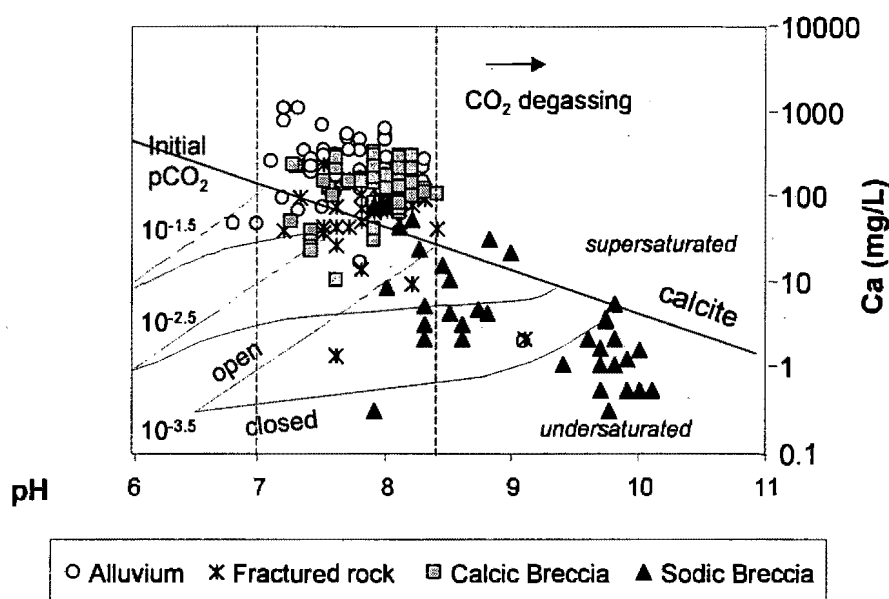


Figure 6.9. Scatterplot of calcium concentration against pH for all Calvinia groundwater samples. Also shown on the diagram are the theoretical trendlines for evolution of waters towards equilibrium with calcite under closed and open system conditions for varying initial partial pressures of CO_2 at 25°C (see Figure 6.1). Dashed lines show the pH range between 7 and 8.3 for most of the samples and the arrow the direction of pH drift if CO_2 degassing is allowed before measuring laboratory pH readings.

Figures 6.7 and 6.8 illustrate the tendency for major ion trends in the calcic breccia pipes to follow those of the alluvial groundwater, while sodic breccia waters appear to be extreme end-members of the trends in the fractured rock system. A scatterplot of potassium against chloride on a logarithm scale gives one of the clearest indications of this relationship (Figure 6.10).

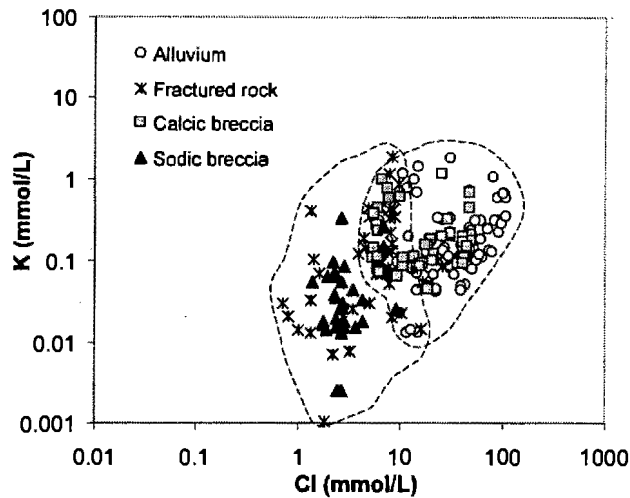


Figure 6.10. Logarithmic plot of potassium versus chloride concentrations showing grouping of calcic breccia pipes with alluvial systems and sodic breccia pipes with fractured rock groundwater systems.

Evidence from major ion composition, mineral saturation status and stable isotope data points towards a similar origin for the groundwater in the alluvial aquifer system and that in the Golf Course and Witkop breccia pipes. Considering the close proximity of these pipes to the Oorlogskloof drainage channel and the floodplain deposits along the river (Figure 3.1), it seems likely that infiltration from the alluvial aquifer system is a major source of recharge to the calcic breccia pipes. The inflow of shallow groundwater with a high solute content and seepage down the permeable breccia, effectively masks the chemical character of any deeper water in these pipes, which may have undergone local water-rock interactions.

The inflow of groundwater from the alluvial system is probably responsible for the higher salinity and lower ^{14}C content near the top of the Golf Course breccia pipe. Stable isotope data suggest that the water in the pipe has undergone some degree of evaporation before infiltration. Samples collected during drilling and test pumping of borehole 59 show a decrease in solute concentration and an increase in relative water age with depth (Figure 6.11), consistent with local recharge of high salinity water from the surface.

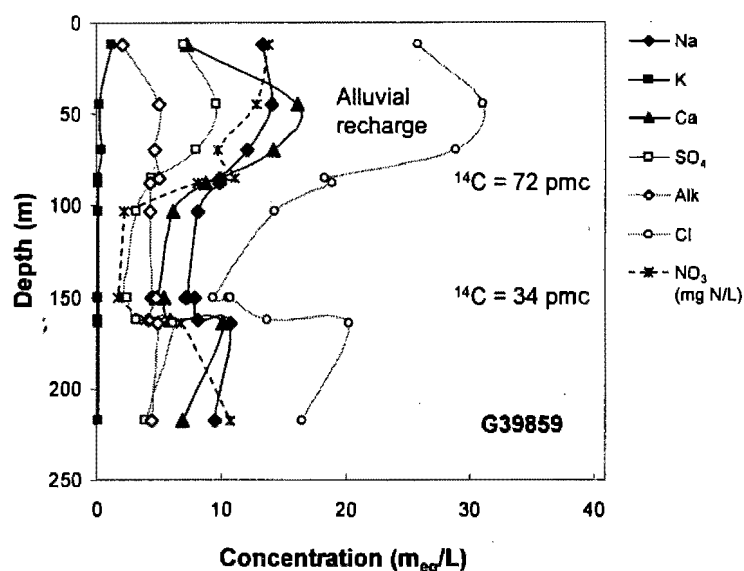


Figure 6.11. Change in concentrations of major cations and anions, nitrate and radiocarbon with depth in the Golf Course breccia pipe. These data for borehole G39859 were taken from Woodford, 1994 and the NWQDB.

Fluoride concentrations do not appear to change with depth and all samples collected during drilling of borehole 59 had low concentrations between 0.4 and 0.6 mg/L. Lower salinity water between 100 and 150 metres below surface may occur where the breccia pipe intercepts fresher groundwater from the fractured rock aquifer system. A highly fractured zone occurs from 99 m to 188 m below surface (see geological logs in Appendix A). The fractured rock groundwater may be considerably older than the alluvial water at the top of the pipe, resulting in mixing of old and young waters and, therefore, a lower ^{14}C concentration in the deeper part of the pipe.

Groundwater from the Witkop breccia pipe has even higher salinity than that at the Golf Course and shows little change with depth in boreholes 648 or 649. The water in this pipe appears to be almost entirely alluvial in origin. The influence of young alluvial recharge is seen in the Ca/Mg/Na-Cl water type and the relatively young ^{14}C signature measured at both the start and end of the pumping test at 646. The $\delta^{18}\text{O}/\text{Cl}$ relationship for this borehole (Figure 3. 18) also suggests the combination of Cl^- leaching and evaporative concentration of salts, characteristic of the alluvial groundwaters. Fluoride concentrations in the Witkop pipe are slightly higher than at the Golf Course, ranging from 0.8 to 1.4 mg/L.

Samples from other boreholes drilled through the alluvium into the underlying shales and dolerites also tend to have a strong alluvial component to their character, having elevated salinity and mixed cation-chloride water type. The improved yield of boreholes in the alluvial system over those in the shales is the reason why the majority of boreholes in the region are drilled through alluvial deposits (see Figure 3.1).

Fewer data are available for Airfield and Bakenskop from which to determine the origin of the groundwater in these breccia pipes. No radiocarbon data were collected for either the Bakenskop or Airfield pipes from which to gauge the relative ages of these waters.

The Airfield breccia is similar to the calcic pipes, but the salinity, pH and major ion content of this breccia pipe fall within the typical compositional range for groundwaters from dolerite/shale contact zones. The Airfield pipe is located outside the area of the alluvial deposits and is, therefore, not likely to receive local recharge from the alluvial system. Instead, it probably forms part of the fractured rock aquifer system, with the groundwater in the pipe not being modified significantly by water-rock interactions that are specific to the breccia. This breccia pipe contains metasomatised shales with chlorite and minor sulphides, but no reported apophyllite. It was noted by the geological team to be “poorly mineralised” (Chevallier, pers. comm.). The geological logs (Appendix A) show that most of the Tierberg Formation, which is the host rock for the secondary mineralisation at Kopoasfontein, has been eroded away at the Airfield breccia pipe.

The Bakenskop pipe appears to be a hybrid of the sodic and calcic types and it is suspected that some alluvial groundwater has mixed with a deeper water, having a composition similar to that of the sodic breccia pipes. The Na-Cl water type of Bakenskop lies on a mixing line between the sodic breccias and the Ca/Mg/Na -Cl type of the alluvial waters in a Piper diagram (Figure 3.9). A sample from borehole 35 also lies between the sodic breccia and alluvium samples on the $\delta^{18}\text{O}/\text{Cl}$ graph (Figure 3.18). Another link between the geochemistry of Bakenskop and the sodic breccia pipes at Witwal and Kopoasfontein is the fluoride concentration which ranges from 2.3 to 12 mg/L, increasing with depth during drilling of borehole 57. Slightly elevated Cr, Zn, Pb and Mo concentrations in this groundwater suggest that some oxidation of metal sulphides has occurred in the mineralised breccia.

Bakenskop groundwater has a slightly higher salinity and much lower pH than the sodic breccia pipes, which may be further evidence of a shallow alluvial component. The origin of the remaining deep groundwater component, which the Bakenskop breccia pipe appears to share with the pipes of Witwal and Kopoasfontein, is the subject of the following section.

6.6 The origin of groundwater in the Kopoasfontein breccia pipe

Several alternative sources may be considered for the origin of the groundwater in the Kopoasfontein breccia pipe, including trapped palaeowaters, local rainwater recharge or inflow from fractured rock aquifers. The solutes in the groundwater may also be transported with the inflow to the breccia or acquired by water-rock interactions inside the pipe. Evidence for and against the various models for the Kopoasfontein breccia pipe are discussed in this section. Alluvial groundwaters have already been rejected as possible recharge sources for the sodic breccia pipes, mainly because of the high salinity of these waters.

Figure 6.12 shows a cross section constructed from south to north through the Calvinia valley, illustrating the various groundwater flow systems in the region and their possible influence on the Kopoasfontein breccia pipe.

6.6.1 Trapped palaeowaters

Woodford (1994) observed the uniform drawdown inside breccia pipes and their very slow recovery after pumping tests and concluded that these were features of a system with limited storage and negligible recharge. This could suggest that the breccia pipes contain trapped palaeowaters that are unconnected with the surrounding aquifers. Abstraction from the breccia pipe would then amount to mining of this groundwater. Long residence times of the groundwater in contact with the breccia pipe minerals would allow sufficient time for the solution chemistry to be modified by slow silicate dissolution reactions. Palaeowaters may be of hydrothermal, connate, diagenetic, or meteoric origin.

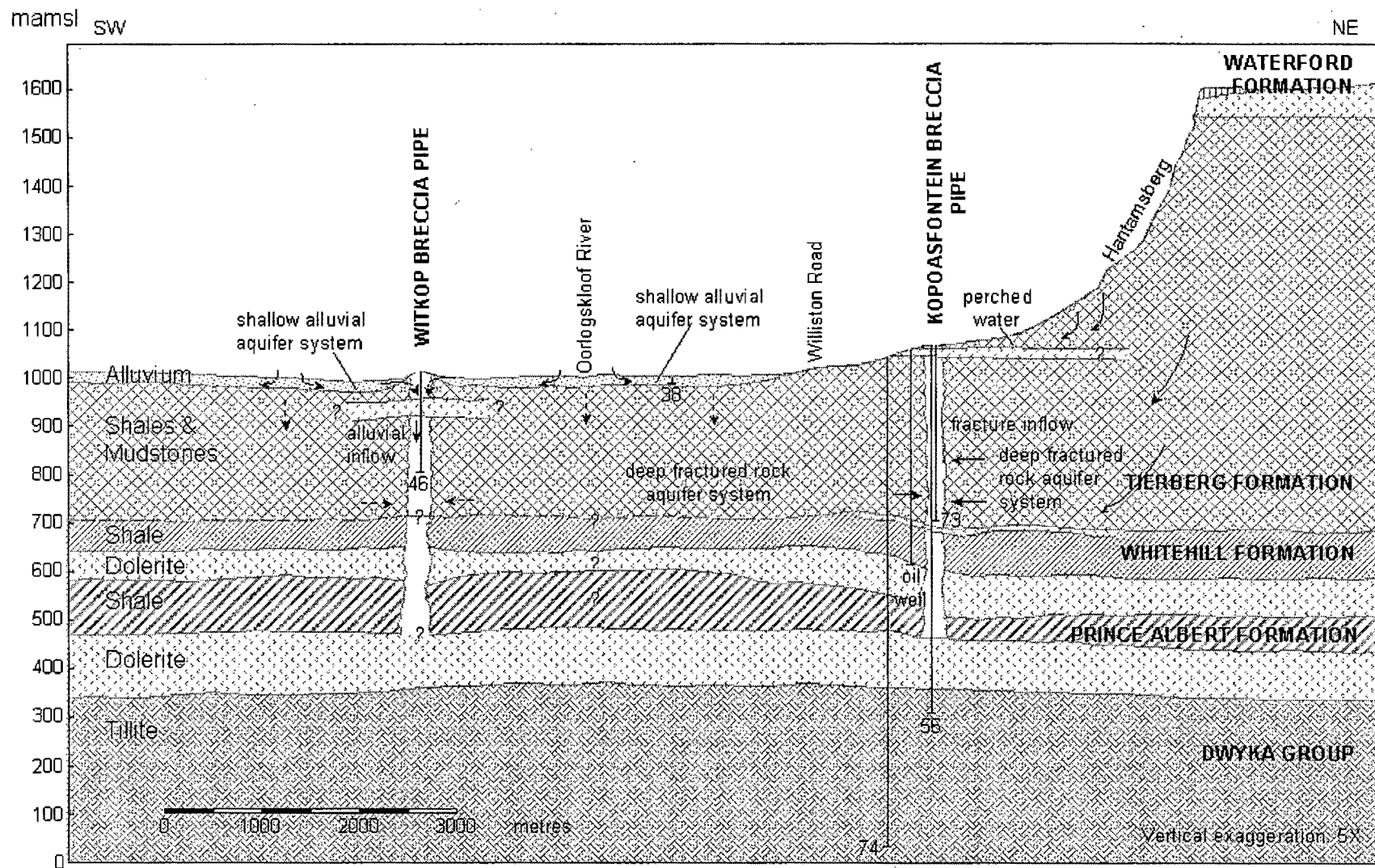


Figure 6.12. Cross section from southwest to northeast through the Calvinia valley, showing the various groundwater systems and their influence on the Kopoasfontein and Witkop breccia pipes.

Magma, which provided the heat source for hydrothermal alteration in the Kopoasfontein breccia pipe, intruded the Karoo sediments around 200 million years ago. Apophyllite crystallisation occurred during the final phase of hydrothermal activity and would be of slightly younger age. Stable isotope ratios for the groundwater, however, do not show any evidence of oxygen isotope exchange with the rocks that would be expected to occur at temperatures above 80°C (Issar, 1995) and it is anticipated that none of the groundwater is old enough to have been influenced directly by the Jurassic hydrothermal activity. Slightly elevated groundwater temperatures in the Kopoasfontein breccia pipe are not related to a magmatic heat source, but probably reflect the normal geothermal gradient and the fact that Kopoasfontein groundwaters have a deeper origin than those in the surrounding boreholes.

No fluid inclusions were found in any of the apophyllite crystals from Kopoasfontein, so these could not be used to determine the composition of the hydrothermal fluids that passed through the breccia pipe. Since deeply circulating meteoric waters are often associated with the formation of apophyllite, it may be surmised that heated phreatic waters formed a large component of the hydrothermal fluids and these were not merely the final volatile differentiate released from an igneous melt. It is envisaged that a hydrous fluid phase with high silica and significant fluorine and ammonia would be needed to crystallise the Kopoasfontein apophyllite, with the fluorine and nitrogen most likely to have been derived locally from the organic material in the Whitehill Formation. The original hydrothermal fluids have in all likelihood long since escaped from the system, vast quantities having been lost as gases during the venting which caused brecciation. The only influence of the hydrothermal fluids on the modern groundwater chemistry would then be through interaction with the elements trapped in the altered mineral assemblage of the breccia pipe.

Although sodic breccias have a Na-HCO₃/Cl type, which may be typical of the final product of groundwater evolution under deep, confined, sedimentary basin conditions, such as the Australian Great Artesian Basin (Herczeg *et al.*, 1991), they lack the high salinities generally associated with sedimentary basinal brines. The low salinity of the groundwaters also suggests that these are not evolved connate waters trapped during deposition of the Karoo sediments in the brackish environment of the Ecca Sea. Palaeowaters associated with the deposition and diagenesis of the Ecca Group sedimentary rocks would be older than the dolerite intrusions and much of this water

may have boiled off during the magmatic event that formed the breccia pipes.

The presence of low, but measurable ^{14}C in the sodic breccia pipe, indicates that although the water is, on average, older than that in the calcic breccia pipes, it is not all ancient palaeowater and there has been considerable addition of groundwater to the Kopoasfontein and Witwal breccia pipes over the last 50 000 years.

Perhaps the strongest argument against the occupation of the sodic breccia pipes by palaeowaters is a hydraulic, rather than a geochemical one. By the time feasibility studies for artificial recharge at the Kopoasfontein site were begun in 1998, the water level in the pipe had recovered to its rest position of 16 m below surface (Cavé, 1999). This means that the amount in excess of 22 550 m³ of water that was removed from the pipe during the 1994 pumping tests (Woodford, 1994) had been fully replaced by natural inflow to the pipe over the intervening four years. The volume replaced represents a significant portion of the estimated 57 000 to 74 000 m³ capacity of the permeable portion of the pipe (Murray and Tredoux, 1998b) and yet there was no significant change in water chemistry or stable isotope composition that might suggest that the inflow to the pipe after the pumping test was from a different source from the groundwater already resident in the breccia.

6.6.2 Local meteoric recharge

Stable isotope ratios in the sodic breccia pipes fall very close to the meteoric water line for the western Karoo area, suggesting that the groundwater originates from recent atmospheric sources and that the water infiltrates fairly rapidly without undergoing evaporation (Figure 3.17). Rainwater would also provide a suitable freshwater source for the low salinity waters. It was initially thought that the high permeability of the brecciated sediments could allow rapid recharge to the pipe during rainfall events. The groundwater composition would then be modified by water-rock interactions in the pipe.

The presence of an impervious dolerite sill near the top of the breccia pipe, however, prevents recharge of the Kopoasfontein breccia pipe by vertical infiltration of atmospheric precipitation at the site. A perched groundwater body in the weathered zone above the sill, which is not

connected to the deeper groundwater, provides strong evidence that the groundwater in the main body of the pipe is locally confined and does not receive direct recharge from above.

Infiltration at the site may recharge the perched aquifer, but this shallow groundwater does not feed the sodic waters of the breccia pipe, except for a small amount which trickles down the uncased boreholes drilled through the sill. The perched water is of similar $\delta^{18}\text{O}$ and δD isotope composition, but is of higher salinity and differs in chemical composition from the breccia pipe groundwater. The meteoric water which feeds the breccia pipe must, therefore, be brought in from further away by fracture flow below the upper capping sill of the breccia.

The eventual recovery of the groundwater level after test pumping also argues against direct filling of the pipe by rainwater infiltration. Approximately 1000 mm of rainfall was measured over the time between the end of the pump test and the beginning of the artificial recharge studies, an amount that would be insufficient to replace the 22 550 m³ of groundwater that was removed, even if 100% recharge occurred.

6.6.3 Inflow from fractured rock aquifers

An association has been made in Section 6.5 between the geochemistry of groundwater in the fractured rock aquifers around Calvinia and that in breccia pipes classified in this study as being of “sodic type”. The characteristics of major and minor aqueous species in these two waters are not indistinguishable, but the fractured rock environment and its low salinity groundwaters provide a more likely source for the inflow of waters to the sodic breccia pipes than the shallow alluvial aquifer system. Mass balance calculations (Section 6.4) suggest that it is possible to derive the composition of the Kopoasfontein groundwater from that of boreholes close to the Hantamsberg mountains in the fractured rock aquifer system.

While the fractured rock groundwaters and the sodic breccia pipe waters share a similar major anion composition, predominantly a mixture of HCO_3^- and Cl^- with relatively low SO_4^{2-} , it is the strong Na^+ dominance of the breccia pipes which differentiate them from the Ca^{2+} - and Mg^{2+} -rich fractured rock groundwaters. The low Ca^{2+} and Mg^{2+} in the Kopoasfontein pipe are intricately linked through carbonate equilibria with the high pH and high F^- which distinguish these samples

from all others in the area.

The proposed model for the origin of the Kopoasfontein breccia pipe groundwater includes:

- (1) recharge of the fractured rock aquifer system by atmospheric precipitation, infiltrated fairly rapidly through an unsaturated zone that does not have a high content of readily soluble phases or carbonate minerals. The most likely recharge zone in the study area is along the base of the Hantamsberg mountains, but there may be a regional recharge area for the deeper parts of the fractured rock system which lies further away.
- (2) slow transport through the fractured rock aquifer and reaction with silicate phases in the shales and dolerites under closed system conditions and acquisition of a $\text{Na-HCO}_3/\text{Cl}$ major ion composition through a combination of feldspar weathering and calcium removal by $\text{Na}^+ - \text{Ca}^{2+}$ cation exchange. Some fluoride may have been added through release from primary silicates and clay minerals.
- (3) inflow from local fractured rock groundwater systems through the sides of the breccia pipe below the upper dolerite sill. The breccia pipes may also offer a pathway of low resistance for the upward transport of groundwaters from a deep, possibly regional, flow system in the Karoo. Such deep waters would have travelled further along the evolutionary pathway than most of the waters intercepted by other boreholes around Calvinia. The existence of a second cross-cutting dolerite sill above the Whitehill Formation, at 380 metres below surface, could prevent groundwater below this depth from entering the breccia pipe. The deep groundwaters would, therefore, originate from the base of the Tierberg Formation.
- (4) further modification of water composition by chemical interactions with the hydrothermal mineral assemblage inside the pipe over significant residence times inside the breccia pipe. Changes include a further rise in pH and fluoride concentration, addition of sulphate by sulphide oxidation after oxygen was allowed into the pipe and mobilisation of trace species, such as arsenic.

Evidence in favour of an old, deep groundwater source includes the groundwater temperature of about 5 - 7 °C hotter than the others in the region, which suggests that the water follows a deep flowpath before reaching the breccia pipe, and the low ^{14}C activity in the groundwater. Several dissolved components of the Kopoasfontein groundwater, such as high Si and F^- concentrations,

are typical of the effects of long residence times in a non-carbonate aquifer, where slow silicate weathering reactions control the water chemistry. Carbonate speciation calculations, based on pH and total alkalinity measurements, show that these waters are likely to be at equilibrium with a partial pressure of CO_2 that is well below atmospheric concentration, near 10^{-5} atm. This implies that Kopoasfontein groundwaters are likely to have evolved for some time in a system closed to CO_2 .

A few samples of the $\text{Na-HCO}_3/\text{Cl}$ water type with elevated F^- concentrations were also noted in the database, which are not recorded as being from breccia pipes, for example DW12, JV1, 80, and 50. This suggests that the major cation composition is not uniquely associated with the mineralogy of the Kopoasfontein pipe, but occurs at other locations in the fractured rock system. Although these are localised occurrences that may originate from unmapped breccias, they could also arise from fractures intercepting the same deep system² that feeds the Kopoasfontein and Witwal breccias.

An additional increase in dissolved silica and fluoride content and rise in pH is uniquely associated with the Kopoasfontein mineral assemblage, since these measurements are higher here than at any of the other $\text{Na-HCO}_3/\text{Cl}$ groundwater sites. Records from the NGWDB suggest that Si and F^- decreased slightly after recovery from the pumping tests. Major ion chemistry remained unchanged, with the exception of SO_4^{2-} concentrations, which have been increasing since the first removal of groundwater from Kopoasfontein during 1994 allowed oxygen to enter the deeper parts of the pipe (Figure 6.13).

² An oil exploration borehole adjacent to the Kopoasfontein site, however, did not seem to yield the expected water composition from this hypothetical “deep flow system”. A record from the NWQDB shows that the 455 m deep borehole (Oil 1) outside the breccia pipe, produced a Na-Cl/SO_4 water type of pH 7.2, with a much lower F^- (2.2 mg/L) and Si (4.4 mg/L) concentration than inside the breccia. Unfortunately, there is no information about how this borehole was constructed and sampled, and the water may be bailed stagnant water or a mixed groundwater. If this analysis is a true reflection of the fractured rock aquifer system around the breccia pipe, then it provides a strong argument for the modification of water composition by water-rock interactions inside the pipe.

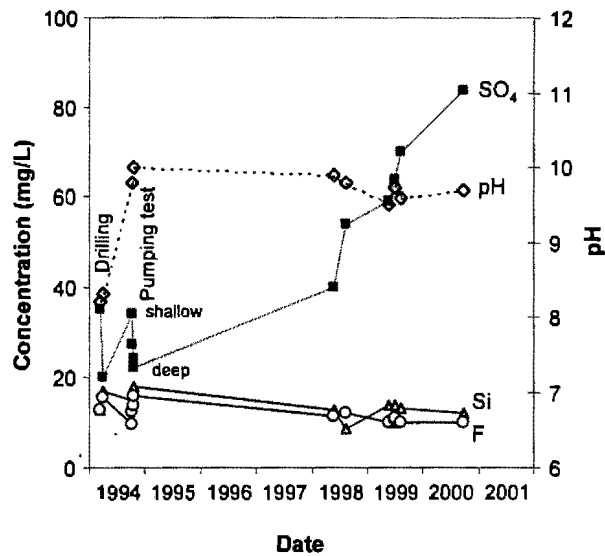


Figure 6.13. Change in concentration of sulphate, fluoride and silicon and pH with time in groundwater samples from borehole 73 at Kopoasfontein.

Data for arsenic concentrations in Calvinia groundwaters are scarce, but the mobilisation of this element is also a characteristic feature of the Kopoasfontein breccia pipe, which would be related to interactions within the pipe. The non-mineralised breccia pipe at the Airfield yields water that is typical of unmodified, fractured rock groundwater, while the mineralised Golf Course breccia pipe also produces groundwater with elevated As concentrations.

6.6.4. The origin of fluoride in Kopoasfontein groundwater

A combination of dissolution studies, mass balance calculations, thermodynamic estimates and groundwater chemistry observations have shown that fluorapophyllite dissolves in dilute aqueous solutions, releasing F^- ions at rates that are relatively rapid for layer silicate dissolution, but that it is unlikely to be the sole source of dissolved F^- in the Kopoasfontein groundwater. Apophyllite dissolution is stoichiometric in neutral to alkaline solutions and significant quantities of silica and calcite precipitation are required to remove the excess Ca and Si from solution if all F^- in the groundwater originates from dissolved apophyllite. The concentration of F^- is also in excess of the stoichiometric quantity in relation to K^+ and NH_4^+ which would be released by dissolving the Kopoasfontein apophyllite, although the behaviour of these ions is not conservative.

A very simplistic mass balance calculation shows that for 74 000 m³ of pure water to reach a fluoride concentration of 11 mg/L, it would need to dissolve 38 tons of fluorapophyllite. If the average porosity of the rock is 10%, then 74 000 m³ of water will occupy 740 000 m³ of rock. Even if only 0.1% of the rock is composed of apophyllite, this would be 740 m³ of the mineral, (or 1665 tons, using a density of 2.35 g/cm³) so 34 tons would be only 2% of the total amount present in the breccia pipe. It is, therefore, not unreasonable to conclude that the Kopoasfontein breccia pipe contains enough fluorapophyllite to contribute at least part of the dissolved fluoride.

Weathering of apophyllite has probably occurred in the upper portion of the Kopoasfontein breccia pipe, where open system conditions prevail in the unsaturated zone. The fluoride concentration, however, increases with depth, suggesting that another source of dissolved fluoride is contributed in the lower part of the pipe. Apophyllite is not recognised in the upper 30 m of the breccia pipe where most of the fracture-filling material is calcite, above the rest water level of 15 mbgl, or calcite and chlorite, below the water table. It is suspected that all apophyllite in the weathering zone has been altered to these secondary phases. Deeper in the pipe, below 80 mbgl, the apophyllite crystals are clear and appear to be well-formed and largely unweathered.

The system is closed to CO₂ below the water table and the pH close to 10. The solubility of the mineral is extremely sensitive to pH and estimated saturation indices suggest that apophyllite dissolution in the deeper Kopoasfontein groundwater is thermodynamically unfavourable. Fluorapophyllite precipitation has also not been observed at ambient temperatures and the deposition of apophyllite from supersaturated solutions does not provide a realistic mechanism for controlling the maximum concentration of fluoride in solution.

It appears that it is the lack of an efficient sink for the removal of fluoride, rather than a particularly reactive fluoride source, which is controlling the elevated fluoride concentrations in sodic breccia pipes from Calvinia. Samples with elevated fluoride generally belong to a Na-dominant water type and it is the very low Ca²⁺ activity that allows F⁻ to reach high concentrations without exceeding fluorite solubility (Figure 6.14).

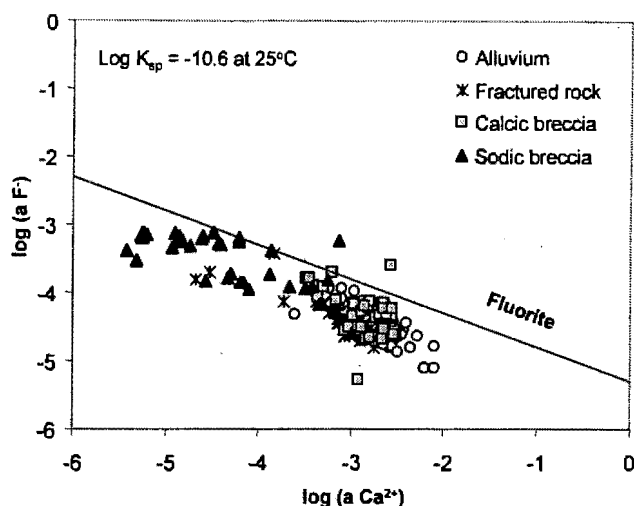


Figure 6.14. Scatterplot of fluoride and calcium activities in all Calvinia groundwater samples showing inverse relationship between Ca^{2+} and F^- and undersaturation with respect to fluorite.

Since apophyllite may not contribute all of the fluoride at Kopoasfontein, and since other locations where no apophyllite has been recorded, also produce groundwaters with elevated dissolved fluoride, there must be (an) additional source(s) of fluoride in the Karoo rocks. Fluorite itself is one possible source, which may be responsible for fluoride in groundwater, particularly in the shallow alluvial aquifers.

A more likely source is F isomorphously substituted for structural OH in silicate minerals. A fluorine concentration of 420 mg/kg was determined for the dolerite sill at 380 m in the Kopoasfontein breccia pipe (Cavé, 1999) and could be resident in traces of biotite and amphiboles in the dolerites. Much of the fracturing in the Karoo shales is associated with dolerites and weathering of these unstable primary silicate minerals could release fluoride to the fractured rock groundwater system. Chevallier has also found vesuvianite in the Airfield breccia pipe and tourmaline in the Downes pipe (pers. comm.) which may be hosts for fluorine.

Because it is associated with clay structures, the natural concentration of fluorine in fine textured sedimentary rocks, such as the Eccca Group shales and mudstones, can also be high (McBride, 1994; p. 332). The presence of fluorapophyllite in the Kopoasfontein breccia pipe indicates that there are likely to have been significant amounts of fluorine present in the Karoo sediments

before the magmatic events that led to the hydrothermal activity in the pipe. Geptner and Petrova (1990) have shown that fluorapophyllite mineralisation is not possible by simple chemical reconstitution of basaltic rocks (e.g. dolerite), which are the usual source rock for this mineral, without a supplementary supply of fluoride and potassium (or ammonium), presumably derived from reaction with the country rock.

Much of the fluorine in the Karoo fractured shale environment may be associated with the micaceous clay minerals, especially illite, in the sedimentary rocks. It is probably no coincidence that the two samples from the Kopoasfontein breccia core which released the least fluoride in leaching tests and contained the least F in the bulk analysis (Cavé, 1999) were kaolinitic samples that made up sample KF4 (see Chapter 4) and contained no detectable illite.

A proposed mechanism for the production of high fluoride groundwaters at Kopoasfontein involves a combination of fluoride brought in by the inflow to the pipe by sodium-dominant groundwaters, release of fluoride by weathering and ligand exchange with F-rich illite and dissolution of fluorapophyllite.

6.7 Implications for artificial recharge at Kopoasfontein

The Kopoasfontein site was selected for artificial recharge based on the observations of the original pumping tests in 1994. Minimal recovery of the water level in the 20 days following a constant discharge test suggested that the pipe has very poor hydraulic connection with its surroundings. This implied that there would be minimal inflow to the breccia pipe below the upper dolerite sill and, more importantly from a water storage perspective, minimal losses by seepage out of the pipe. The native groundwater in the pipe was recognised to be non-potable, because of the high pH and fluoride concentrations, but it was reasoned that this could be overcome by dewatering the pipe of what was assumed to be palaeowater and replacing this with fresh, treated drinking water. The stored water should not evolve to the same composition as the original groundwater, provided the minerals in the pipe are chemically inert, because its residence time in the pipe would be negligible in comparison with that of the fossil groundwater.

Mixing simulations were run with PHREEQC-1.5 software (Parkhurst, 1995) to choose the most appropriate source of water for injection and leaching tests performed on core samples to investigate the reactivity of the rocks as part of the initial feasibility studies (Cavé, 1999; Cavé, 2000). Fluoride, arsenic and possibly nitrogen were identified as potential problems at this stage, warranting further investigations into their origin.

This extended study has shown that the geochemistry of the groundwater in the breccia pipe is not consistent with that of a palaeowater and that there is some modern inflow to the pipe. This inflow is most likely to originate from fairly deep within the fractured rock aquifer system around the pipe and to transport additional fluoride into the breccia pipe. The rate of inflow is, however, slow in comparison to the rate of injection when filling the pipe and the positive hydraulic pressure of the stored water in the pipe should prevent the ingress of the local groundwater once the pipe has been filled.

Laboratory dissolution rates have been measured for apophyllites as a function of pH, but there are various problems in applying these directly to the field situation, not least of which is the inability to measure the surface area of the apophyllite in the breccia pipe. Where the accumulation of fluoride in the stored water is concerned, however, the dissolution tests have indicated that fluorapophyllite reacts slowly in neutral to alkaline solutions and should not pose a major risk for short-term water storage in contact with the mineral. The Kopoasfontein apophyllite also contains ammonium, but there is no realistic threat that this constitutes a source of nitrate contamination.

Fluorapophyllite is not likely to be the only source of fluoride in the system, however, and other mineral sources are likely to contribute to the fluoride concentration in the natural Kopoasfontein groundwater. Although fluorapophyllite does not threaten the water quality, some of the additional fluoride sources may still cause unacceptable concentrations in Calvinia drinking water, if there is significant mixing of inflowing groundwater with the water stored in the breccia pipe. Fluoride monitoring and, if necessary, treatment will have to be incorporated into the management of the artificial recharge scheme.

Two other geochemical processes may become problematic in the operation of an artificial recharge scheme at Kopoasfontein. The first is a slight increase in salinity of the injected water above that of the native water in the pipe, noted when logging EC after the pilot injection run. Salinity may be stored in the form of soluble salts in the unsaturated zone at the top of the pipe and dissolved by the rising water table. Mixing of the injection water with the higher salinity preched groundwater above the capping dolerite sill, may also be responsible for the 20 mS/m rise in EC. The second cause for concern is the oxidation of sulphide minerals in the pipe. Drilling, pumping tests and dewatering have allowed the ingress of oxygen into a system previously isolated from atmospheric gases. This has altered the redox environment and destabilised sulphide species in the pipe (see Figure 6.13).

Although some benefit may be obtained in this case by the acidifying action of sulphide oxidation, the negative impact of this geochemical process on the water quality is likely to outweigh any positive results. Oxidation of iron released from pyrite and pyrrhotite may eventually cause clogging problems in the system, particularly if conditions remain alkaline where ferric hydroxides are highly insoluble. The sulphides are also the most likely hosts for arsenic in the Kopoasfontein breccia pipe and their degradation may release additional quantities of this toxic element to the groundwater.

6.8 Concluding remarks

The research project described in this thesis set out to investigate the connection between the geochemistry of an alkaline, fluoride-rich groundwater and the brecciated, hydrothermally-altered sedimentary rock body which hosts it. Among the objectives that have been achieved is the establishment of how this water is related to other groundwater sources in the area, in terms of geochemical evolution sequences and mixing trends, and the answering of key questions related to the origin of the high pH and dissolved fluoride. The properties and weathering behaviour of apophyllite were chosen as a focus area for study, because of its prominence in the breccia pipe and the paucity of existing data for this mineral, which offered an excellent opportunity to make a meaningful contribution to the field of low-temperature silicate weathering research.

Using a combination of existing water quality data, field measurements, water and rock analyses, laboratory batch tests and geochemical modelling tools, this work has tested the hypothesis that local water-rock interactions in the Kopoasfontein breccia pipe are responsible for the unusual groundwater composition, and found it to be partly true. Reactions of pure recharge water with minerals in the breccia pipe cannot *solely* account for the simultaneous high pH, low calcium and high fluoride in solution. Inflow of external groundwater, after silicate dissolution and carbonate precipitation along a flow path closed to atmospheric CO₂ within the fractured rock aquifer system, ion exchange reactions of Ca²⁺ for Na⁺ and fluoride dissolution from other mineral sources in the Karoo shales and dolerites are likely to contribute to the final groundwater composition. The local water-rock interactions probably cause final modifications to the inflowing groundwater chemistry, however, resulting in additional increases in pH and fluoride and dissolution of sulphate and arsenic species.

In addressing the key questions set out in Section 1.2, this work has found that:

Is fluorapophyllite the mineral phase controlling dissolved fluoride concentrations?

- ▶ fluorapophyllite can reasonably be expected to release some dissolved fluoride to the groundwater, but it is not the dominant control on fluoride concentrations. The low calcium concentrations and high pH environment prevent the efficient removal of fluoride, probably derived from a variety of sources, by maintaining undersaturation with respect to fluorite.

Can nitrogen in the groundwater be mineralogically derived?

- ▶ high concentrations of nitrogen (0.4 wt%) occur in hydrothermally altered Tierberg shales and the Kopoasfontein apophyllite also has a high degree of NH₄ substitution. These findings support the conclusion that NH₄⁺ in the deep groundwater is from a geological source, rather than recharged from near-surface biological nitrogen sources.

What geochemical reactions are responsible for the high pH?

- ▶ closed system conditions, where the weathering reactions of silicate minerals (including apophyllite) and secondary carbonate equilibria occur in an environment controlled by low pCO₂ (below 10⁻⁴ atm), are conducive to the evolution of a pH close to 10.

Do all breccia pipes yield groundwaters that are distinct from the local aquifer systems? and Do breccia pipes of similar mineralogy produce similar groundwater compositions?

- breccia pipes connected to the alluvial aquifer system have a chemical composition dominated by the high salinity inflow from the alluvium. Poorly-mineralised pipes, such as the Airfield breccia also contain groundwater with a composition that is not distinctive from that of the surrounding aquifers. Only the hydrothermally-mineralised, “sodic” Witwal and Kopoasfontein breccia pipes produce characteristic groundwaters.

This study of the groundwater geochemistry at Calvinia has improved the understanding of the geohydrology of dolerite breccia pipes, where previously very little was known about these systems. The findings are expected to have wider application in the western Karoo, where several such pipes are known to occur, and to facilitate the selection of more suitable sites for water storage in this semi-arid region, should the Calvinia recharge experiments prove successful.

Apophyllite investigations have uncovered an exceptionally ammonium-rich variety of the mineral at Kopoasfontein and characterised the behaviour of various members of the apophyllite series during thermal decomposition and aqueous dissolution at room temperature. The laboratory measurement of apophyllite dissolution rate and stoichiometry and its pH and compositional dependence, as well as the derivation of an estimated solubility constant at 25°C, broaden the understanding of the geochemical behaviour of this mineral

Geochemical investigations at Kopoasfontein have also uncovered topics that are not yet well understood and invite further research. Detailed studies of the ion exchange capacity, exchange site occupancy and selectivity of ion exchange reactions could be of benefit in unravelling their role in the regulation of cations in the system. Repeated reference has been made to additional sources of fluoride and, while illite has been suggested as a likely candidate, a rigorous study of this mineral is needed for confirmation. The source of As in the system has still to be positively identified and the mechanism(s) for its mobilisation investigated. Various biogeochemical reactions could be implicated in the release of As, regulation of CO₂ partial pressure and transformations of N and may even provide a mechanism for the enhancement of ammonian apophyllite dissolution rates. The study of these reactions provides an opportunity to improve the current understanding of geochemistry of the Kopoasfontein groundwater system.

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GLOSSARY OF TERMS

alteration: changes in the chemical or mineralogical composition of a rock, usually produced by hydrothermal solutions or weathering.

artificial recharge: process whereby water is induced to enter the subsurface at rates exceeding those at which groundwater recharge would naturally occur.

aquifer: strata or a group of interconnected strata comprising saturated earth material capable of conducting groundwater and of yielding usable quantities of groundwater to borehole(s) and/or springs (a supply rate of 0.1 L/s is considered as a useable quantity).

authigenic: (of mineral constituents) formed in a rock at the site where the rock is found. It is applied chiefly to sedimentary material.

basalt: dark-coloured, fine-grained basic igneous rock, essentially composed of calcic plagioclase and pyroxene.

brackish: water that contains between 1 000 and 10 000 mg/L of dissolved solids.

breccia: coarse-grained rock composed of broken, angular rock fragments enclosed in a fine-grained matrix, or held together by mineral cement.

Carboniferous: the time interval between 360 and 290 Ma.

clast: an individual fragment of a larger rock mass, removed by the physical disintegration of the larger mass.

connate water: water trapped in the pore space of sediment at the time of its deposition.

detrital: minerals, sediments or rocks derived from transport of solid grains from pre-existing rocks, in contrast to chemical or biological precipitates.

diagenesis: physical and chemical processes affecting a sediment or sedimentary rock after it is deposited, excluding those processes at sufficiently high temperature to be considered metamorphic.

discharge: outflow of subsurface water, including water in the vadose zone and saturated zones, to land surface, to surface water or to the atmosphere.

drawdown: the difference between the observed water level during pumping and the non-pumping water level.

dolerite: a medium-grained basic igneous rock of basaltic composition, composed essentially of pyroxene, plagioclase and Fe-Ti oxides.

dyke: a tabular body of intrusive igneous rock which cuts across the layering or structural planes of the host rock.

evaporite: a sediment deposited from a saline solution as a result of extensive or total evaporation of the water.

freshwater: water that contains less than 1 000 mg/L dissolved solids.

groundwater: all subsurface water occupying voids within a geological stratum.

granophyre: medium to fine-grained granitic rock, characterised by micrographic intergrowth of quartz and alkali feldspar.

hornfels: fine-grained metamorphic rock composed of mineral grains of the same size. Hornfels is formed by thermal metamorphism and solid state crystal growth within the contact zone surrounding an igneous intrusion.

hydrothermal: of, or pertaining to heated water, to its actions, or to products related to its actions.

igneous rock: rock that has solidified from molten rock material.

intrusion: igneous rock formed by emplacement of molten rock or a plastic solid into pre-existing rock.

Jurassic: the period of geological time extending from 210 to 140 Ma, occupying the middle portion of the Mesozoic Era.

lamprophyric: descriptive of a group of dark- to medium-dark coloured, igneous rocks that typically occur as dykes and small intrusions. They are porphyritic (contain large crystals in a fine-grained groundmass of smaller crystals or glass), with large crystals of biotite-phlogopite and/or amphibole. Lamprophyres usually show signs of hydrothermal alteration and calcite and chlorite may be present in the groundmass.

leucocratic: (of igneous rocks) light-coloured, containing between 0 and 35% of dark minerals.

magma: molten rock.

magmatic differentiation: internal diversification processes that separate an initially homogeneous magma into two or more daughter magmas of different chemical composition.

metasomatism: a process of practically simultaneous capillary solution and deposition by which a new mineral of partly, or wholly differing chemical composition may grow in the body of an old mineral or mineral aggregate.

meteoric water: water derived from the atmosphere (usually in geologically recent time).

palaeo-: prefix denoting old or ancient.

permeability: refers to the ease with which water can pass through a porous medium and is defined as the volume of water discharged from a unit area of an aquifer under unit hydraulic gradient in unit time (expressed as $\text{m}^3/\text{m}^2/\text{d}$ or m/d).

Permian: the period at the end of the Palaeozoic Era, from 290 to 250 Ma.

porosity: ratio of the volume of void space to the total volume of the rock.

primary aquifer: an aquifer in which water moves through the original interstices of the geological formation.

pumping test: a method of parameter measurement that is specifically suited to the determination of transmissivity and storativity in confined and unconfined aquifers.

recharge: process of the addition of water to the groundwater system by natural or artificial processes.

secondary aquifer: an aquifer in which water moves through the secondary interstices, which are a result of post-depositional processes, such as joints and faults.

secondary mineral: a mineral formed after the rock enclosing it has been formed. The process usually involves alteration of a primary mineral by metamorphism, weathering or solution.

sill: a tabular igneous intrusion with boundaries conformable with the planar structure of the surrounding rock.

tholeiite: a variety of basalt that is poor in alkalis and is characterised by the presence of orthopyroxene in addition to calcic plagioclase and clinopyroxene.

tillite: unsorted, unstratified sedimentary rock derived from glacially transported or deposited material.

trachytic: descriptive of a fine-grained, extrusive alkaline igneous rock, approximately silica-saturated and with a wide compositional range. Its main components are alkali feldspar with minor mafic minerals. Trachytes are the extrusive equivalent of syenite.

vug: an unfilled cavity in a rock or mineral vein, commonly not joined to other cavities, often lined with euhedral vapour-phase crystals of differing mineralogy to the surrounding rock.

vadose zone: unsaturated zone below the surface, but above the groundwater table.

wellhead: the area immediately surrounding a borehole where groundwater is abstracted.

zeolite: group of hydrated aluminosilicate minerals corresponding chemically to feldspars plus water or minus silica. Some zeolites have high cation-exchange capacities, and are used in industry for water softening or as molecular sieves.

**APOPHYLLITE WEATHERING AND THE
AQUEOUS GEOCHEMISTRY OF A
KAROO BRECCIA PIPE**

Lisa Caryn Cavé

**VOLUME II
APPENDICES**

February, 2002

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APPENDIX A

BOREHOLE CONSTRUCTION DETAILS AND DRILLING LOGS

A.1 Kopoasfontein geohydrological research site

The research site at Kopoasfontein consists of a cluster of boreholes and associated infrastructure constructed on the farm property for exploration and geohydrological research. The artificial recharge testing comprises boreholes dedicated to water injection, water level monitoring and a deep abstraction borehole to recover the injected water (G39973). Details of the boreholes at the Kopoasfontein research site, including their purpose and method of construction are summarised in Table A.1. The last two digits of the G-number identifier assigned by DWAF are used as borehole labels in figures and tables and in discussions from the main body of this thesis. A map of the borehole positions at the site appears in Figure 3.3.

Most of the boreholes were drilled using the air rotary percussion method, but two deep boreholes, G39856 and G39974, were drilled by a wire-line core rig to obtain geological samples. Borehole casing and slotted screens for the groundwater boreholes are constructed of steel. Several boreholes have open hole construction and are uncased below the upper weathered zone. All groundwater boreholes are fitted with a steel collar in a concrete block and closed with a steel cap when not in use. The injection pipes on boreholes G39852 and G39854B are plastic and the pipes connected to the submersible pump used for borehole G39973 are made of galvanised steel.

Table A.1 Borehole information for the Kopoasfontein geohydrological research site

Borehole Identity (DWAF)	Surface Lithology	Purpose	Total Depth (m)	Equipped	Casing	Construction	Depth below surface to water strikes (m) and maximum blow yield (bracketed)	Date drilled	Source
					Plain (m) Slotted (m)	BH diameter Casing (mm)			
G39851A	breccia	monitoring	108	water level recorder	no data	200 165	no data	1992	1
G39852	breccia	injection	150	injection pipes	0 - 12.0 -	200 165	64, 71, 95, 133 (16.5 L/s)	1992	2, 3
G39853	dolerite	exploration	130	capped	0 - 4.5 -	200 165	84 (01. L/s)	1992	2, 3
G39854B	dolerite	injection	141	injection pipes/capped	no data	200 165	(±50 L/s)	1998	1
G39855	shale	monitoring	150	water level recorder	0 - 12.0 -	200 165	30, 60 (1.1 L/s)	1992	2, 3
G39856	breccia	geological exploration	755	capped	0 - 20	141 46	geology core	1992	4
G39973	breccia	abstraction	360	submersible pump	0 - 10.5 10.5 - 182 182-255	200 200 165	26, 59, 86-133, 140, 161, 193, 199, 210, 247, 259 (80 L/s, 35L/s after casing)	1994	2, 3
G39974	shale	geological exploration	1016	capped	0 - 20	141 46	geology core	1994	4
Private (KF1)	shale	stock watering	6?	wind pump	no data	no data	(0.6 L/s)	pre - 1983	1, 5

Information sources:

1. Field observations (1998 - 2000)
2. Woodford (1994)
3. National Groundwater Database (Department of Water Affairs and Forestry)
4. Woodford *et al.* (in prep.)
5. Seward (1983)

A1.1 Geological logs

Table A.2 Geological log for borehole G39973.

DRILLER:	RC Drilling (Smith's Mining) J van der Merwe
COORDINATES:	Latitude 31.48536, Longitude 19.90031 (GPS 2D, Accuracy = 100m)
DRILLING DATES:	08-03-1994 to 30-03-1994
TOTAL DEPTH:	360 m
COLLAR ELEVATION:	1065.316 mamsl
WATER LEVEL (16-05-1994):	16.10 m
Depth (m)	Lithology
0-8	Baked, metasomatised grey/green mudstone and siltstone. <i>Brecciated - vugs filled with calcite</i> . Weathered/jointed to 6 m, thereafter weathered on joint surfaces only.
8-23.5	Melanocratic, very fine to fine grained dolerite. Weakly jointed and weathered to 10.5 m. Weakly jointed 20-21 m.
23.5-24	Metasomatised/brecciated, highly baked, light grey siltstone.
24-31	Highly baked, metasomatised, brecciated, grey/maroon mudstone. <i>Breccia vugs filled with calcite + chlorite</i> . 26-29 m mixed mudstone and melanocratic, very fine grained dolerite.
31-49	Baked, metasomatised, brecciated, dark grey to black mudstone and shale. <i>Minor open breccia vugs filled with calcite and chlorite</i> . Minor apophyllite and pyrrhotite. 35-39 m - weakly jointed (blocky).
49-51	Highly baked, metasomatised, brecciated, grey/maroon mudstone (hornfels).
51-60	Baked, metasomatised, dark grey to black shale. <i>Minor open breccia vugs filled with calcite + chlorite</i> . 60 m - jointed (blocky).
60-61	Baked, metasomatised, grey/maroon mudstone.
61-81	Baked, metasomatised, dark grey to black mudstone and shale. <i>Minor breccia vugs filled with calcite + chlorite</i> . 66-67 m weakly jointed (blocky). Minor thin zones of grey/maroon siltstone. 74 m - brecciated/jointed (blocky). Minor pyrrhotite.
81-82.5	Baked, metasomatised, highly brecciated, light grey to maroon/grey siltstone. <i>Breccia vugs filled with calcite + chlorite</i> .
82.5-87	Baked, metasomatised, dark grey to black shale.
87-217	Highly baked, metasomatised, brecciated, mottled, maroon/grey mudstone to light grey-grey/green siltstone. <i>Open breccia vugs, lined with chlorite and apophyllite, minor pyrrhotite</i> . 96-165 m highly brecciated, <i>abundant open vugs- abundant chlorite, apophyllite and pyrrhotite</i> . 175 m onwards, only <i>minor open breccia vugs</i> , generally hairline erratic fracturing and shattering, filled with chlorite. 196-197 m - <i>open vugs</i> .
217-242	Baked, metasomatised, remobilised, dark grey/maroon to grey/green, mottled siltstone and very fine grained sandstone. <i>Minor open breccia vugs</i> , lined with chlorite. Minor dark grey mudstone. 232-236 m highly baked creamy white shale.
242-305	Highly baked, metasomatised, brecciated, mottled, grey/green to maroon/grey mudstone. <i>Very minor open breccia vugs</i> . 279 m - well brecciated. Hornfels texture to 279 m
305-360	Baked, metasomatised, dark grey to grey/green shale.

Data source: Woodford, pers. comm.

Table A.3 Geological log for borehole G39852.

DRILLER: Department of Water Affairs and Forestry COORDINATES: Latitude 31.4851, Longitude 19.9012 DRILLING DATES: 06-06-1992 to 10-06-1992 TOTAL DEPTH: 150 m COLLAR ELEVATION: WATER LEVEL (11-06-1992): 27.700 m (0.1m casing elevation) (09-07-1992): 26.030 m	
Depth (m)	Lithology
0-0.5	Red/brown clay silt to very fine sand.
0.5-8	Weakly weathered/jointed, grey/green mudstone. Thin (<0.2 m) highly weathered horizons, clay in joints.
8-15	Slightly weathered/jointed, dark grey/black shale. Weakly baked.
15-21	Baked, weakly jointed, dark grey to grey siltstone. Maroon discolouration. <i>Pyrite</i> staining.
21-32.5	Melanocratic, very fine to fine, ophitic (speckles feldspar) dolerite. Slightly jointed.
32.5-33.5	Baked, light grey/green siltstone. (Breccia pipe?)
33.5-36	Mesocratic, fine-grained dolerite. Appears metasomatised.
36-55	Weakly baked, dark grey to black shale. Minor thin (<0.5 m) silty layers.
55-62	Weakly baked, dark grey mudstone.
62-150	<i>Breccia pipe</i> material. Light grey/green to grey/green/maroon siltstone. Well baked. 63 m - well jointed (blocky, ϕ 60 mm). 66 m - jointed (blocky, ϕ 20 mm), minor <i>calcite</i> in joints. 68 m onwards - metasomatised. 71 m - jointed (blocky, ϕ 20 mm). Individual fractures, rather than fracture zones. 73-74 m - minor <i>calcite</i> + <i>pyrrhotite</i> . 74 m onward - hornfelsic texture. 75 m - well jointed (blocky, ϕ 20 mm). 80 - 86 m - mineralised, <i>pyrrhotite</i> (max ϕ 3 mm). 88 m - jointed, <i>apophyllite</i> + <i>pyrrhotite</i> , thin (10 mm) interbedded very fine quartzite. 96 m - hornfels, <i>apatite</i> (?crystal) with alteration halo, <i>calcrete</i> -like matrix. 99-122 m - hornfelsic, grey/maroon siltstone. 125 m - weakly jointed + <i>apophyllite</i> . 133 m - as per 96 m, weakly jointed. 136 + 138 m - weakly jointed (conchoidal) + minor <i>apophyllite</i> on joint surfaces.

Data source: Woodford, pers. comm.

Table A.3 Geological log for borehole G39854.

DRILLER:	Department of Water Affairs and Forestry
COORDINATES:	Latitude 31°29'08.3", Longitude 19°54'05.1"
DRILLING DATES:	08-07-1992 to 20-07-1992
TOTAL DEPTH:	150 m
COLLAR ELEVATION:	1064.353
WATER LEVEL (24-07-1992):	20.785 m
	(21-08-1992): 26.555 m
Depth (m)	Lithology
0-1	Weathered/jointed, mesocratic, fine-grained dolerite.
1 -5.8	Baked, weathered/jointed olive green mudstone.
5.8-19	Melanocratic, very fine to fine grained dolerite.
19-20	Baked, light grey/maroon siltstone.
20-25	Weakly baked, dark grey mudstone.
25-150	Dark grey to black shale. Slightly baked to 29 m. Minor thin (<0.5 m) silty horizons. 67 m onwards - slightly baked. 80 m - slightly jointed. 100 m - slightly jointed + <i>pyrite</i> staining. 134-136 m - thin layers jointed grey/green quartzite. 135 m - jointed (blocky ϕ 20 mm). 137 m - jointed, fill <i>quartz</i> (apophyllite?), slightly weathered. 142 m - <i>quartz</i> + <i>pyrrhotite</i> mineralisation. 143 - 146 m - weakly jointed + minor <i>calcite</i> .

Data source: Woodford, pers. comm.

Note: Borehole G39854 had collapsed by 1998 and was replaced by G39854B drilled approximately 20 m closer to G39973 by the Worcester drilling branch of the DWAF in November 1998. Drilling logs were not available for the new borehole, but drilling chips supplied to the author consisted largely of breccia pipe material with *pyrrhotite* and abundant apophyllite. A new observation borehole (73obs) was also drilled into breccia pipe material approximately half way between G39852 and G39854B in November 1999.

Geological logs for boreholes G39856 and G39974 are shown on Figure A.1.

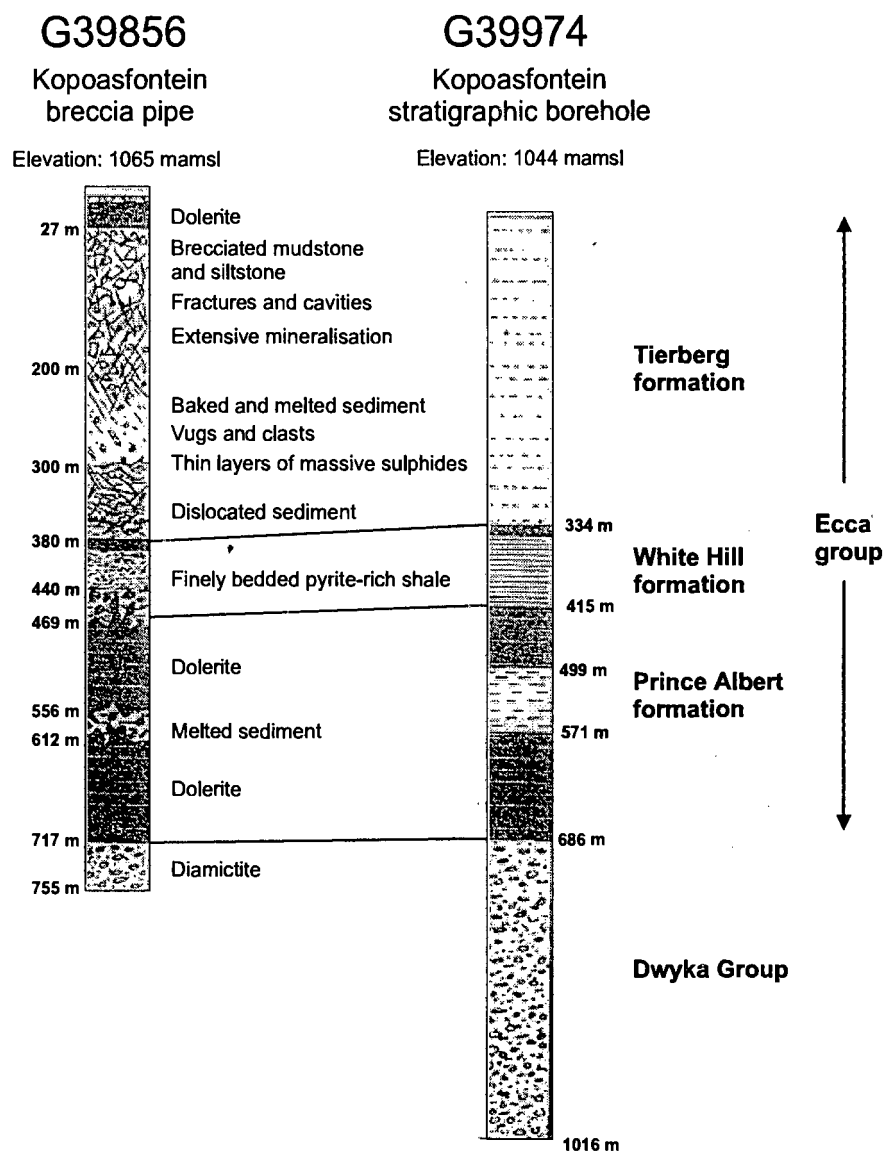


Figure A.1. Lithological sequence of boreholes 56 and 74 at Kopoasfontein, as logged by Chevallier and Balaban (pers. comm.).

Mineralogy logs

The main metallic and non-metallic minerals associations in borehole G39956 are recorded in Table A.5.

Table A.5 Mineralisation record for core borehole G39856 (Chevallier and Balaban, pers.comm., 1995)

Depth (m)	Mineral bulk (cm)	Mineral associations
45.0		pyrrhotite + pyrite (remobilized?)
51.0		pyrite + gypsum (breccia texture)
102.35		pyrite + quartz + calcite (+ ?apophyllite)
119		pyrrhotite + pyrite + sphalerite + chalcopyrite + chlorite + galena
119.5		pyrrhotite + pyrite + sphalerite
122.35		pyrite + chalcopyrite + pyrrhotite + chlorite + apophyllite (+ ?zeolite)
158.50		chalcopyrite + pyrite + pyrrhotite + quartz + (covellite) (+ ?apophyllite)
163.85		chalcopyrite + pyrite + pyrrhotite + secondary Cu minerals
169.50		pyrrhotite + pyrite + quartz + calcite + chalcopyrite + apophyllite + chlorite
191.45		chalcopyrite + pyrite + pyrrhotite + calcite + quartz + galena + sphalerite + apophyllite + gypsum (+ ?chlorite)
313.10	0.5 - 0.7	chalcopyrite + pyrrhotite + pyrite + carbonates + chlorite
405.50	1.5 - 2.5	pyrite + (pyrrhotite) + carbonate (calcite?)
436		pyrite + marcassite + carbonate
438.50		pyrite + chalcopyrite
449.50		pyrite + calcite + quartz + gypsum (+ ?fluorite)
533.50		pyrite + sphalerite + quartz + calcite + chlorite + gypsum
537.95		chalcopyrite + (gold) + quartz + calcite + pyrite + gypsum
538.50		pyrite + calcite + gypsum
719	10	pyrrhotite + chalcopyrite + (?sphalerite)

A1.2 Porosity logs

A neutron probe was used to log the average porosity of the aquifer at borehole G39973.

Table A.6 Aquifer porosity log for borehole G39973.

Depth (m)	Average porosity ¹ (%)
0 - 113	20 [#]
113 - 182	20
182 - 220	10
220 - 255	10 → 6
255 (small cavity)	3
255 - 360	1

¹ Porosity = volume of voids/ total volume of material

[#] estimated porosity, neutron probe measurement not possible above this level = position of water table at time of measurement.

Data source: Barry Venter (Department of Water Affairs and Forestry).

A2 Other breccia pipes

A total of twenty-six boreholes were drilled into breccia pipes during a joint exploration programme by DWAF and the Council for Geoscience from 1992 to 1996. Several of these boreholes have been included in the data set for the geochemical investigation of breccia pipes in the Calvinia area in this thesis. Most of the boreholes were constructed using percussion drilling techniques, but a 1000 m deep diamond-drilled geological core was also collected from the Platberg site on the farm Enkelde Wilgenboom (also called the Airfield breccia pipe in this thesis because of its proximity to the Calvinia landing strip).

Construction details (Table A.7) and drilling logs (Figure A.2) for some of these boreholes were supplied by DWAF and the Council for Geoscience (Chevallier, pers. comm.). Further information on borehole position, drilling depth and intended use of the groundwater may be found in the data tables of Appendix D.

Table A.7. Construction details for some boreholes drilled in Calvinia breccia pipes.

Borehole Identity (DWAF)	Breccia pipe	Purpose	Total Depth (m)	Equipped	Casing	Construction	Depth below surface to water strikes (m) and maximum blow yield (bracketed)	Date drilled	Source
					Plain (m) Slotted (m)	BH diameter Casing (mm)			
G39648	Witkop	municipal supply	200	submersible pump	0 - 6 -	165 -	20-25, 30-36, 41(8.5L/s), 65-68	1991	2,3
G39846	Witkop	stock watering	103	?	0 - 19 -	165 -	54-58, 60-67, 75, 97, 109 (8.6 L/s)	1991	2, 3
G39649	Witkop	?	141	?	0 - 10 -	165 -	21, 76 (1.7 L/s)	1991	2, 3
G39861	Witwal	municipal supply	196	submersible pump	0 - 12 -	165 -	66, 83, 133, 141 (14.2 L/s)	1993	1, 2, 3
G39860	Witwal	not in use	170	capped	0 - 6 -	165 -	28, 86, 113-114, 161 (4.6 L/s)	1993	1, 2, 3
G39858	Witwal	not in use	150	capped	0 - 12 -	165 -	29, 45-48, 81, 95, 114 (1.7 L/s)	1993	1, 2, 3
G39961	Witwal	not in use	181	capped	0 - 6 -	203 -	92 (0.1 L/s)	?	2, 3
G39859	Golf Course	municipal supply	217	submersible pump	0 - 21 21 - 45	203	26-28, 45, 70, 88, 97, 103-109, 146+151, 162-164 (31 L/s)	1993	1, 2, 3
G39862	Golf Course	not in use	194	capped	0 - 12	165	10-11, 33-35, 90, 151, 193 (9.3 L/s)	1993	1, 2, 3
G39635	Bakenskop	not in use	187	capped	?	?	?	1991	1, 3
G39857	Bakenskop	not in use	150	capped	?	200	?	1993	1, 3

Table A.7 (continued). Construction details for some boreholes drilled in Calvinia breccia pipes.

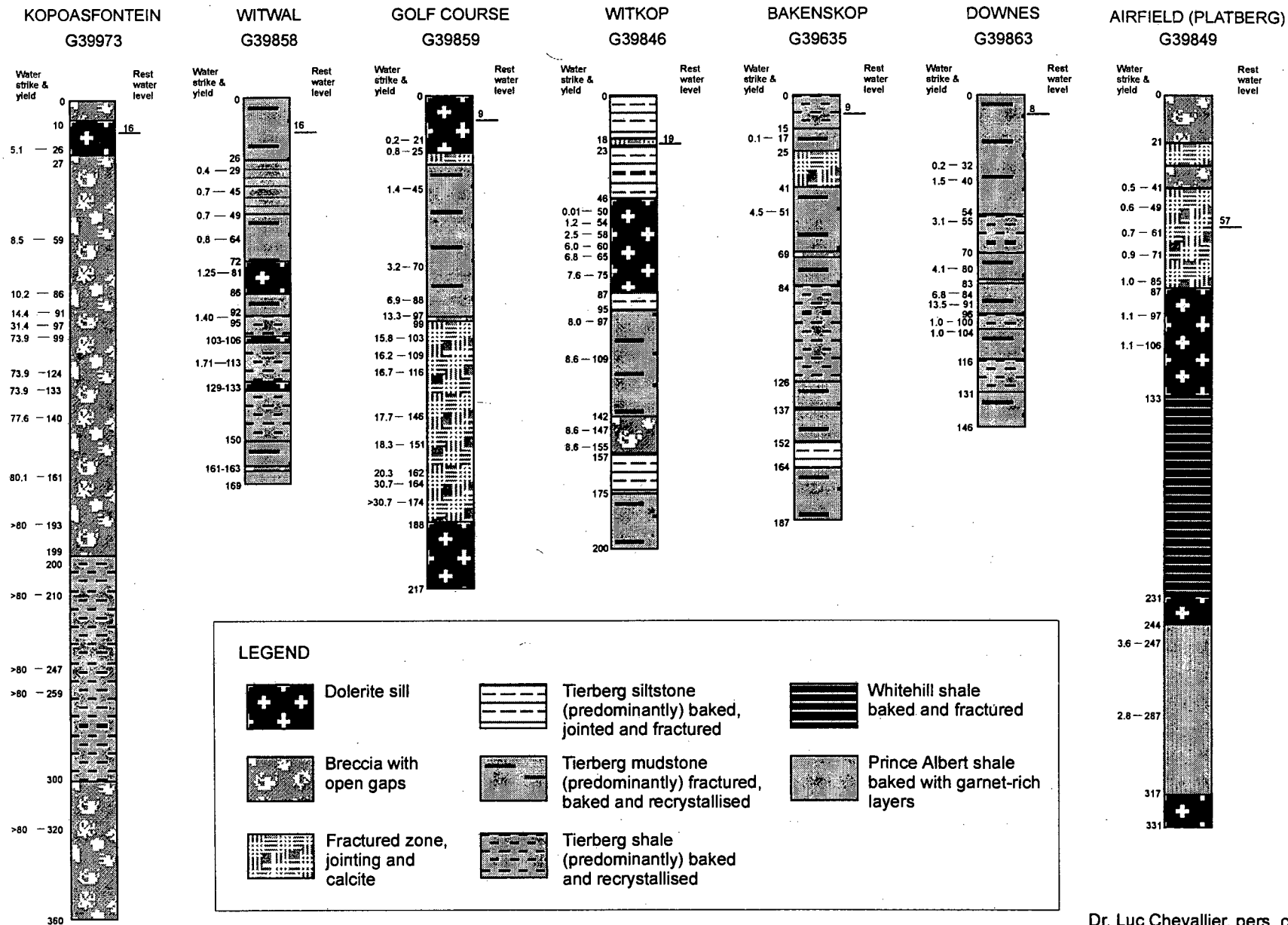
Borehole Identity (DWAF)	Breccia pipe	Purpose	Total Depth (m)	Equipped	Casing	Construction	Depth below surface to water strikes (m) and maximum blow yield (bracketed)	Date drilled	Source
					Plain (m) Slotted (m)	BH diameter Casing (mm)			
G39848	Airfield	not in use	91	capped	?	?	?	1992	1, 3
G39849	Airfield	not in use	301	capped	?	?	?	1992	1, 3
G39980	Airfield (Platberg)	geological core	1000	capped	0 - 19 -	140 to 68	70-80,	1995/96	4

Information sources:

1. Field observations (1998 - 2000)
2. Woodford (1994)
3. National Groundwater Database (Department of Water Affairs and Forestry)
4. Chevallier (pers.comm.)

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Dr. Luc Chevallier, pers. comm., 1999.

Figure A.2. Geological logs for percussion drilled boreholes in breccia pipes near Calvinia.

APPENDIX B
SAMPLING TRIP REPORTS

B1 Field trip 1: 7 - 8 July 1999

Five boreholes fitted with fixed pumping equipment were sampled during the first sampling trip. This included 73 and KF1 at the research site, 59 at the Golf Course, 61 at Witwal farm and an unlabelled borehole on the farm Jaagvlakte, assigned the name JV1. Wind pumps abstract water from KF1 and JV1 while 73, 59 and 61 are equipped by the Calvinia Municipality with submersible pumps. The pump at 73 was installed at 127 m below surface.

Borehole pumps at 59 and 61 were each run for 30 minutes and the electrical conductivity readings monitored until they stabilised, before taking any samples. At the time of sampling, boreholes KF1, 73 and JV1 were in use, and purging of stagnant groundwater was not required. KF1 was being pumped into a reservoir for livestock watering, JV1 for water supply to the farmstead and 73 was being used to dewater the breccia pipe for artificial recharge experiments.

Pumping at borehole 73 began in June 1999 and 1600 m³ of groundwater was removed by 16 June 1999, dropping the water table in the pipe from its rest level of 15 m to 34 m below surface. The pump was then stopped and restarted on 7 July 1999 when it was run continuously for approximately 30 hours before collecting the water sample. The water level in the breccia pipe, measured at 51A, using an electronic dipmeter, dropped from 33.5 m to 59.9 m below surface over this 30 hour period where a volume of 850 m³ was removed. At the same time, the water table outside the pipe, at borehole 53, was measured at 29.4 m below surface.

Field parameters including temperature, pH, alkalinity and electrical conductivity were measured at the wellhead at the time of sample collection. Temperature was measured with a calibrated mercury thermometer and pH and electrical conductivity using portable Radiometer field instruments. These instruments were set to the measured water temperature and calibrated in the field using pH 6.86 (CSIR¹ phosphate buffer) and pH 8.96 or pH 10.0 (BDH) buffers and 0.01M

¹ Calibration solutions made up by CSIR Water Programme Analytical Laboratory

KCl electrolyte solution (CSIR). Measurements were taken with the electrodes suspended in flowing groundwater that was pumped into a clean, open 5 L plastic bucket. Readings were recorded once these had stabilised. Field alkalinity was measured by potentiometric titration of a 20 mL water sample with 0.01 M HCl immediately after sample collection using the preselected end point method for total alkalinity (Appendix C). The pH meter was recalibrated using pH 4.0 and pH 6.86 (CSIR) buffers for the titration.

Groundwater samples for laboratory analyses were collected in clean, unused, 250 mL plastic screw cap bottles, which were first rinsed at least three times with the water to be collected. Untreated samples were collected for major and minor ionic constituents and stable isotopes by filling the bottles to the brim and sealing tightly to create as little air head space as possible. One bottle from each borehole was treated with 4 drops of HgCl_2 solution to retard microbiological activity which could affect the concentration of nutrient anions. A separate 250 mL sample was filtered in the field through a $0.45\mu\text{m}$ microporous membrane filter using a Millipore syringe apparatus and acidified with 0.2 mL trace element grade 6M HNO_3 to preserve trace metals for analysis. Filtered samples ($0.45\mu\text{m}$) were also collected in 25 mL glass bottles, to avoid contamination by plastics, and poisoned with a drop of HgCl_2 to arrest biological degradation of dissolved organic carbon. Sample blanks were also prepared by adding the preservatives HgCl_2 or HNO_3 to deionised water under the same conditions. Samples were stored and transported in a cool box with ice packs for a maximum of 48 hours until they reached the laboratory and then refrigerated at 4°C until analysis.

B2 Field trip 2: 18 August 1999

Field measurements of physical and chemical parameters in boreholes 53, 54B, and 55 were made in August 1999 using a HydroLab® MiniSonde® 4a water quality multiprobe which could be lowered down the boreholes to log water quality profiles. The pump at borehole 73 was in operation at this time and an unfiltered, untreated water sample was collected by the author from borehole 73, after 1 hour of pumping, for analysis at the CSIR analytical laboratories. No other water samples were collected during the depth profiling exercise.

The multiprobe has temperature and pressure sensors and electrodes for the measurement of dissolved oxygen, redox potential, pH and electrical conductivity. A Freshflow™ circulator is used to stir the water for improved reproducibility of readings. The instrument is capable of collecting data at depths from 0 to 200 m below the water table.

The multiprobe was calibrated in the laboratory using pH 6.86 and pH 9 (CSIR) buffer solutions, 0.01M KCl electrolyte and redox buffers made from hydroquinone solutions at pH 4 and 9 (CSIR). These buffers were used to check the calibration again in the field before measurement. Dissolved oxygen was calibrated in air at the site for atmospheric pressure at the altitude of the borehole, 1060 m above sea level. The multiprobe was connected to a portable computer and programmed to collect readings at 30 second intervals. The probe was then lowered on a nylon rope to the water table and allowed to descend a fixed length after every 1 minute interval. In this way duplicate readings were collected at each depth interval down the borehole. The probe was then recovered and the data file downloaded to a portable computer.

When the depth profiles were taken, 11 970 m³ of groundwater had been dewatered from the breccia pipe and the water level at 51A and 54B was 94.7 and 94 m below ground level respectively. Since the total depth of 51A is 108 m, the water column in this borehole was too short for sampling, but borehole 54B was used to collect a 40 m depth profile at 2 m intervals inside the breccia pipe. The water table at the edge of the breccia pipe was then at 59.4 m below surface and a 90 m depth profile of borehole 55 was collected from 60 m to 150 m below ground level, using a 5 m interval between readings. Outside the pipe at borehole 53, the water table was measured at 30 m below surface. This represents a very steep 65 m drop in the water table over a distance of only 300 m between 51A and 53, caused by the pumping at 73, indicative of the very low hydraulic conductivity between the two boreholes. A 100 m profile was recorded at 5 m intervals from 30 to 130 metres below surface down borehole 53.

B3 Field trip 3: 17 - 18 November 1999

By the time of the November sampling trip, the pump at 73 had been removed to attend to a blockage in the borehole. No abstraction from the breccia pipe occurred at this time. The water table at 51A had recovered to only 90 m below surface after the earlier dewatering had removed

22 000 m³. A maximum water table depth of 115.5 m below surface had been reached one month previously, when the water table intercepted the pump cut-off level. The level of 90 m below ground surface was too deep for sample collection at 73 with the available equipment. The water table was measured at 61 m below surface at the edge of the breccia pipe (borehole 55) and 32 m below surface outside the pipe (borehole 53).

Water samples were collected from boreholes 53 and 55 at the research site and other breccia pipe boreholes 62 at the Golf Course, 58 and 60 at Witwal, and 57 at Bakenskop using a 1.5 litre teflon bailer with a ball valve mechanism, since no pumping equipment is installed at these holes. The bailer and sample bottles were rinsed several times with the water to be sampled, but no purging of the boreholes is feasible with this grab sampling method. This reduces the reliability of the samples as an accurate reflection of the aquifer chemistry. Borehole 60 was not capped at the time of sampling and appeared to have been contaminated by a dead animal, so this sample was discarded. Borehole 59 at the Golf Course and borehole 61 were also sampled during this sampling trip, using the installed pumping equipment.

Temperature and pH were measured at the wellhead, following the same calibration procedure as for field trip 1 in July 1999, but without the water flowing during measurement for the bailed samples. Electrical conductivity measurements were also taken, but were later rejected when a large discrepancy was found between these values and those measured with the more accurate laboratory meter. Unfiltered, filtered, poisoned and acidified samples were collected in the same manner as for the first sampling trip. In addition, samples were prepared to preserve sulphide ions for iodometric titration. This involved addition of 10 drops of a 0.1M zinc acetate solution to a 250 mL unfiltered groundwater sample, followed by pH adjustment, adding 2 drops of 0.1 M NaOH.

APPENDIX C
ANALYTICAL METHODS AND DATA QUALITY

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C.1 Analysis of aqueous solutions

C.1.1 pH and electrical conductivity

Laboratory measurements of pH in groundwater samples were made using a Metrohm combination glass calomel electrode and Metrohm 691 pH meter or a Radiometer combination pH electrode connected to a DTS8000 multi-titration system. Electrical conductivity (EC) was measured using a Crison Micro CM 2201 meter, conductivity probe and automatic temperature sensor. Portable Radiometer instruments were used in the field at Calvinia, with the exception of down-borehole logging where a Hydrolab MiniSonde 4a multiprobe was employed.

Apophyllite dissolution studies were conducted in several different laboratories in Cape Town, Stellenbosch and Boulder and the measurement of pH was made with the available instrumentation in each case. All reference electrodes were filled with a solution of KCl, with the exception of the preliminary dissolution studies (Section 5.7.2) in the Chemistry Department, UCT, where a 0.1M NaCl solution was used.

Principle

The pH of a solution is a measure of the hydrogen ion activity $\alpha(\text{H}^+)$ in solution:

$$\text{pH} = -\log \alpha(\text{H}^+) \dots\dots\dots (\text{C.1})$$

The glass membrane electrode used to measure pH generates an electrical potential in response to the H^+ activity in solution. When combined with a reference electrode of known constant potential, the potential difference between the two electrodes can be measured by a potentiometer (pH meter) to determine the solution pH. Combination electrodes have a glass electrode and reference electrode combined in one probe. The pH is measured relative to the known H^+ activity of one or more pH buffer solutions which are used to calibrate the pH meter.

Electrical conductivity, (EC), or specific conductance, is the reciprocal of the electrical resistivity of a solution. The more ions a solution contains, the lower its resistivity and the higher its conductivity. Electrical conductivity is, therefore, a convenient approximate way to measure

salinity. Electrical conductivity is measured using a conductivity cell consisting of two electrodes of known surface area and separation, from which a cell constant is calculated. The cell constant of the Crison conductivity cell was 1.03.

Procedure

Where the pH meter was not equipped with internal temperature compensation, the instrument was first set to the measured solution temperature. All pH meters were calibrated using standard buffer solutions (Metrohm, Radiometer, BDH or CSIR buffers) that bracketed the expected pH range of the samples, following the manufacturers' instructions. Buffers were equilibrated to the same temperature as the samples before use. The calibration slope reported was always greater than 0.92.

A small volume of unfiltered water was decanted into a clean vessel and the pH probe immersed in the sample to a depth great enough to cover the glass bulb. For dissolution batch test solutions, the pH probe was inserted directly into the reaction vessel in most instances. The sample was swirled gently to ensure homogeneity while the reading stabilised. The pH was recorded once a stable signal had been reached.

Calibration of the laboratory and field electrical conductivity meters was checked with a 0.01M KCl solution, using the tabled conductivity values in Standard Methods (Clesceri *et al.*, 1998). If necessary, the cell constant was adjusted to calibrate the instruments. The Crison laboratory instrument has a built-in temperature compensation feature and reports the electrical conductivity at a reference temperature of 20°C. The conductivity probe was immersed in a small volume of unfiltered water to a depth great enough to cover the conductivity cell. The EC meter was operated in continuous mode and the measurement recorded once the reading remained constant for ± 20 seconds. The sample was gently swirled to ensure homogeneity while the reading stabilised.

Sources of error

Standard Methods for the Examination of Water and Wastewater (Clesceri *et al.*, 1998) reports the following interferences with pH measurement:

- ▶ Reactions with sediment, hydrolysis and oxidation in the sample bottle may alter the

laboratory measured pH from that at the time of collection.

- ▶ Loss of dissolved gases, absorption of laboratory fumes, and precipitation of calcium carbonate or other salts may also change the pH appreciably.
- ▶ Significant error can result if the temperature of the buffers and samples differ appreciably (more than 5°C).

Turbidity, colour, organic or colloidal material, oxidising and reducing substances do not interfere with the accuracy of pH measurement.

Precision of the methods

Duplicate pH readings were taken for all water samples, and in some cases a third reading was taken using a different pH meter. All pH data in the thesis is reported as the mean value of two or more readings. Table C.1 reports precision data for the measurement of pH in the Calvinia groundwater samples. Analysis of a test sample by 34 laboratories resulted in a standard deviation of 0.12 for a sample of mean 8.26 pH units (Clesceri *et al.*, 1998).

Table C.1 Precision data for replicate analyses of pH.

Sample	Reading 1 Radiometer ^a	Reading 2 Metrohm ^b	Mean	Standard Deviation	Relative standard deviation (%)
73	9.71	9.75	9.73	0.03	0.3
59	7.53	7.61	7.57	0.06	0.8
61	8.42	8.45	8.44	0.02	0.3
KF1	7.29	7.35	7.32	0.04	0.6
JV1	9.06	9.11	9.09	0.04	0.4
61	8.95	8.88	8.92	0.05	0.6
60	8.36	8.34	8.35	0.01	0.2
58	9.04	9.02	9.03	0.01	0.2
59	7.24	7.23	7.24	0.01	0.1
62	7.42	7.34	7.38	0.06	1.0
57	7.53	7.5	7.52	0.02	0.3
55	9.8	9.8	9.80	0.00	0.0
53	7.97	7.9	7.94	0.05	0.6

^a Metrohm 691 pH meter calibrated with Metrohm pH 4 and pH 7 buffers using autocalibrate routine.

^b Radiometer pH meter calibrated manually with Metrohm pH 7 and BDH pH 9 buffers.

Electrical conductivity measurements on the groundwater samples were also taken in duplicate. Precision for the measurements is reported in Table C.2. The relative standard deviation for one of the repeat measurements of sample 61 is very high, indicating that one of the readings is probably in error. The precision of commercial EC meters is commonly between 0.1 and 1.0%,

and a reproducibility of 1 to 2% is expected after an instrument has been calibrated (Clesceri *et al.*, 1998).

Table C.2 Precision data for replicate analyses of EC.

Sample	Reading 1	Reading 2	Mean	Standard Deviation	Relative standard deviation (%)
73	88.6	87.6	88.1	0.71	0.8
59	160	167.3	163.7	5.2	3.2
61	157	134.5	145.8	15.9	10.9
JV1	76.1	78	77.1	1.3	1.7
KF1	117	119.9	118.5	2.1	1.7
62	224	224	224.0	0.0	0.0
59	253	251	252.0	1.4	0.6
61	91.7	92.5	92.1	0.6	0.6
60	62.5	63	62.8	0.4	0.6
58	62	61.8	61.9	0.1	0.2
57	334	335	334.5	0.7	0.2
55	67.3	67.4	67.4	0.1	0.1
53	86.1	86.5	86.3	0.3	0.3

C.1.2 Alkalinity

Alkalinity was determined on unfiltered water samples using either the stepwise titration method for low alkalinity samples devised by Gran (1952) or potentiometric titration to a preselected end point pH following Method 2320B 4c in Standard Methods (Clesceri *et al.*, 1998). Phenolphthalein alkalinity was determined by titration to pH 8.3 if the original pH of the sample was above this value and total alkalinity to pH 4.5. An automatic Radiometer DTS8000 titration system comprising a TTT85 titrator with pH combination electrode and ABU autoburette was used for the titrations. The acid titrant was 0.01 M HCl prepared from Merck Titrisol standard solution ampoules using deionised water. Field alkalinity titrations were performed by manual titration to a preselected end point of pH 4.5 using a portable Radiometer pH meter and a field burette.

Principle

Total alkalinity is defined as the equivalent sum of the bases that are titratable with strong acid. In most natural water systems, Total alkalinity is given by the following expression (Drever, 1997):

$$\text{Alkalinity} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{B(OH)}_4^-} + m_{\text{H}_2\text{SiO}_4^{2-}} + m_{\text{HS}^-} + m_{\text{organic anions}} + m_{\text{OH}^-} - m_{\text{H}^+} \quad (\text{C.2})$$

where m_i is the molar concentration of species i .

Gran titration function

Titration functions are used to bypass the difficulty of identifying the true equivalence point pH. In the pH region below an equivalence point there is a region in which the expression formulated by Gran (1952) plots linearly with respect to the volume of standard strong acid added. If the linear portion of the plot is extrapolated to a function value of zero, the corresponding volume of acid added will give the volume that would have been needed to titrate to the equivalence point. This gives the alkalinity initially present in the sample (Loewenthal *et al.*, 1986).

In natural terrestrial water systems, the dominant weak acid-base system is the carbonate system, existing as H_2CO_3 , HCO_3^- and CO_3^{2-} ions in solution. The total alkalinity equation is therefore:

$$\text{Alkalinity} = m_{\text{HCO}_3^-} + 2m_{\text{CO}_3^{2-}} + m_{\text{OH}^-} - m_{\text{H}^+} \quad \dots\dots\dots (\text{C.3})$$

In the region below the total alkalinity equivalence point, the concentrations of CO_3^{2-} and OH^- are negligible and $m_{\text{H}^+} \gg m_{\text{HCO}_3^-}$ so that equation C.3 approximates to:

$$\text{Alkalinity} \approx -m_{\text{H}^+} \quad \dots\dots\dots (\text{C.4})$$

After adding v ml of strong acid in the region between $3 > \text{pH} > 4$,

$$\text{Alkalinity} = \frac{(v_{eq} - v) C_a}{v_i + v} \quad \dots\dots\dots (\text{C.5})$$

where C_a is the molarity of the standard strong acid titrant;

v_i is the initial volume of the sample; and

v_{eq} is the volume of strong acid required to titrate the sample to the equivalence point.

From equations C.4 and C.5:

$$m_{H^+}(v_i + v) = (\widehat{v_{eq}} - v) C_a \quad \dots\dots\dots (C.6)$$

Converting to H^+ activity by multiplying both sides of equation C.6 by the H^+ activity coefficient, γ_{H^+} , allows the equation to be expressed in terms of pH, i.e.

$$FI = 10^{-pH}(v_i + v) = (v_{eq} - v) C_a \gamma_{H^+} \quad \dots\dots\dots (C.7)$$

The Gran Titration Method thus involves the addition of strong acid to a pH below the equivalence point, followed by small increments of added acid for which the volume added, v , and pH measured are recorded. These are substituted into equation C.7 to give values for FI, which are then plotted against the total volume of strong acid added.

The straight line obtained is then extrapolated back to $FI = 0$, and the corresponding volume of strong acid added at this point determined. This is the equivalence volume for the total alkalinity end point, from which the alkalinity of the sample is calculated using the equation:

$$Alkalinity = \frac{v_{eq} C_a}{v_i} \times 100 \text{ (mg/L as } CaCO_3) \quad \dots\dots\dots (C.8)$$

Procedure 1: preselected end point method

An end point pH of 4.50, recommended for routine or automated analyses, or when silicates are suspected, was chosen for this method (Clesceri *et al.*, 1998). Twenty millilitre unfiltered water samples were measured by pipette into a clean glass beaker for field titrations and 10 mL samples into plastic titration vessels for laboratory titrations. A teflon-coated stirrer bar was placed in each sample and a magnetic stirrer used to agitate the samples during the titration. Samples were titrated directly to pH 4.50 using 0.01M HCl, with the addition of smaller acid aliquots as the end point was approached. Samples with pH greater than 8.3 were first titrated to this end point to

determine the phenolphthalein alkalinity. Deionised water was used for a blank titration in the laboratory following the same method. The alkalinity of the deionised water blank was subtracted from the calculated sample alkalinities.

Procedure 2: Gran stepwise method

Ten millilitre aliquots of each sample were titrated against 0.01 M HCl with constant stirring by a magnetic stirrer. The samples were titrated down to a pH of 4.0, followed by stepwise increments of -0.2 pH units down to a pH of 3.2. Deionised water was used for a blank titration following the same method. The alkalinity of the deionised water blank was subtracted from the calculated sample alkalinities.

Sources of error

- ▶ The measured alkalinity value may vary significantly with the end point pH used. Gran functions are intended to overcome the difficulty of identifying the point at which all acid neutralising capacity of the sample is expended.
- ▶ Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes can react with additions of standard acid and contribute excess alkalinity.
- ▶ Anions of weak organic and inorganic acids other than the carbonate system also contribute to alkalinity. These introduce error if they are not considered when converting alkalinity measurements to carbonate or bicarbonate concentrations.
- ▶ Precipitation in the sample bottles between the time of sample collection and analysis may lead to underestimation of alkalinity.
- ▶ Soaps, oily matter, suspended solids or precipitates may coat the glass electrode and cause a sluggish response (Clesceri *et al.*, 1998). Since alkalinity titrations involve pH measurement, they are also subject to the potential sources of error in the measurement of pH.

Precision of the methods

Clesceri *et al.* (1998) claim that no general statement can be made about the precision of alkalinity determinations, because of the great variation in sample characteristics. The precision of the methods is expected to be much greater than the uncertainties involved in sampling and

sample handling before the analysis.

Two water samples analysed in triplicate show that the precision of the preselected end point method using the automated titration is very good (Table C.3). Gran titrations did not yield significantly different results (Table C.4) from the pH 4.5 method for the higher alkalinity groundwater samples from the first sampling run (July 1999) and so only the more efficient preselected end point method was used for duplicate analyses of the second sample set (November 1999).

Table C.3. Precision data for triplicate alkalinity titrations to preselected pH 4.5 end point.

Sample	Titration 1 mg/L as HCO_3^-	Titration 2 mg/L as HCO_3^-	Titration 3 mg/L as HCO_3^-	Mean	Std. dev.	RSD (%)
61	216	219	215	216	0.58	0.3
KF1	319	321	320	320	0.91	0.3

Table C.4. Comparison of alkalinity data obtained using a preselected end point method and the Gran function calculation.

Sample	Preselected mg/L as HCO_3^-	Gran method mg/L as HCO_3^-	Sample	Preselected mg/L as HCO_3^-	Gran method mg/L as HCO_3^-
73	181	182	KF1	320	318
59	270	270	JV1	233	232
61	216	215	Town	36	34.1

C.1.3 Ion chromatography

Principle

Ion chromatography is a liquid-solid chromatographic method for the separation of ionic analytes which are detected conductimetrically. Dilute electrolyte solutions are injected into a liquid eluent stream, which is pumped through a column containing a solid stationary phase. The ionic components of the sample progress through the column at different rates and therefore enter the detector at different times.

Procedure

Major cation and anion concentrations in all groundwater samples and the solutions from batch

tests 1 and 3 were measured by ion chromatography (IC) using Dionex equipment. Ammonium analyses for batch test 2 were also performed by this technique. Samples were filtered through $0.45\mu\text{m}$ microporous membrane filters and groundwater samples were diluted with deionised water to attain an EC below 10 mS/m before analysis. Dionex Ongaard-P polyvinylpyrrolidone cartridges were used before injection to remove organic compound which might foul the column. These procedures could have caused removal of nutrients and dilution or adsorption of certain constituents to below detection levels.

Cation analysis was calibrated for the species Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} using standard solutions prepared by the author from dried, analytically pure chloride salts with routine checks using sequential dilutions of a Dionex certified multi-cation standard solution. Dionex CS12A Separator and CG12A Guard columns were used with 11 mM H_2SO_4 eluent at a flow rate of 1 mL/min and sample loop volume of $25\mu\text{L}$ for a run time of 15 minutes for the analyses. Detection was by a Dionex CD20 electrical conductivity detector, using a CSRS-I cation self-regenerating suppressor to suppress eluent conductivity.

Anion analysis was calibrated for the species F^- , Cl^- , Br^- , NO_2^- , NO_3^- , PO_4^{3-} and SO_4^{2-} using standard solutions prepared by the author from dried, analytically pure sodium salts with routine checks using sequential dilutions of a Dionex certified multi-anion standard solution. Ten microlitre samples were injected into a Dionex IonPac AS14 column and eluted with Na_2CO_3 (3.5 mM)/ NaHCO_3 (1.0 mM) solution at a flow rate of 1.2 mL/min for a run time of 12 minutes. Detection was by electrical conductivity (Method 4110, Clesceri *et al.*, 1998) using an ASRS-II AutoSuppression system to suppress eluent conductivity. Samples preserved in the field were used for anion determination, with duplicate untreated samples run for Cl^- determination which is affected by the addition of HgCl_2 .

Sources of error

Any ionic substance that produces a detector response, and has a retention time coinciding with that of an analyte, or near enough to cause peak overlap, may interfere with the determination. Low molecular weight organic acids, such as formic acid, may interfere with the determination of fluoride and chloride, for example. Also a high concentration of any one ion may interfere with the resolution, and sometimes the retention, of others (Clesceri *et al.*, 1998). Most samples

require dilution for determination of major ions by ion chromatography, which can introduce additional error.

Limit of detection

Generally, the minimum detectable concentrations for anions by this method are near 0.1 mg/L for Br^- , Cl^- , NO_3^- , NO_2^- , PO_4^{3-} and SO_4^{2-} using a 100 μL sample loop and 10 $\mu\text{S}/\text{cm}$ full scale setting on the conductivity detector. Lower detection limits may be obtained with electronic peak area integration and a larger scale setting (Clesceri *et al.*, 1998).

Accuracy of the method

Analyses of Dionex standard cation and anion solutions were used to measure the accuracy of the IC method once the instrument had been calibrated from stock solutions. The results are displayed in Table C.5 for the July and October 1999 analyses.

Anion data gives a better fit for calibration curves than cation data and produces more accurate readings in July 1999 and the opposite in October 1999. Magnesium and calcium data were frequently found to be of poor quality and most calcium and magnesium analyses were repeated using an atomic emission or absorption technique (ICP-AES or FAAS). The nutrient anions, NO_2^- , NO_3^- and PO_4^{3-} were also problematic and new stock solutions were prepared before analysing the water samples whenever possible. Phosphate analyses were repeated by colorimetry.

A groundwater sample from borehole 73 was submitted to the CSIR water laboratory in Stellenbosch for analysis by atomic absorption spectrophotometry (FAAS) and wet chemical techniques. The results are compared with those obtained by IC in Table C.6. Data accuracy is poor where solute concentrations are low, especially for cations e.g. K^+ , NH_4^+ , Ca^{2+} . This is partly due to the dilution of the samples needed to lower the sodium and chloride concentrations to avoid damaging the IC columns. Ion chromatography is not an ideal method for the analysis of samples with vastly differing ion concentrations. Anion data measured by IC appears to be of better quality than cation data.

Table C.5. Calibration data for ion chromatographic method used for analysis of groundwater samples in July 1999 and batch test samples in October 1999. R² values describe the “goodness of fit” of the calibration samples to a linear or quadratic function used to calculate sample concentrations from peak areas. The accuracy of the measurements is described by the percentage difference between measured concentrations and expected concentrations of standard solutions.

July 1999							October 1999					
Cations	Calibration	R ²	Range ^a (mg/L)	Expected (mg/L)	Measured (mg/L)	Diff. %	Calibration	R ²	Range ^a (mg/L)	Expected (mg/L)	Measured (mg/L)	Diff. %
Li	linear	0.997	0 - 5	1.25	1.31	2.3	linear	1.000	0 - 5	0.526	0.51	-3.0
Na	linear	0.998	0 - 25	6.25	6.38	1.0	linear	1.000	0 - 25	1.99	2.06	3.5
NH ₄	quadratic	0.994	0 - 5	1.25	1.44	7.1	quadratic	1.000	0 - 5	2.48	2.36	-4.8
K	linear	0.963	0 - 5	1.25	1.00	-11	linear	0.997	0 - 5	4.97	4.93	-0.8
Mg	quadratic	0.997	0 - 5	0.59	0.76	13	linear	0.999	0 - 5	2.45	2.18	-11
Ca	quadratic	0.996	0 - 25	6.25	6.38	1.0	linear	0.997	0 - 25	5.29	6.94	31
Anions	Calibration	R ²	Range ^a (mg/L)	Expected (mg/L)	Measured (mg/L)	Diff. %	Calibration	R ²	Range ^a (mg/L)	Expected (mg/L)	Measured (mg/L)	Diff. %
F	linear	0.999	0 - 10	1.25	1.27	0.6	linear	0.999	0 - 10	0.985	0.849	-14
Cl	linear	0.999	0 - 37.5	4.69	4.41	-3	linear	0.998	0 - 37.5	1.485	1.306	-12
NO ₂	linear	0.999	0 - 20	2.5	2.75	4.7	linear	1.000	0 - 20	0	0	n.d.
Br	linear	0.999	0 - 10	1.25	1.31	2.2	linear	0.999	0 - 10	0	0	n.d.
NO ₃	linear	0.998	0 - 20	2.5	3.05	9.9	linear	0.997	0 - 20	5	3.339	-33
PO ₄	linear	0.998	0 - 20	2.5	3.23	13	linear	0.998	0 - 20	7.55	7.591	0.5
SO ₄	linear	0.998	0 - 40	5	4.99	-0.2	linear	0.996	0 - 40	7.55	7.829	3.7

^a Range of concentrations for which the instrument was calibrated.

Table C.6. Comparison of IC results for sample 73 with those obtained by other methods at the CSIR laboratory.

Cations	IC (mg/L)	Other (mg/L)	Diff (%)	Anions	IC (mg/L)	Other (mg/L)	Diff (%)
Na	155	165	3.1	F	9.9	11	5.3
NH ₄	2.7	0.8	-54	Cl	98	102	2.0
K	0.3	0.6	33	NO ₂ + NO ₃	<0.1	<0.1	n.d.
Mg	1.4	1.2	-7.7	PO ₄	<0.1	<0.01	n.d.
Ca	13	3.4	-59	SO ₄	66	64	-1.5

Precision of the method

Repeatability of IC measurements was generally good, with a relative standard deviation of less than 5% for most measurements, except where concentrations were near the detection limit.

C.1.4 Fluoride ion selective electrode

The ion selective electrode (ISE) is preferred over the ion chromatography method for the determination of fluoride ion concentrations in solution. The technique was employed for repeat F⁻ analyses of the groundwater samples, analyses of NaOH fusions of apophyllite samples and analyses of the solutions from the second apophyllite batch test.

Principle

The fluoride selective electrode employs a laser-type doped lanthanum fluoride crystal across which a potential is established by fluoride solutions of different concentrations (Clesceri *et al.*, 1998).

Procedure

For the groundwater samples, fluoride standards of concentrations 1, 2, 5, 10 and 20 mg/L F⁻ were made up in deionised water from a 100 mg/L F⁻ stock solution of NaF. Five millilitres of a concentrated buffer (Orion TISAB III) was added to 50 mL of each standard in 100 mL glass beakers. Using these standards, a Corning 255 ion analyser was calibrated by an automatic 5-point calibration method to measure fluoride activity in mg/L. Fifty millilitre samples were then treated with 5 mL TISAB III buffer and the activity of fluoride in each solution measured

automatically by the ion analyser and electrode pair.

The TISAB III buffer contains an ionic strength adjustment buffer and CDTA (cyclohexylenediaminetetraacetic acid) complexing agent. The purpose of the buffer is to adjust the ionic strength of the solution and to complex ions which may interfere with the determination of fluoride. The buffer also contains acetic acid to produce an optimum pH (between 5 and 8) for fluoride measurement.

Smaller samples of 5 ml were used for the analysis of apophyllite solutions and the fluoride calibration range extended from 0.125 to 50 mg/L F^- concentrations. The fluoride electrode was directly coupled to a voltmeter in this case and a manual calculation was performed to convert millivolt readings to fluoride concentrations, using the linear relationship between the electrode response and the natural logarithm of fluoride ion activity. The readings showed good linearity over the calibration range, producing R^2 values between 0.994 and 0.999. Some deviation from the linear relationship was observed for the lower end of the concentration range (< 0.25 mg/L).

Sources of error

The fluoride electrode measures the activity of fluoride in solution, rather than concentration. However, the ionic strength adjustment buffer provides a constant ionic strength background, buffers the pH in a suitable range, and breaks up fluoride complexes, such that the activity closely approximates the concentration. Common interferences with fluoride determination include aluminium and iron complexes, OH^- and poorly ionised HF at low pH (Clesceri *et al.*, 1998). CDTA preferentially complexes interfering cations, while acetic acid/sodium acetate in the buffer keeps the pH between 5.3 and 5.5. This pH is unfavourable for HF and OH^- species. Clesceri *et al.* (1998) report a -0.1 mg/L error at 1.0 mg/L fluoride in the presence of 3.0 mg/L Al^{3+} . Alkalinity, chloride, phosphate and sulphate only interfere at concentrations above 7000 mg/L.

Limit of detection

The electrode method is suitable for fluoride concentrations from 0.1 to more than 10 mg F/L (Clesceri *et al.*, 1998). Below 0.1 mg F^- /L the calibration curve is non-linear.

Accuracy of the method

Analysis of a USGS reference water sample M102 by the ISE method gave a concentration of 1.11 mg/L. The reference value for this sample is 1.1 mg/L.

Precision of the method

Duplicate measurements were taken for some of the fluoride samples using the ISE technique. The data in Table C.7 shows the excellent reproducibility of these results.

Table C.7. Precision of fluoride measurements using the ion selective electrode.

Sample	Reading 1 (mV)	F ⁻ (mg/L)	Reading 2 (mV)	F ⁻ (mg/L)	Mean F ⁻ (mg/L)	Std. dev.	RSD (%)
M102	95.9	1.10	95.7	1.12	1.11	0.01	1.3
JL4_2	113.6	0.37	113.4	0.38	0.38	0.01	1.9
GJ2_2	43.7	10.5	43.7	10.5	10.50	0.00	0.0
KF7_2	122.9	0.24	124.1	0.23	0.24	0.01	3.0
PT10_2	116.6	0.32	116.5	0.33	0.33	0.01	2.2
GJ10_3	115.2	0.24	116.9	0.22	0.23	0.01	6.1
JL2_3	35.45	12.4	35.4	12.5	12.45	0.07	0.6
KF2_3	30.7	15.7	30.3	16.1	15.90	0.28	1.8
PT4_3	114.6	0.25	114.8	0.25	0.25	0.00	0.0
GJ7_4	125.7	<0.125	125.2	<0.125	n.d.	n.d.	n.d.
JL2_4	26.7	19.0	26.1	19.5	19.25	0.35	1.8
KF10_4	129.5	<0.125	127.9	<0.125	n.d.	n.d.	n.d.

C.1.5 Iodometric titration for sulphide

Principle

Iodine oxidises sulphide in acid solution. Iodine is added in excess to the sample and the unreacted iodine determined by back titration against a standard thiosulphate solution. In the presence of a starch indicator, the solution colour disappears once all the iodine has reacted.

Procedure

Groundwater samples collected during the November 1999 field trip were treated in the field by adding 10 drops of 0.1 M zinc acetate solution and 2 drops 0.1 M NaOH to 250 mL samples to preserve dissolved sulphide for analysis. In the laboratory, the treated samples were filtered to trap the ZnS precipitate. The supernatant liquid was discarded and the filter returned to the original sample bottle, to which 100 mL deionised water and 2 mL 6N HCl were added. The

samples were then shaken for 30 minutes to dissolve the precipitate. A back¹ titration with 0.025 N sodium thiosulphate was performed after addition of excess standardised 0.0186 N iodine solution following the iodometric method (Method 4500-S²⁻ F, Clesceri *et al.*, 1998). A field blank was treated and analysed in the same manner as the groundwater samples. Sample 61 was the only sample where concentrations detected were above those of the blank. All other samples are reported as being below the method detection limit.

C.1.6 Ascorbic acid colorimetric technique for phosphate

Principle

Ammonium molybdate and potassium antimonyl tartrate form phosphomolybdic acid on reaction with orthophosphate in acid medium. This heteropoly acid is reduced to an intensely coloured molybdenum blue by reaction with ascorbic acid and can be determined spectrophotometrically. Analysis of unfiltered water samples gives total reactive phosphorus concentrations.

Procedure

Phosphate analysis of groundwater samples, originally determined by ion chromatography, was repeated using an ascorbic acid colorimetric method (Method 4500-P E, Clesceri *et al.*, 1998), because of the poor accuracy of the IC determinations. Calibration standards of 0.1, 1, 2 and 5 mg P/L were used.

Four millilitres of the colour reagent was added to 25 mL unfiltered groundwater samples and the absorbance at 880 nm read after 15 minutes of colour development using a Sequoia-Turner 340 spectrophotometer. Two drops of 5N H₂SO₄ were initially added to high-pH samples 73 and JV1. All samples were outside the calibration range, measuring below 0.1 mg/L PO₄³⁻ as P and are reported as being below the detection limit.

C.1.7 Molybdosilicate colorimetric technique for silicon

A colorimetric technique was used for the analysis of molybdate-reactive silica (monomeric silica) in groundwater samples and solutions from dissolution batch tests 1 and 3. Silica standards prepared from sodium metasilicate salts were analysed by ICP-AES as an independent measure

of their concentrations. Other silicon analyses from batch test 2 and apophyllite digestions were also conducted by ICP-AES.

Principle

Ammonium molybdate at pH approximately 1.2 reacts with silica to form coloured heteropoly acid complexes. The intensity of the yellow colour that develops is proportional to the concentration of the molybdate reactive silica.

Procedure

Standard solutions of 1, 2, 5, 10 and 20 mg/L silica were prepared by appropriate dilution of a 1000 mg/L SiO₂ stock solution (Na₂SiO₃ · 5H₂O). Fifty millilitre aliquots of the standards and samples were treated with 2 mL ammonium molybdate reagent and 1 mL 1+1 hydrochloric acid, followed after 7 minutes by 2 mL oxalic acid, as set out by Clesceri *et al.* (1998) (Method 4500-Si D). Smaller samples were used for batch test solutions and the reagents scaled down accordingly. Samples at high pH required additional HCl for colour development. Where samples gave adsorption values above the calibration range, the measurements were repeated after appropriate dilution.

The absorbance of the yellow colour that developed was measured at a wavelength of 410 nm after a further 5 minutes of colour development using a Sequoia-Turner 340 spectrophotometer. Distilled water was used to set the spectrophotometer zero and a blank reading was taken from 50 mL distilled water with the same colorimetric reagents added. The blank should account for any silicon introduced by the reagents or glassware.

Silicon concentrations were calculated from a linear function obtained using the calibration standards, including a correction for the change in volume caused by the addition of the reagents. Good linearity was found for the concentration-absorbance relationship over the calibration range from 0 - 20 mg/L, with R² values ranging from 0.998 to 1.000 for the various analytical runs. A 50 mg/L standard was rejected since the calibration deviated from linearity at this high concentration.

A Merck certified 1000 mg Si/L standard in 5M NaOH was used for later analyses after ICP-AES

showed the original standards to be inaccurate. Silicon data from the first groundwater sampling run was corrected using the new measured concentrations of the laboratory prepared standards.

Sources of error

- ▶ Glassware and reagents can both contribute silica. As far as possible, silica-free reagents and distilled water were used and solutions and samples stored in plastic bottles.
- ▶ Tannin, large amounts of iron, colour, turbidity, sulphate and phosphate may interfere with silica determination by this method. The addition of oxalic acid decreases interference by phosphate and tannin.
- ▶ Phosphate also produces coloured heteropoly acids in contact with ammonium molybdate, but the addition of oxalic acid is intended to break down the molybdophosphoric acids and prevent their interference.

Limit of detection

Approximately 1 mg SiO₂/L can be detected (Clesceri *et al.*, 1998).

Precision of the method

Repeat analyses of four water samples showed good reproducibility of the silicon measurements by this technique (Table C.8).

Table C.8. Precision data for analysis of silicon in groundwater samples by the molybdosilicate method.

Sample	Measurement 1 (mg Si/L)	Measurement 2 (mg Si/L)	Mean (mg Si/L)	Std. dev.	RSD (%)
57	8.1	8.0	8.1	0.02	0.2
61	7.3	7.1	7.2	0.12	1.6
60	10.0	10.1	10.0	0.05	0.5
58	9.6	9.6	9.6	0.00	0.0

C.1.8 Phenanthroline colorimetric technique for iron

Groundwater samples collected in July 1999 were analysed for total dissolved iron using a colorimetric technique. The samples were filtered through 0.45 µm in the field and acidified by the addition of 200µL concentrated reagent grade HNO₃ per 250 mL sample. A blank was

prepared by addition of the same acid to deionised water in one of the sample bottles. Iron redox states could not be determined since the samples were only analysed two weeks after collection.

Principle

Ferrous iron forms an orange-yellow complex with phenanthroline in an ammonium acetate/acetic acid buffer, enabling the concentration to be determined colorimetrically from the absorbance at 510 nm

Procedure

The analytical procedure follows method 3500-Fe D 4a) in Standard Methods (Clesceri *et al.*, 1998). Standards of 1, 2, 5 and 10 mg/L Fe were used for calibration. Water samples and the field blank (25 mL each) were boiled to less than 10 mL in glass conical flasks after the addition of 1 mL HCl and 0.5 NH₂OH.HCl to reduce all iron to the ferrous form. The samples were decanted into 25 mL volumetric flasks and treated with 5 mL ammonium acetate/acetic acid buffer and 2 mL 1,10-phenanthroline solution, then filled to the mark with deionised water. The absorbance was read after 12 minutes colour development. The blank sample showed that some iron contamination was present in the acid or deionised water used in the procedure.

After blank correction, all samples fell close to the 0.1 mg/L detection limit of the technique and outside the range of the lowest calibration standard. Repeat analysis by ICP-AES also gave values <0.1 mg/L for all groundwater samples. The values reported in the thesis are taken from the more sensitive ICP-MS analysis.

C.1.9 Inductively coupled plasma - mass spectroscopy (ICP-MS)

Field-filtered (0.45µm) and acidified groundwater samples were used for trace element analysis by ICP-MS. The acid used was concentrated reagent grade HNO₃ supplied by the ICP-MS laboratory and added to the 250 mL water samples after filtration, using a 200 µL autopipette. A blank sample was also prepared from deionised water by adding the same HNO₃ reagent as was added to the filtered water samples on site. Analyses were performed on a Perkin-Elmer ELAN 6000 ICP-MS.

Principle

A high temperature argon plasma source is used to ionise sample atoms, which are passed through an interface into the source region of a quadrupole mass spectrometer and detected simultaneously by their different charge to mass ratios.

Procedure

Aliquots of each sample were diluted either 1:1 (samples with EC <10 mS/m) or 1:10 (higher EC samples) with 2% nitric acid to make up 30 mL. The 30 mL samples were then divided into two 15 mL replicates for analysis. Data reported for trace element concentrations is the mean value of the two measurements. The blank was analysed along with the other samples to account for any elements which may be contributed by the acid. Concentrations in the blank above 1 µg/L for Al and Zn were subtracted from the measured concentrations of the samples.

Sources of error

ICP-MS produces a relatively simple spectrum, with fewer opportunities for interference, compared with the complex optical spectra of atomic absorption or emission techniques.

- ▶ **Spectral interference:**

arises from ions other than the analyte ions (M^+) which form in the plasma from the plasma gas atoms or atmospheric gases. These complicate the ICP-MS spectrum. Examples of ions causing spectral interference are Ar^+ , Ar_2^+ , ArO^+ , ArH^+ , $M-Ar^+$, O^+ , O_2^+ , OH^+ , H_2O^+ , N_2^+ , MO^+ , $M-H^+$, $M-OH^+$ and doubly charged analyte ions.

- ▶ **Isobaric effects:**

arise from the overlap of molecular peaks with common analyte peaks e.g. $^{75}As^+$ and $^{40}Ar^{35}Cl^+$. Correction factors are applied to reduce these effects.

- ▶ **Matrix effects:**

Samples and standards were prepared in the same 2% HNO_3 to minimise matrix effects. Components in the matrix which ionise easily can suppress the analyte ionisation.

Accuracy and precision of the method

A NIST-1640 standard water sample of known concentration was analysed before and after the analytical run to check the accuracy of the results. The results presented in Table C.9 give the published values for the NIST standard, the measured concentrations and the mean and standard

deviation for the two measurements during the run. The percentage difference was calculated between the mean measured concentrations and the published data. Values for Al, Fe, Zn, and Pb differ by more than 10% from the certified concentrations. Relative standard deviations between the two readings were below 10% for all but Li.

Table C.9. Precision and accuracy data for ICP-MS analyses from determination of NIST-1640 standard solution. Data are in $\mu\text{g/L}$ unless otherwise specified.

Element	Reading 1	Reading 2	Mean	Std. dev.	RSD (%)	Published	Diff. (%)
Li	56	47.1	51.55	6.29	12.2	50.7	1.68
B	298	283	290.5	10.61	3.7	301.1	3.52
Al	64.9	62.1	63.5	1.98	3.1	52	22.12
Cr	38.2	38	38.1	0.14	0.4	38.6	1.30
Mn	122	119	120.5	2.12	1.8	121.5	0.82
Fe	43.4	43.4	43.4	0.00	0.0	34.3	26.53
Co	20.7	20.2	20.45	0.35	1.7	20.28	0.84
Ni	28.3	27.1	27.7	0.85	3.1	27.4	1.09
Cu	91.1	88.4	89.75	1.91	2.1	85.2	5.34
Zn	64.2	63.1	63.65	0.78	1.2	53.2	19.64
As	27.2	26.4	26.8	0.57	2.1	26.67	0.49
Se	21.7	22.3	22	0.42	1.9	21.96	0.18
Rb	2.14	2.08	2.11	0.04	2.0	2	5.50
Sr	125	122	123.5	2.12	1.7	124.2	0.56
Mo	47.7	47.7	47.7	0.00	0.0	46.75	2.03
Cd	23.2	23.3	23.25	0.07	0.3	22.79	2.02
Cs	0.2	0.18	0.19	0.01	7.4	n.d.	n.d.
Ba	149	147	148	1.41	1.0	148	0.00
Tl	0.049	0.055	0.052	0.00	8.2	n.d.	n.d.
Pb	33.1	32.4	32.75	0.49	1.5	27.89	17.43
U	0.83	0.81	0.82	0.01	1.7	n.d.	n.d.

C.1.10 Inductively coupled plasma - atomic emission spectroscopy (ICP-AES)

This technique was used for repeat analysis of Ca, Mg, Al, Fe and Si in groundwater samples at the Chemical Engineering Department, UCT and for analysis of K, Ca and Si in apophyllite digests and samples from dissolution batch test 2. Trace species in the apophyllite samples, Na, Mg, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr, V and Zn were also determined by this method after high temperature fusion and acid digestion of the samples.

Principle

A high temperature argon plasma source is used to ionise sample atoms. The plasma is an efficient excitation source for atomic or ionic emission spectra. The light emitted from the ICP

is focussed onto the entrance slit of a monochromator (sequential analysis) or polychromator (simultaneous analysis) that effects dispersion of the emission wavelengths for detection using a photomultiplier tube. Calibration solutions are used to relate the emission intensity to analyte concentrations.

Sources of error

There are various interferences that may affect the accuracy of analysis (Clesceri *et al.*, 1998), including:

- ▶ **Spectral interference:**
arises from light emission from sources other than the analyte element. Examples are direct spectral line overlaps, broadened wings of intense spectral lines, ion-atom recombination continuous emission, molecular band emission and stray scattered light from the emission of elements at high concentration. Selection of different analytical wavelengths, background corrections and the use of computer software to effect empirical corrections may help to reduce the inaccuracy of spectral interference.
- ▶ **Non-spectral interference:**
Physical interference may be associated with sample nebulisation and transport processes. Chemical interferences are caused by molecular compound formation, ionisation effects and thermochemical effects associated with sample vaporisation and atomisation in the plasma. Matrix matching of samples and standards is used to reduce physical and chemical interference.

Limits of detection

Detection limits for the analytes reported by the ICP-AES laboratory in Boulder, where the apophyllite samples were analysed, are shown in Table C.10. Limits for Fe, K and Sr are estimated detection limits for these elements from Clesceri *et al.* (1998).

Accuracy and precision

No information on the accuracy or precision of the data was supplied by the laboratories contracted to undertake ICP-AES analyses.

Table C.10. Detection limits for elements determined by ICP-AES.

Element	Detection limit ($\mu\text{g/L}$)	Element	Detection limit ($\mu\text{g/L}$)	Element	Detection limit ($\mu\text{g/L}$)
Al	60	Cr	1	Ni	1
As	50	Cu	1	Pb	6
Ba	0.5	Fe	7	Se	50
Be	0.1	K	100*	Si (SiO_2)	40
Ca	50	Mg	80	Sr	0.5
Cd	5	Mn	0.1	V	20
Co	1	Na	60*	Zn	1

* sensitive to operating conditions.

C.1.11 Persulphate ultraviolet oxidation method for dissolved organic carbon (DOC)

Dissolved organic carbon was analysed on filtered ($0.45\mu\text{m}$) groundwater samples from Calvinia by the Water laboratory of the CSIR, Stellenbosch.

Principle

The analysis of total organic carbon involves oxidation of organic matter to carbon dioxide gas which can be quantified. Dissolved organic carbon is distinguished from total organic carbon by filtering the samples before analysis. An initial step requires inorganic carbonate species to be stripped off, as these can also contribute to CO_2 evolution.

Sources of error

Incomplete stripping of inorganic carbonate can lead to overestimation of DOC, while incomplete oxidation of organic carbon can cause underestimation (Mike Louw, analyst, pers. comm.). Large complex organic molecules such as tannins, lignins and humic acid may be oxidised slowly because persulphate oxidation is rate limited. Oxidation is also slowed by the preferential oxidation of chloride. At a chloride concentration of 0.1%, oxidation of organic matter may be completely inhibited (Clesceri *et al.*, 1998).

Limit of detection

The lower limit of detection for DOC by this method using an autoanalyser system is

approximately 1 mg C/L (Mike Louw, analyst, pers. comm.).

Precision of the method

Information on the precision of total organic carbon determination by this method was obtained from Clesceri *et al.* (1998). The results in Table C.11 are based on the analysis of seven replicate determinations of three unknown samples, and two samples spiked with a known quantity of potassium acid phthalate.

Table C.11. Precision data for seven replicate measurements of DOC on five water samples (Clesceri *et al.*, 1998).

	Mean (mg C/L)	Standard deviation (mg C/L)	Relative standard deviation (%)	Recovery (%)
<i>Unknown samples</i>				
Spring water	0.35	0.02	6	
Tap water	2.46	0.02	1	
Wastewater	5.32	0.23	4	
<i>Spiked samples</i>				
0.50 mg C/L	0.53	0.03	6	106
12.46 mg C/L	11.53	0.21	2	93

C.1.12 Stable isotopes of hydrogen and oxygen

Oxygen-18 and deuterium analyses of groundwater samples collected by the author were undertaken by the UCT stable isotope laboratory. Additional data for historical samples was supplied by the CSIR Quaternary Dating Research Unit (QUADRU), Pretoria.

Principle

As it is often difficult to measure the absolute abundance of a single isotope, isotope data are reported as a ratio to some abundant isotope of the same element or as positive or negative deviations of these isotope ratios (R) away from a standard. The relative difference is designated by δ (normally expressed in parts per thousand, ‰).

$$\delta_x = \frac{R_x - R_{std}}{R_{std}} \times 1000 \quad \dots\dots\dots (C.9)$$

R is the particular isotope ratio (for example $^{18}\text{O}/^{16}\text{O}$ or $^2\text{D}/^1\text{H}$) for the sample and standard. Mass spectrometry is used to measure the isotope ratios of samples and known standards.

Procedure

Water samples had to be converted to the appropriate gases for measurement by a gas-source mass spectrometer i.e. H_2 for δD and CO_2 for $\delta^{18}\text{O}$. Water was reduced with Zn following the procedure of Venneman and O’Niel (1993) to produce hydrogen, or equilibrated with CO_2 and the CO_2 analysed (Socki *et al.*, 1992).

Stable isotope ratios were then measured on the sample gases using a dual-inlet mass spectrometer, which allows for alternate measurement of the sample and a fixed reference gas for enhanced precision. The reference gas has a known isotope composition for hydrogen and oxygen relative to VSMOW (Vienna Standard Mean Ocean Water), the international reference material for these isotope ratios (Chris Harris, UCT stable isotope laboratory, pers. comm.).

Precision of the method

Analytical precision on $\delta^{18}\text{O}$ values is usually better than $\pm 0.2\text{‰}$. For deuterium the error is slightly larger, typically around 1‰ (Clark and Fritz, 1997).

C.2 Rock and mineral analysis

C.2.1 X-ray diffraction analysis (XRD)

X-ray diffraction analysis was used for mineral identification of clay minerals in shale samples from Kopoasfontein and for identification of sulphide minerals and apophyllite in concentrated samples from hand specimens. The technique was also employed for the measurement of unit cell dimensions for apophyllite mineral specimens, using either powdered or single crystal samples.

Principle

X-ray diffraction techniques allow the qualitative and quantitative determination of crystalline solid materials, by measuring the distance between the atomic planes in the crystal lattice.

Samples are irradiated with X-rays from a tube source using a monochromator and slits to ensure that radiation of a single known wavelength (λ) is incident on the specimen. X-ray wavelengths are of the same order of magnitude as the spacing of crystal planes (d) and thus a change in path length of the X-ray beam reflected off successive atomic planes causes constructive or destructive interference of the reflected radiation for a given angle of incidence (θ). The conditions for constructive interference are given by Bragg's law:

$$n\lambda = 2d \sin \theta \quad \dots\dots\dots (C.10)$$

where n is an integer denoting the spectral order. Since λ is known, the crystal plane spacing (d) can be calculated for those angles (θ) where the reflection intensity maxima are encountered.

A goniometer is used to rotate the sample through a measured angle (2θ) in the path of the incident X-ray beam and the reflected X-ray intensity for each angle is measured by a proportional counter. X-ray reflection peaks can occur from those crystallographic planes which lie parallel to the specimen surface. Using a powdered sample, a great number of crystal particles are arranged in random orientation, ensuring that each crystallographic plane will lie parallel to the surface in a fair number of the grains. Single crystals are rotated while X-ray reflections are collected.

Plotting the measured intensity against 2θ angle (or corresponding crystal d spacing) produces a diffractogram from which the minerals in the sample can be characterised. Crystalline compounds are identified by the characteristic spacings of their crystal planes in different orientations. Each compound has a distinctive pattern of XRD spectral lines which are used to identify the compound from a database of stored XRD spectra.

C.2.1.1. Clay mineral identification in shales

The clay mineralogy of four composite samples from the geological core borehole 56 was analysed by XRD. Separation of the clay size fraction was employed as a first step to remove other minerals which might interfere with the detection of the phyllosilicate phases.

Separation of the clay fraction

Composite rock core samples were hand crushed and ground in an agate mortar and pestle in acetone. A 50 g subsample of each was sonicated in 200 mL distilled water at 145W power for 2 minutes and the suspended fraction decanted. Sonication was repeated with more distilled water, accumulating approximately 1.5 L of decantate for each sample. The suspension was poured through a $63\ \mu\text{m}$ sieve into a 1 L settling column. Stokes law was used to calculate a settling distance of 17.4 cm for particles of $2\ \mu\text{m}$ diameter over 12 hours in distilled water at 24°C . The suspension was carefully siphoned off to this depth, collecting the $< 2\ \mu\text{m}$ size fraction. Calcium chloride (14.7 g $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$) was added to flocculate the dispersed clays and the volume made up to 1 L with distilled water to give a 0.1 M CaCl_2 solution. After 4 hours a clear supernatant could be syphoned off and discarded and the clay concentrated by centrifugation (2000 rpm for 5 minutes). Calcium chloride was removed by 3 rinses of distilled water, after which the supernatant remained cloudy after centrifugation at 6000 rpm for 5 minutes. After a further 5 minutes centrifugation at 6000 rpm, the supernatant was discarded leaving the solid clay sample.

Diagnostic treatments of clay samples for XRD

Diagnostic treatments have been developed that allow distinction to be made between the various expanding and non-expanding phyllosilicates using XRD (Whittig and Allardice, 1986). Subsamples of the Kopoasfontein clay fractions were subjected to four different treatments to facilitate clay mineral identification.

Potassium saturation of exchange complex

The solid clay concentrate was divided into 2 approximately equal portions. One portion was shaken up with 1 M KCl solution, followed by centrifugation (6000 rpm for 5 minutes) and decanting of the solution, the process being repeated for a total of 4 KCl washings. The potassium saturated material was then rinsed with 50% ethanol, 99% ethanol and then 95% acetone, with centrifugation between each washing, until no chloride was detected in the decanted acetone by AgNO_3 test.

Heat treatment

Potassium saturated clay mineral samples mounted on ceramic tiles were heated in a furnace to 550°C for 1 hour and allowed to cool for 10 minutes before XRD analysis.

Magnesium saturation of exchange complex

The second portion of each clay concentrate was diluted with about 20 mL distilled water and dropwise addition of 0.1M HCl used to adjust the pH to between 3.5 and 4 to avoid later precipitation of $\text{Mg}(\text{OH})_2$. After centrifugation and discarding the acid solution, a 0.5M MgCl_2 solution was used to saturate the clays. The procedure for clay saturation was the same as that described for the potassium saturated clays.

Solvation with glycerol

Magnesium saturated clay mineral samples mounted on ceramic tiles were placed in a dessicator, the bottom of which was filled with a 50% solution of glycerol. The dessicator was closed and placed in an oven at 50°C for 16 hours. Samples were analysed within 20 minutes of being removed from the glycerol-saturated atmosphere.

Clay sample mounting

Clay samples were mounted on ceramic tiles for analysis using a modification of the filter-membrane peel technique (Drever, 1973). First the material was resuspended by the addition of distilled water and the suspension filtered through a $0.45\mu\text{m}$ filter under vacuum to create a clay layer approximately 2 mm thick on the filter. The wet filter and filter cake was then carefully inverted onto an unglazed ceramic tile and a slight vacuum applied to promote adhesion of the clays to the tile. The sample was dried at 50°C for 10 minutes until the filter became opaque,

when it could be peeled away leaving a smooth analytical surface of preferentially oriented clay mineral particles on the ceramic tile. The purpose of inverting the filtered cake is to produce a clean, smooth surface which is representative of all particle sizes in the clay concentrate for XRD analysis. Filtering directly through the ceramic tile could produce an analytical surface which is biased towards the smaller size fractions that remain in suspension longest.

X-ray diffraction analysis

Samples were irradiated with Copper K_{α} X-ray radiation of wavelength 0.154056 nm ($K_{\alpha 1}$) and 0.154439 nm ($K_{\alpha 2}$), at a $K_{\alpha 2}/K_{\alpha 1}$ intensity ratio of 0.500. The radiation was generated by a PW2233 Cu NF X-ray tube at a generator current of 25 mA with a 40 kV applied voltage.

The intensity of diffracted radiation from the sample surface was detected by a PW3011 detector after passing through a Diffracted Beam PW1752 monochromator and 0.1 mm receiving slit. An angle range from 2° to $70^{\circ} 2\theta$ was scanned using a step size of 0.1° and the intensity of the diffracted X-rays counted for 1 second at every step. Glycerol solvated samples were only run from 2 to 30° to look for shifts of the $\{001\}$ smectite peak, which occurs in the low angle range. Diffractograms of the X-ray intensity pattern against 2θ angle were used to identify the dominant clay minerals, using diagnostic reflections from planes perpendicular to the c crystallographic axis.

C.2.1.2. Identification of sulphide minerals

Single crystals of metallic sulphide minerals were isolated by hand from drilling fragments (Kopasfontein borehole 54B) and milled for 2 minutes on a fast speed setting in a Siebtechnik carbon-steel swing mill. The powdered sulphides were poured into a square cavity in an aluminium sample holder and gently pressed against a piece of filter paper using a stamp machined to fit the cavity. This produced a randomly orientated sample with a smooth analytical surface and no backing material once the sample holder was lifted from the paper and inverted.

The random powder sample was irradiated under the same conditions as the clay mineral samples and X-ray diffraction data collected over a scanning range of 5 to $75^{\circ} 2\theta$. The X-ray diffractogram was analysed using X-pert software (Philips Analytical) and the measured d -spacings used to match the XRD spectrum with that of pyrrhotite-4C (17-0200) in the database.

C.2.1.3. Positive identification and cell determination of apophyllites

Crystals of apophyllite were isolated from hand specimens for characterisation. Crystals were separated by scraping off rock surfaces by hand with a stainless steel spatula, or separating out apophyllite crystal fragments after lightly crushing the sample between paper sheets using a hammer. For the Kopoasfontein sample, a Dremel hand-held engraving tool was used to dislodge apophyllite crystals from the rock. Several well-formed crystals were set aside for single crystal XRD analysis.

The remainder of the mineral samples were crushed using a small stainless steel piston mortar and then ground to a finer grain size using automatic agate or alumina mortar and pestle sets for 15 minutes or more. The Kopoasfontein sample was also milled in a small stainless steel swing mill (Siebtechnik) for 20 s. The fine mineral powder obtained was used in powder XRD analyses.

Several techniques were employed to mount the powdered apophyllite samples. A random powder mount of Kopoasfontein apophyllite was prepared by lightly pressing a powdered apophyllite sample into a perspex sample holder. Other powder samples were pressed into brass (LC12, LC13, LC15) or silicon wafer (LC3) holders to produce random oriented samples or mixed into a slurry with methanol and evaporated on silicon wafers (LC1, LC2, LC4, LC9, LC14) to produce oriented samples. A small amount of aluminium powder was added to the samples as an internal standard to allow the diffraction peaks to be corrected for the effects of poor sample alignment.

Powder samples were irradiated with $\text{Cu K}\alpha_1$ radiation and scans run from 2 to $65^\circ 2\theta$ at a scan rate of 0.05° per second. Specialised X-ray analytical software was used to determine crystal d-spacings, match the apophyllite samples to reference spectra and refine unit cell dimensions for the powder samples.

X-ray diffraction data sufficient for accurate cell determinations were collected using single crystal samples at the XRD facility of the Chemistry Department, UCT. Data were gathered at room temperature, using a Nonius Kappa CCD diffractometer. Several thousand reflections were collected for each crystal by rotating it 50° about the phi axis while irradiating the samples with 1.5kW graphite-monochromated Mo radiation.

A primitive tetragonal lattice was used to index all diffraction patterns used for cell dimension determinations by powder and single crystal techniques.

C.2.2 X-Ray Fluorescence Spectrometry (XRFS)

Major elements and fluoride determinations in Kopoasfontein apophyllite and arsenic determination for the sulphide mineral concentrate were performed by XRFS. The analyses were performed at the Department of Geological Sciences, UCT.

Principle

The characterisation of X-ray spectral information is employed by XRF to determine the elemental composition of solid samples. X-ray spectra are created by the interaction of an X-ray source with the electrons of the sample atoms. The excitation source causes ejection of an inner-shell electron from a sample atom, creating a vacancy in the electron shell and leaving the atom in an excited state. During de-excitation, an electron transition occurs from an outer electron shell to fill this vacancy. The change in energy associated with the transition takes the form of X-ray radiation which is detected and analysed. The electronic configuration of each element is unique and thus the atoms of an element produce a characteristic set of X-ray spectral lines for the elements in the portion of the sample undergoing excitation.

Wavelength dispersive XRF uses the rotation through a measured angle (2θ) of a crystal of known interplanar spacing (d) to separate the X-ray energy of different wavelengths (λ) from the sample, in accordance with the Bragg equation, C.10. A proportional counter detector then measures the intensity of the radiation at each wavelength in turn as the analysing crystal is rotated. The intensity is plotted against wavelength (or rotation angle) to produce a spectrum of peaks from which the elements in the sample are determined qualitatively, or quantitatively if the instrument is calibrated for each element.

Sample preparation

A powder briquette of the sulphide minerals was prepared from 8 g of powdered sample mixed with 2 g (20%) Hoescht analytical grade wax in a Turbula mixing mill for 30 minutes. The mixture was then pressed at 10 tons on a steel die to produce a cylindrical briquette.

Kopoasfontein apophyllite was milled in a small stainless steel swing mill (Siebtechnik) for 20 seconds and the powder used to make two glass fusion disks and a powder briquette for XRFS analysis. The powder briquette was made from 2g oven-dried apophyllite (110°C) with 2 drops 4% Mowiol solution as binder pressed under 10 tons. Crystalline boric acid was used as a backing for the thin briquette. Wax has a tendency to interfere with the analysis of fluoride and so was not used in the making of the powder briquette.

Duplicate glass fusion disks were prepared for major element determination. Approximately 3 g of apophyllite was weighed out accurately into a platinum crucible and the weight loss due to evaporation of absorbed water measured after drying in an oven overnight at 110°C. The dried apophyllite was then placed in a furnace and the temperature stepped up 200°C every 2 hours to a maximum of 950°C where the sample was held overnight. The slow temperature ramping was used to ensure that all the fluorine in the mineral structure was driven off. After roasting the mass loss (LOI) was once again recorded after cooling the sample in a desiccator. The roasted sample was weighed out into two portions of exactly 0.7000 g and 6.000 g of 57:43 anhydrous lithium metaborate: lithium tetraborate flux (Sigma) mixed thoroughly with each. The flux had been dried overnight at 450°C and stored in a desiccator before use. Fusion disks were prepared using an automatic Claisse *Fluxy*. The sample-flux mixtures were poured into two platinum crucibles of the *Fluxy* and 4 drops of a 0.25mg/L Claisse wetting agent added to each. An automatic heating programme was followed to fuse the samples into transparent glass disks.

Analysis

The following information on the XRFS analyses has been extracted from Willis (1996):

Major elements were determined by a standard major element run using fusion disks, analysed on a wavelength dispersive spectrometer with dual target Mo/Sc X-ray tube. Iron, manganese and titanium were measured with the tube at 100 kV, 25 mA. The other elements (Ca, K, P, Si, Al, Mg, Na and S) were determined with the tube at 40 kV, 65 mA. Peak-only measurements, rather than peak scanning, were made on the elements Fe through Mg. Analytical conditions are given in Table C.12.

Fusion disks made up with 100% Johnson Mathey Specpure SiO₂ were used as blanks for all

elements except Si. Fusion disks made up from Johnson Matthey Specpure Fe_2CO_3 and CaCO_3 were used as blanks for Si. Intensity data was collected using the Phillips X40 software. Matrix corrections were made on the elements Fe through Mg using the de Jongh model in the X40 software. Theoretical alpha coefficients used in the de Jongh model for all other elements on the analyte element were calculated using the Phillips on-line ALPHAS program. Na_2O is not included in the matrix corrections in the de Jongh model, and no matrix corrections were made to the sodium intensities.

Table C.12. Analytical conditions for determination of major elements using a Philips PW1480 WDXRF spectrometer.

Element/ line	Collimator	Crystal	Detector	PHS		Counting time (s)	Concentration range*
				LWL	UPL		
FeK $_{\alpha}$	F	LiF(220)	FL	16	70	150	0-17
MnK $_{\alpha}$	F	LiF(220)	FL	15	70	150	0-0.22
TiK $_{\alpha}$	F	LiF(200)	FL	28	70	150	0-2.75
CaK $_{\alpha}$	F	LiF(200)	FL	36	70	20	0-12.5
K K $_{\alpha}$	F	LiF(200)	FL	36	70	50	0-15.5
P K $_{\alpha}$	C	GE(111)	FL	25	75	100	0-0.36
SiK $_{\alpha}$	C	PE(002)	FL	32	74	100	0-100
AlK $_{\alpha}$	C	PE(002)	FL	25	75	80	0-17.5
MgK $_{\alpha}$	F	PX-1	FL	30	74	150	0-46
NaK $_{\alpha}$	F	PX-1	FL	30	78	200	0-9

* Concentrations expressed as wt% oxide.

Arsenic and fluoride were determined on powder briquettes using a Mo/Sc X-ray tube. Analytical conditions for the elements determined in the Kopoasfontein samples are listed in Tables C.13 and C.14. The MoK $_{\alpha}$ Compton peak was used to determine the mass absorption coefficients of the samples at the MoK $_{\alpha}$ (C) wavelength and the Compton peak mass absorption coefficient value used to correct for absorption effects on the As analyte wavelengths. Primary and secondary mass absorption coefficients for the F analyte wavelengths were calculated from major element compositions.

Table C.13. X-ray tubes and X-ray path settings for the determination of F and As using a Philips PW1480 WDXRF spectrometer.

Element/line	X-ray tube			X-ray path
	Target	kV	mA	
MoK _α (Compton)	Mo/Sc	90	30	vacuum
AsK _α	Mo/Sc	90	30	vacuum
F K _α	Mo/Sc	40	70	vacuum

Table C.14. Instrumental conditions for determination of F and As using a Philips PW1480 WDXRF spectrometer.

Element/ line	Colli- mator	Crystal	Detector	PHS		Counting time (s)	Background position relative to peak	Concen- tration range*
				LWL	UPL			
MoK _α (C)	F	LiF(220)	SC	32	74	200		
AsK _α	F	LiF(200)	FS	25	75	200	3.62	
F K _α	C	PX-1	FL	25	80	400		0-54

* = all concentrations expressed as part per million (ppm or mg/kg).

Measured intensity data were processed through the program TRACE to correct gross peak intensities for background and spectral overlap and to make mass absorption coefficient corrections. First order calibration lines with zero intercept were calculated using six or more international rock standard reference materials (SRMs) for each element. The lower limit of detection was calculated for each element in each specimen using the equation:

$$LLD (mg/kg) = \frac{6}{m} \sqrt{\frac{I_b}{T_{total}}} \dots\dots (C.11)$$

- where m = net peak/ gross concentration;
- I_b = background count rate under the peak in cps;
- T_p = counting time for peak in seconds;
- T_b = total counting time for background in seconds and T_{total} = T_p + T_b.

Sodium and arsenic concentrations are reported as <LLD, where measured concentrations were calculated to be below the lower limit of detection.

C.2.3 Ion microprobe analysis of Kopoasfontein apophyllite crystals

Single crystals of apophyllite from Kopoasfontein were mounted in resin discs and polished on both sides to expose smooth crystal surfaces, then carbon coated for chemical analysis by ion microprobe. A beam current of 40 nA was used for the analysis of 20 spots on five apophyllite crystals. Ten readings were taken using a defocussed beam, but this did not prevent large mass losses by volatilisation. The analyses were undertaken at the Department of Geological Sciences, UCT.

C.2.4 Total nitrogen analysis

Total nitrogen analyses on rock and mineral materials were performed at the USGS laboratories in Boulder using an Antek 900N Nitrogen Analyser. The technique involves pyrolysis of a carefully weighed out solid sample at 1050°C and chemoluminescent detection of the evolved nitrogen gases. Analyses were performed in duplicate or triplicate and the mean values reported. Ammonium analysis of Kopoasfontein apophyllite was repeated on a sample submitted to the Sea Fisheries Research Institute in Cape Town.

C.2.5 Fusion and digestion of apophyllites

Apophyllite samples were fused by two high temperature methods using a lithium metaborate flux and acid-digested for the determination of major and minor components by ICP-AES. A separate low temperature fusion in sodium hydroxide was used to prepare digests for fluoride analysis by ISE.

C.2.5.1 Union College method (Union College, current)

Lithium metaborate flux was oven-dried overnight at 600°C and cooled and stored in a desiccator. Accurately weighed amounts of 0.580 g flux and 0.120 g powdered apophyllite were mixed in glass vials and transferred to graphite crucibles. The mixture was then fused in a preheated furnace at 980°C for 10 minutes, swirling for 5 seconds after 4 minutes and 7 minutes to ensure all apophyllite reacted with the flux. The mixture was removed from the furnace and immediately tipped into a magnetically-stirred beaker of acid while still molten. The acid used was made up by adding 15 mL of 12N trace metal grade HCl to 75 mL of double distilled water in a plastic beaker. Stirring for approximately one hour was required to dissolve the glass fusion bead. The acid was carefully transferred to a 250 mL glass volumetric flask and the beaker rinsed several times into the flask with double distilled water before making up to the mark. The acid digests were stored in acid-washed, dried plastic bottles until analysis by ICP-AES.

Duplicate fusions were performed for samples LC6, LC7, LC 8, LC10 and LC11 to check the precision of the method (Table C.15). The two samples in each case gave very similar concentrations of major elements in apophyllite, showing the method to be highly reproducible. Only for trace analytes of low concentrations did the results differ by more than 6%.

Table C.15. Reproducibility of Union College digestion method. Analyses were performed on duplicate samples fused and digested in acid before ICP-AES analysis. Data is reported in mg/L.

	Al	Ca	Fe	K	Mg	Na	SiO ₂
LC6_1	0.616	78.92	0.081	19.1	0.0090	0.422	250
LC6_2	0.637	79.58	0.064	19.3	0.0085	0.414	240
Mean	0.626	79.25	0.073	19.2	0.0088	0.418	245
Std. dev.	0.015	0.46	0.012	0.14	0.0004	0.006	7.1
RSD (%)	2.4	0.58	17	0.74	4.0	1.4	2.9
LC7_1	0.7085	78.225	0.067	22.9	0.0088	0.487	240
LC7_2	0.7215	78.275	0.070	23.1	0.0090	0.479	250
Mean	0.7150	78.250	0.069	23.0	0.0089	0.483	245
Std. dev.	0.0092	0.0354	0.002	0.14	0.0002	0.006	7.1
RSD (%)	1.3	0.05	3.1	0.61	2.0	1.3	2.9
LC8_1	0.435	78.25	0.045	24.3	<0.009	0.580	260
LC8_2	0.415	78.30	0.041	23.1	<0.009	0.568	240
Mean	0.425	78.28	0.043	23.7		0.574	250
Std. dev.	0.014	0.035	0.003	0.85		0.009	14.1
RSD (%)	3.3	0.05	6.6	3.6		1.5	5.7
LC10_1	0.8335	76.85	0.036	23.25	<0.009	0.820	240
LC10_2	0.8330	77.55	0.056	23.15	<0.009	0.829	250
Mean	0.8333	77.20	0.046	23.20		0.825	245
Std. dev.	0.0004	0.495	0.014	0.071		0.006	7.1
RSD (%)	0.04	0.64	30.7	0.30		0.77	2.9
LC11_1	0.5375	77.83	0.065	22.90	0.009	0.765	250
LC11_2	0.5485	78.08	0.069	22.85	<0.009	0.797	250
Mean	0.5430	77.95	0.067	22.89		0.781	250
Std. dev.	0.0078	0.177	0.003	0.035		0.023	0.00
RSD (%)	1.4	0.23	4.2	0.15		2.9	0.0

C.2.5.2 Walsh method (Walsh, 1980)

A second acid digest method was employed for those samples where larger quantities of apophyllite were available, as a means of checking data reliability. Samples LC6, LC7, LC8 and LC13, used in the dissolution experiments, were prepared by this method.

Accurately weighed amounts of 0.50 g apophyllite and 2.00 g lithium tetraborate flux were mixed

together in platinum crucibles using a metal spatula. The mixtures were fused over a bunsen burner for approximately 40 minutes until gas bubbles were no longer formed and the melt homogenised. The crucible was then cooled and the entire crucible placed in a 250 mL plastic beaker containing 100 mL double deionised water and 7 mL 69% redistilled reagent grade HNO₃ to give an approximately 5% HNO₃ solution. A small teflon-coated magnetic stirrer bar was placed inside the crucible and the solution stirred for approximately 3 hours to dissolve the fused sample. The acid digests were then made up to 250 mL in glass volumetric flasks using double distilled water and decanted into acid-washed, dried plastic storage bottles.

Table C.16 compares results obtained using the two different high temperature fusion methods. The data is compared after conversion to weight % oxide in the solid, because different masses of sample are used for the two methods. Silica data has not been corrected for SiF₄ losses.

Table C.16. Comparison of data from Union College and Walsh fusion methods for apophyllite digestion. Data are reported in wt % except for Sr in mg/kg.

	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	Na ₂ O	SiO ₂	Sr
LC6: Union College ¹	0.250	23.39	0.018	4.77	0.016	51.64	13.71
Walsh	0.227	24.48	0.015	4.86	0.090	48.00	13.99
Difference (%)	9.1	4.5	18	1.8	480	7.1	2.0
LC7: Union College ¹	0.284	23.04	0.017	5.73	0.034	51.52	8.42
Walsh	0.251	23.78	0.022	6.31	0.090	49.50	9.00
Difference (%)	12	3.1	25	9.3	62	4.0	6.5
LC8: Union College ¹	0.169	23.08	0.009	5.91	0.060	52.66	<5.0
Walsh	0.174	23.78	0.016	6.49	0.140	50.00	1.00
Difference (%)	2.7	2.97	44	8.9	57	5.1	
LC13: Union College	0.557	19.38	0.321	2.65	0.11	50.5	48.42
Walsh	0.498	21.65	0.286	2.84	0.14	47.0	41.99
Difference (%)	11	10	11	6.9	23	6.9	13

¹ Reported values are the means from duplicate analyses.

Major element data were usually within 10% difference between the two methods, but differences were much larger for minor components such as Na and Fe. The Union College method produced consistently higher Si and lower Ca values than the Walsh method.

C.2.5.3 Fabbri and Donati low temperature method (Fabbri and Donati, 1981)

Considerable loss of fluorine was expected from the high temperature fusions, so a separate low temperature alkali fusion method was employed to prepare all the apophyllite samples for fluoride analysis. Accurate amounts of 0.20 g apophyllite and 2.00 g NaOH were measured out and mixed together in Ni crucibles. The mixtures were then fused in a preheated furnace at 500°C for 20 minutes, shaking the melt after 5 minutes to ensure good mixing. Crucibles were then cooled, filled with water and transferred to 100 mL glass beakers. The beakers were placed on a hot plate and the water boiled for 10 minutes before filtering the solutions through Whatmann No. 41 filter paper into 100 mL glass volumetric flasks for dilution with double distilled water. Samples were decanted into plastic bottles for storage and further five or ten times dilutions used to decrease fluoride concentrations to the working range required for analysis by ion selective electrode.

The reproducibility of the sodium hydroxide digestions is not as good as that of the high temperature acid digestion techniques (Table C.17). One of the fusions for sample LC7 also appears to be in error. The data from the second fusion has been used as this was performed under more controlled conditions.

Table C.17. Comparison of fluoride data from duplicate digestion of apophyllite samples using the method of Fabbri and Donati (1981). Concentrations are the mean values from replicate analyses using different dilutions (2, 5 or 10 times) reported as wt% in the original solid.

Sample	LC6	LC7	LC8	LC13
Digestion 1	1.72	1.42	1.34	2.17
Digestion 2	1.61	2.22	1.95	2.19
Difference	0.11	0.80	0.61	0.02

C.2.6 Thermal analysis

Apophyllite samples were submitted to the USGS thermochemical facility for thermogravimetric analysis (TGA) and differential thermal analysis (DTA) and qualitative mass spectrometric analysis of evolved gases (EGA). The instrument used was a Mettler TGA/SDTA851e outfitted to a small furnace and coupled to a Balzers quadrupole mass spectrometer. Kopoasfontein

apophyllite was also analysed by TGA and DTA to 600°C at the Department of Chemical Engineering, UCT.

Principle

Thermal analysis is a term covering a group of analytical techniques that determine some physical parameter, such as energy, mass, dimension and evolved volatiles, as a dynamic function of temperature. Solid phases can undergo several changes on heating which can serve as diagnostic properties for the qualitative and quantitative identification of substances or can reveal information about their structure and chemical stability. Reactions such as evaporation of adsorbed water occur at low temperature, while oxidation of reduced ions occurs at intermediate temperatures and loss of crystal lattice OH at high temperature. Reactions may be exothermic or endothermic and often involve phase changes or crystal changes during the course of heating

Thermogravimetric analysis (TGA) is a technique whereby a sample is continuously weighed as it is being heated or cooled at a controlled rate. Differential thermal analysis (DTA) determines energy changes between a sample and reference material as the two are heated at a controlled rate so that phase transitions that do not involve a change in mass are recorded as exotherms or endotherms (Tan *et al.*, 1986).

Procedure

Approximately 20 mg of finely ground apophyllite was weighed out. A 70 μ L aluminium oxide crucible was tared on the TGA balance in flowing argon gas (75 mL/min) before opening the furnace and adding the sample to the crucible. The argon flow was then restarted and the mass of the sample recorded on the TGA balance. Each run was started with a 5 minute isothermal segment in flowing argon to make sure all air was removed from the sample and furnace before starting the dynamic segment of the run. Heating rates of 1, 5 and 10°C/min were used for Kopoasfontein apophyllite and 10°C/min for all other samples.

TGA and DTA curves were recorded automatically while samples were heated from ambient temperature to 1050°C. The single differential thermal analysis (SDTA) used for the apophyllite samples was calibrated by the melting points of indium and aluminium.

For EGA, the gases evolved from the sample entered a heated (200°C) silica capillary which transferred them to the mass spectrometer. Runs were computer controlled to synchronise with the TGA and were set up to scan for selected atomic mass units between 1 and 74 that could correspond to parent molecules H₂O, CO₂, SO₄ and NH₄. Data were reduced using the Mettler STAR System software. The TGA, SDTA and EGA curves are reproduced in Appendix G.

C.2.7 Apophyllite pretreatment for dissolution batch tests

Crushed apophyllite from Kopoas Fontein (KF/LC13), Jalgaon (JL/LC8), Guanajuato, (GJ/LC6) and Paterson (PT/LC7) was sieved through stainless steel sieves to isolate the size fraction <106 µm (150 mesh) and the larger particles returned to an automatic mortar and pestle for further grinding. Ground apophyllite was placed in a beaker and stirred with a teflon-coated magnetic stirrer to separate out magnetic impurities. The mineral samples were washed twice with distilled water and sonicated for 15 minutes in methanol or ethanol to dislodge ultrafine particles which might be adhering to the crushed surfaces. The sonicated material was wet-sieved to remove the <53 µm (270 mesh) size fraction along with any impurities dissolved by the organic solvent. The 53 - 106 µm size fraction was washed twice with double distilled water, oven-dried at 102°C for 2 hours and stored in a glass vial for use in the dissolution experiments.

C.2.8 Surface area measurements

The BET (Brunauer, Emmett and Teller, 1938) method used for the determination of specific surface area is based on the physical adsorption of N₂ gas onto the surface of the solid at a temperature of 77 K. Multilayer physical adsorption is based on the BET equation:

$$\frac{v}{v_m} = \frac{c(P/P_0)}{(1 - P/P_0)[1 + (c - 1)P/P_0]} \quad \dots\dots\dots (C.12)$$

where v = volume of gas adsorbed per unit mass of adsorbent at 298 K and 1 atm;
 v_m = maximum volume of gas adsorbed per unit layer of adsorbent
 (representing a monolayer of adsorbed molecules);
 P/P_0 = partial pressure of gaseous adsorbate; and c is a constant.

A plot of $(P/P_0)/[v(1-P/P_0)]$ versus P/P_0 for the partial pressure range $P/P_0 = 0.05$ to 0.3 produces a straight line from which v_m and c are obtained from the intercept and slope. The BET surface area is then calculated using the equation:

$$A = \left(\frac{v_m}{v_0} \right) N_0 \dot{\alpha} \qquad \dots\dots\dots (C.12)$$

- where A = specific surface area of the solid (m^2/g);
- $\dot{\alpha}$ = area of one adsorption site, estimated to be $16.2 \text{ \AA}^2$ for N_2 ;
- v_0 = volume of one mole of the adsorbing gas (22.4 L at 273 K); and
- N_0 = Avagadro's number.

The BET area is always larger than the geometric area (calculated by assuming the minerals are simple geometric forms such as spheres or cubes) and commonly changes significantly during a dissolution experiment (Drever, 1997).

The surface area of Kopoasfontein apophyllite ($50 - 100 \text{ }\mu\text{m}$ particle size) used in batch tests 1 and 3 was determined at the Department of Chemical Engineering, UCT. A 4.1588g sample of the material was used. The N_2 gas absorption was measured for relative pressure changes from 0.0636 to 0.9933 and desorption from 0.9933 to 0.1210 at a saturation pressure of 760 mm Hg . The measured BET parameters are given in Table C.18. The estimated error of about 0.6% is based on the error of the slope and is not as reliable as error estimates from repeat analyses.

Table C.18. Parameters used in the multipoint BET determination of surface area for Kopoasfontein apophyllite, used in batch dissolution studies 1 and 3.

Relative pressure	Volume adsorbed (cc/g STP)	$1/[VA (P_0/P - 1)]$	Results
0.0636	0.0783	0.8672	Slope = 9.424 ± 0.060
0.0797	0.0839	1.033	y-intercept = 0.276 ± 0.008
0.1197	0.0965	1.410	$c = 35.155$
0.1597	0.1067	1.781	$V_m = 0.1031 \text{ cc/g STP}$
0.200	0.1158	2.158	$R^2 = 0.99945$
			Area = $0.4488 \pm 0.0028 \text{ m}^2/\text{g}$

The BET surface area of samples from Kopoasfontein (KF/LC13) and Jalgaon (JL/LC8) used in the second batch dissolution test were determined at the USGS laboratories in Denver. Data from the sampling reports is shown in Table C.19.

Table C.19. Multipoint BET surface area determination for LC8 and LC13 used in batch test 2.

JL/LC8			KF/LC13		
Sample mass	1.4522 g		Sample mass	1.0755 g	
Saturation pressure	641.05 mm Hg		Saturation pressure	641.05 mm Hg	
Free space	4.079 cc STP		Free space	2.884 cc STP	
Evacuation time	1.0 minute		Evacuation time	1.0 minute	
Equilibration time	5 seconds		Equilibration time	5 seconds	
Relative pressure	Pressure (mm Hg)	Volume adsorbed (cc/g STP)	Relative pressure	Pressure (mm Hg)	Volume adsorbed (cc/g STP)
0.0501	32.12	0.077	0.0502	32.15	0.051
0.0977	62.66	0.086	0.0978	62.67	0.061
0.1451	93.03	0.093	0.1452	93.08	0.068
0.1920	123.08	0.098	0.1925	123.41	0.075
0.2394	153.48	0.103	0.2399	153.77	0.080
0.2868	183.88	0.109	0.2872	184.10	
Slope	12.695		Slope	15.588	
y-intercept	0.0193		y-intercept	0.2371	
c	659.44		c	66.748	
V _m	0.0787 cc/g STP		V _m	0.0632 cc/g STP	
R ²	0.9997		R ²	0.9998	
Surface area	0.342 m ² /g		Surface area	0.275 m ² /g	

Samples LC6 and LC7 could not be determined since the available material was below the 1 m² surface area needed for the determination.

Precision of the method

Surface area measurements by the BET method typically have an error of 5 to 15% (J. Ganor, *pers. comm.*).

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APPENDIX D
CHEMICAL DATA FOR ALL GROUNDWATER SAMPLES
FROM THE CALVINIA STUDY AREA

Table D.1. Groundwater data for samples from boreholes in sodic breccia pipes – borehole information.

SODIC BRECCIA PIPES									
Name	DWAF No.	Date sampled	Farm	Location	Lithology	Use	Latitude	Longitude	Elevation (m)
51	G39851	26/05/1992	Kopoasfontein		breccia -Na	Domestic	31.48556	19.90083	1065
51	G39851	03/06/1992	Kopoasfontein		breccia -Na	Domestic	31.48556	19.90083	1065
51	G39851	04/06/1992	Kopoasfontein		breccia -Na	Domestic	31.48556	19.90083	1065
51	G39851	12/08/1992	Kopoasfontein		breccia -Na	Domestic	31.48556	19.90083	1065
52	G39852	06/06/1992	Kopoasfontein		breccia -Na	Domestic	31.485	19.9022	1065
52	G39852	10/06/1992	Kopoasfontein		breccia -Na	Domestic	31.485	19.9022	1065
52	G39852	12/10/1997	Kopoasfontein		breccia -Na		31.485	19.9022	1065
53	G39853	11/06/1992	Kopoasfontein		breccia -Na	Stock	31.48667	19.89806	1065
53	G39853	18/08/1999	Kopoasfontein		breccia -Na		31.48667	19.89806	1065
53	G39853	19/11/1999	Kopoasfontein		breccia -Na		31.4864	19.895	1065
54	G39854	20/07/1992	Kopoasfontein		breccia -Na	Domestic/Stock	31.48556	19.90139	1064.353
54	G39854	12/09/1997	Kopoasfontein		breccia -Na		31.48556	19.90139	1064.353
54B	G39854B	18/08/1999	Kopoasfontein		breccia -Na		31.487	19.9004	1064.353
55	G39855	21/07/1992	Kopoasfontein		breccia -Na		31.48472	19.90056	1065
55	G39855	18/08/1999	Kopoasfontein		breccia -Na		31.48472	19.90056	1065
55	G39855	19/11/1999	Kopoasfontein		breccia -Na		31.48472	19.90056	1065
73	G39973	28/03/1994	Kopoasfontein		breccia -Na	Domestic	31.48528	19.90028	1065.316
73	G39973	10/10/1994	Kopoasfontein		breccia -Na	Domestic	31.48528	19.90028	1065.316
73	G39973	10/10/1994	Kopoasfontein		breccia -Na	Domestic	31.48528	19.90028	1065.316
73	G39973	18/10/1994	Kopoasfontein		breccia -Na	Domestic	31.48528	19.90028	1065.316
73	G39973	18/10/1994	Kopoasfontein		breccia -Na	Domestic	31.48528	19.90028	1065.316
73	G39973	26/05/1998	Kopoasfontein		breccia -Na	Domestic	31.48528	19.90028	1065.316
73	G39973	19/08/1998	Kopoasfontein		breccia -Na	Domestic	31.48528	19.90028	1065.316
73	G39973	24/05/1999	Kopoasfontein		breccia -Na	Domestic	31.48528	19.90028	1065.316
73	G39973	07/07/1999	Kopoasfontein		breccia -Na	Domestic	31.48528	19.90028	1065.316
73	G39973	07/07/1999	Kopoasfontein		breccia -Na	Domestic	31.48528	19.90028	1065.316
73	G39973	18/08/1999	Kopoasfontein		breccia -Na	Domestic	31.48528	19.90028	1065.316
73	G39973	27/09/2000	Kopoasfontein		breccia -Na	Domestic	31.48528	19.90028	1065.316
73	G39973	15/03/1994	Kopoasfontein		dolerite/shale	Domestic	31.48528	19.90028	1065.316
58	G39858	10/05/1996	Calvinia Allotment	Witwal	breccia -Na	Domestic	31.45306	19.81278	

Table D.1 (continued). Groundwater data for samples from boreholes in sodic breccia pipes – macro variables.

SODIC BRECCIA PIPES									
Name	Date sampled	Borehole Depth (m)	Sample Depth (m)	Preservation	Lab. pH	EC (mS/m)	TDS (mg/L)	Ionic strength	Temp. (°C)
51	26/05/1992	18	18	HgCl ₂	7.9	129	928	0.018	
51	03/06/1992	84	84	HgCl ₂	9.6	63.9	446	0.007	
51	04/06/1992	112	112	HgCl ₂	9.7	63.6	434	0.007	
51	12/08/1992	109	100	HgCl ₂	9.9	69.4	495	0.008	
52	06/06/1992	64	64		8.8	67.4	467	0.007	
52	10/06/1992	150	150		10.1	64.9	436	0.007	
52	12/10/1997	150	30		8.5	105	672	0.012	23
53	11/06/1992	84	84	HgCl ₂	8.6	67.6	466	0.007	
53	18/08/1999	130	126.1		8.97	86.5	554		23.7
53	19/11/1999	130	32		7.91	86.3	552	0.010	22.5
54	20/07/1992	135	135	HgCl ₂	9.7	66.3	450	0.007	
54	12/09/1997	135	30		10	78	499	0.009	24.5
54B	18/08/1999	141	140.4		10.1	85.9	550		24.7
55	21/07/1992	60	60	HgCl ₂	9.4	61.7	412	0.006	
55	18/08/1999	150	148.9		9.95	75.5	483	0.000	24.7
55	19/11/1999	162	61		9.77	67.4	431	0.007	23
73	28/03/1994	360	360		8.3	64.5	477	0.007	
73	10/10/1994	360	360	HNO ₃	9.8	76.4	492	0.008	
73	10/10/1994	360	360	HgCl ₂	9.8	73.1	455	0.007	
73	18/10/1994	360	200	HNO ₃	10	70.5	455	0.007	
73	18/10/1994	360	200	HgCl ₂	10	70	441	0.007	
73	26/05/1998	360	127		9.9	76	486	0.008	
73	19/08/1998	360	127		9.8	71	454	0.009	19.5
73	24/05/1999	360	127		9.5	80.7	516	0.006	
73	07/07/1999	360	127		9.73	87.6	561	0.009	24.9
73	07/07/1999	360	127		9.73	82	525	0.009	
73	18/08/1999	360	127		9.59			0.006	
73	27/09/2000	360	127		9.7	84	538	0.009	
73	15/03/1994	26	26		8.2	95.4	704	0.011	
58	10/05/1996				8.6	64.2	499	0.007	

Table D.1 (continued). Groundwater data for samples from boreholes in sodic breccia pipes – cations.

SODIC BRECCIA PIPES										
Name	Date sampled	Na (mg/L)	Na (meq/L)	K (mg/L)	K (meq/L)	Mg (mg/L)	Mg (meq/L)	Ca (mg/L)	Ca (meq/L)	Cations (meq/L)
51	26/05/1992	140	6.09	11	0.27	48	3.95	76	3.79	14.1
51	03/06/1992	138	6.00	1.5	0.04	2	0.16	2	0.10	6.38
51	04/06/1992	134	5.83	1.4	0.04	0.5	0.04	0.5	0.02	6.01
51	12/08/1992	149	6.48	3.4	0.09	2	0.16	0.5	0.02	6.85
52	06/06/1992	142	6.18	1	0.03	2	0.16	4	0.20	6.66
52	10/06/1992	136	5.92	0.6	0.02	0.5	0.04	0.5	0.02	6.11
52	12/10/1997	205	8.92	1.2	0.03	3.2	0.26	10	0.50	9.75
53	11/06/1992	140	6.09	3.8	0.10	0.5	0.04	2	0.10	6.40
53	18/08/1999									
53	19/11/1999	197	8.57	0.75	0.02	0.28	0.02	0.3	0.01	8.68
54	20/07/1992	141	6.13	2.9	0.07	1	0.08	1	0.05	6.47
54	12/09/1997	160	6.96	0.6	0.02	0.1	0.01	1.5	0.07	7.16
54B	18/08/1999									
55	21/07/1992	127	5.52	2.5	0.06	0.5	0.04	1	0.05	5.69
55	18/08/1999									
55	19/11/1999	135	5.87	0.56	0.01	0.48	0.04	0.3	0.01	6.07
73	28/03/1994	144	6.26	2.2	0.06	0.5	0.04	2	0.10	6.55
73	10/10/1994	153	6.66	0.7	0.02	0.5	0.04	1	0.05	6.84
73	10/10/1994	145	6.31	1.1	0.03	0.5	0.04	2	0.10	6.56
73	18/10/1994	143	6.2	0.1	0.00	0.5	0.04	0.5	0.02	6.36
73	18/10/1994	139	6.1	0.1	0.00	0.5	0.04	0.5	0.02	6.23
73	26/05/1998	159	6.9	0.5	0.01	0.2	0.02	1.2	0.06	7.14
73	19/08/1998	170	7.4	1.7	0.04	2.6	0.21	5.3	0.26	8.05
73	24/05/1999	96	4.2	0.7	0.02					4.22
73	07/07/1999	157	6.8	0.7	0.02	1.2	0.10	3.5	0.17	7.28
73	07/07/1999	165	7.2	0.6	0.02	1.2	0.10	3.4	0.17	7.52
73	18/08/1999	104	4.5	0.6	0.02					4.56
73	27/09/2000	179	7.8	0.6	0.02	0.1	0.01	1.6	0.08	8.01
73	15/03/1994	153	6.6	13	0.34	3	0.25	50	2.50	9.80
58	10/05/1996	151	6.57	2.5	0.06	0.5	0.04	3	0.15	6.83

Table D.1 (continued). Groundwater data for samples from boreholes in sodic breccia pipes – anions.

SODIC BRECCIA PIPES									
Name	Date sampled	Cl (mg/L)	Cl (meq/L)	SO ₄ (mg/L)	SO ₄ (meq/L)	HCO ₃ (mg/L)	HCO ₃ (meq/L)	Anions (meq/L)	Balance (%)
51	26/05/1992	244	6.88	107	2.23	281	4.61	14.1	0.01
51	03/06/1992	80	2.26	19	0.40	188	3.08	6.47	-0.74
51	04/06/1992	83	2.34	11	0.23	185	3.04	6.40	-3.2
51	12/08/1992	100	2.82	16	0.33	194	3.18	7.05	-1.4
52	06/06/1992	92	2.60	25	0.52	188	3.08	6.90	-1.7
52	10/06/1992	82	2.31	13	0.27	187	3.06	6.47	-2.9
52	12/10/1997	97	2.74	166	3.46	183	3.00	9.66	0.47
53	11/06/1992	78	2.20	21	0.44	204	3.34	6.81	-3.1
53	18/08/1999								
53	19/11/1999	82	2.31	17	0.35	318	5.21	8.21	2.8
54	20/07/1992	80	2.26	15	0.31	192	3.15	6.53	-0.50
54	12/09/1997	93	2.62	45	0.94	234	3.84	8.03	-5.8
54B	18/08/1999								
55	21/07/1992	70	1.97	29	0.60	162	2.65	6.07	-3.3
55	18/08/1999								
55	19/11/1999	67	1.89	36	0.75	153	2.51	5.59	4.1
73	28/03/1994	93	2.62	20	0.42	199	3.26	7.12	-4.1
73	10/10/1994	96	2.71	34	0.71	195	3.20	7.13	-2.1
73	10/10/1994	94	2.65	27	0.56	172	2.82	6.69	-0.97
73	18/10/1994	85	2.4	24	0.50	195	3.2	6.83	-3.5
73	18/10/1994	85	2.4	22	0.46	176	2.9	6.57	-2.7
73	26/05/1998	93	2.6	40	0.83	184	3.0	7.08	0.46
73	19/08/1998	120	3.4	54	1.1	187	3.1	8.21	-0.94
73	24/05/1999	99	2.8	59	1.2			4.55	-3.8
73	07/07/1999	99	2.8	64	1.3	181	3.0	8.69	-8.8
73	07/07/1999	102	2.9	64	1.3	216	3.5	8.33	-5.1
73	18/08/1999	94	2.7	70	1.5			4.62	-0.68
73	27/09/2000	100	2.8	84	1.8	178	2.9	8.02	-0.04
73	15/03/1994	93	2.6	35	0.73	343	5.6	9.65	0.79
58	10/05/1996	77	2.17	8	0.17	254	4.16	6.66	1.2

Table D.1 (continued). Groundwater data for samples from boreholes in sodic breccia pipes – minor species and ion ratios.

SODIC BRECCIA PIPES										
Name	Date sampled	NO ₃ (mg N/L)	NH ₄ (mg N/L)	F (mg/L)	Fe _T (mg/L)	Si (mg/L)	P (mg/L)	Na/Cl (wt)	Mg/Ca (wt)	SAR
51	26/05/1992	4.9	0.04	0.59		10.8	0.006	0.88	1.04	3.10
51	03/06/1992	0.11	1.0	13.8		20.6	0.035	2.7	1.7	16.5
51	04/06/1992		1.1	15.0		20.6	0.017	2.5	1.7	32.1
51	12/08/1992	0.08	1.3	13.5		15.9	0.065	2.3	6.6	21.1
52	06/06/1992		1.3	13.3		17.4	0.027	2.4	0.82	14.5
52	10/06/1992		1.5	15.6		20.6	0.015	2.6	1.7	32.5
52	12/10/1997		0.5	8.9	0.07	8.8		3.3	0.52	14.4
53	11/06/1992		1.0	15.7		5.7	0.022	2.8	0.41	22.9
53	18/08/1999									
53	19/11/1999			6.3		7.9		3.7	1.5	62.2
54	20/07/1992		1.8	15.5		19	0.028	2.7	1.7	23.9
54	12/09/1997		1.4	12	0.22	17.2		2.7	0.11	34.2
54B	18/08/1999									
55	21/07/1992	1.3	0.1	14.1		8.9	0.035	2.8	0.82	25.9
55	18/08/1999									
55	19/11/1999		1.3	8.4		11		3.1	2.6	35.6
73	28/03/1994	0.05	1.3	15.4		16.7		2.4	0.41	23.6
73	10/10/1994		1.0	9.8		14.7	0.013	2.5	0.82	31.2
73	10/10/1994		1.2	12.5	0.47	14.8	0.033	2.4	0.41	23.8
73	18/10/1994		1.0	13.9		17.3	0.013	2.6	1.7	34.2
73	18/10/1994		1.6	15.8	0.41	18	0.028	2.5	1.7	33.3
73	26/05/1998	<0.1	1.4	11.5	0.14	12.6		2.6	0.27	35.4
73	19/08/1998		1.3	12	0.36	8.6		2.2	0.81	15.1
73	24/05/1999			10		13.7		1.5		
73	07/07/1999		1.7	10.6	0.08	13.8	0.03	2.5	0.57	18.5
73	07/07/1999		0.8	11	0.09	10.1		2.5	0.58	19.6
73	18/08/1999			9.8		13		1.7		
73	27/09/2000	<0.1	1.1	10.1	<0.05	12.1	<0.1	2.8	0.10	37.1
73	15/03/1994		0.88	12.8		12.8	0.007	2.5	0.10	5.68
58	10/05/1996		0.06	3.1		9	0.008	3.0	0.27	21.3

Table D.1 (continued). Groundwater data for samples from boreholes in sodic breccia pipes – saturation indices.

SODIC BRECCIA PIPES										
Name	Date sampled	Calcite	Dolomite	Gypsum	Anhydrite	Fluorite	Chalcedony	Quartz	log $p\text{CO}_2$	Data source
51	26/05/1992	0.65	1.45	-1.69	-1.91	-1.59	0.13	0.56	-2.50	NWQDB
51	03/06/1992	0.36	1.11	-3.88	-4.10	-0.36	0.20	0.63	-4.57	NWQDB
51	04/06/1992	-0.20	0.00	-4.73	-4.95	-0.89	0.16	0.59	-4.72	NWQDB
51	12/08/1992	-0.12	0.75	-4.62	-4.84	-1.04	-0.05	0.38	-5.01	NWQDB
52	06/06/1992	0.14	0.33	-3.38	-3.60	-0.01	0.30	0.73	-3.58	NWQDB
52	10/06/1992	-0.10	0.21	-4.70	-4.92	-0.91	-0.06	0.37	-5.37	NWQDB
52	12/10/1997	0.17	0.15	-2.26	-2.49	-0.01	0.05	0.49	-3.28	CSIR
53	11/06/1992	-0.29	-0.83	-3.74	-3.96	-0.14	-0.17	0.26	-3.32	NWQDB
53	18/08/1999									This study
53	19/11/1999	-1.63	-2.97	-4.67	-4.90	-1.74	0.03	0.46	-2.44	This study
54	20/07/1992	0.11	0.61	-4.30	-4.52	-0.57	0.13	0.55	-4.71	NWQDB
54	12/09/1997	0.42	0.07	-3.75	-3.97	-0.71	-0.07	0.36	-5.08	CSIR
54B	18/08/1999									This study
55	21/07/1992	-0.07	-0.06	-3.95	-4.17	-0.60	-0.09	0.33	-4.34	NWQDB
55	18/08/1999									This study
55	19/11/1999	-0.46	-0.35	-4.42	-4.65	-1.58	-0.11	0.33	-4.95	This study
73	28/03/1994	-0.58	-1.41	-3.75	-3.97	-0.15	0.31	0.74	-3.02	NWQDB
73	10/10/1994	0.15	0.40	-3.98	-4.20	-1.01	-0.03	0.39	-4.84	NWQDB
73	10/10/1994	0.41	0.60	-3.75	-3.97	-0.46	-0.03	0.40	-4.91	NWQDB
73	18/10/1994	-0.10	0.21	-4.45	-4.67	-1.02	-0.08	0.35	-5.16	NWQDB
73	18/10/1994	-0.14	0.12	-4.46	-4.68	-0.88	-0.06	0.37	-5.23	NWQDB
73	26/05/1998	0.22	0.06	-3.83	-4.05	-0.79	-0.16	0.27	-5.05	This study
73	19/08/1998	0.81	1.63	-3.06	-3.29	-0.03	-0.16	0.28	-4.86	Cavé, 1999
73	24/05/1999						0.06	0.49		This study
73	07/07/1999	0.67	1.28	-3.19	-3.41	-0.41	-0.03	0.40	-4.71	This study
73	07/07/1999	0.67	1.29	-3.21	-3.43	-0.40	-0.16	0.26	-4.69	This study
73	18/08/1999						0.01	0.44		This study
73	27/09/2000	0.26	-0.30	-3.39	-3.61	-0.77	-0.07	0.35	-4.74	This study
73	15/03/1994	0.90	0.92	-2.23	-2.45	1.02	0.20	0.63	-2.70	NWQDB
58	10/05/1996	-0.02	-0.46	-3.99	-4.21	-1.40	0.03	0.46	-3.23	NWQDB

Table D.1 (continued). Groundwater data for samples from boreholes in sodic breccia pipes – borehole information.

SODIC BRECCIA PIPES									
Name	DWAF No.	Date sampled	Farm	Location	Lithology	Use	Latitude	Longitude	Elevation (m)
58	G39858	19/11/1997	Calvinia Allotment	Witwal	breccia -Na	Domestic	31.45306	19.81278	
58	G39858	18/11/1999	Calvinia Allotment	Witwal	breccia -Na		31.45306	19.81278	
60	G39860	07/05/1993	Calvinia Allotment	Witwal	breccia -Na	Domestic	31.4515	19.81237	1008
60	G39860	18/11/1999	Calvinia Allotment	Witwal	breccia -Na		31.4515	19.81237	1008
60A	G39860A	30/06/1993	Calvinia Allotment	Witwal	breccia -Na	Domestic	31.4515	19.81237	1008
61	G39861	30/06/1993	Calvinia Allotment	Witwal	breccia -Na	Domestic	31.45111	19.81083	1005
61	G39861	14/09/1994	Calvinia Allotment	Witwal	breccia -Na		31.45111	19.81083	1005
61	G39861	17/09/1994	Calvinia Allotment	Witwal	breccia -Na	Domestic	31.45111	19.81083	1005
61	G39861	17/08/1998	Calvinia Allotment	Witwal	breccia -Na		31.45111	19.81083	1005
61	G39861	07/07/1999	Calvinia Allotment	Witwal	breccia -Na		31.45111	19.81083	1005
61	G39861	18/11/1999	Calvinia Allotment	Witwal	breccia -Na		31.45111	19.81083	1005

Table D.1 (continued). Groundwater data for samples from boreholes in sodic breccia pipes – macro variables.

SODIC BRECCIA PIPES									
Name	Date sampled	Borehole Depth (m)	Sample Depth (m)	Preservation	Lab. pH	EC (mS/m)	TDS (mg/L)	Ionic strength	Temp. (°C)
58	19/11/1997			HgCl ₂	8.3	82.5	607	0.009	
58	18/11/1999	150	15.5		8.99	61.9	396	0.007	22
60	07/05/1993	86	86		8.1	139	924	0.016	
60	18/11/1999	170	14.5		8.26	62.8	402	0.007	22
60A	30/06/1993	161	161		8	59.7	453	0.006	
61	30/06/1993	160	160		8.3	70.1	464	0.007	
61	14/09/1994					72	461	0.007	
61	17/09/1994				8.5	64.8	507	0.007	
61	17/08/1998				8.73	73	467	0.009	22.5
61	07/07/1999				8.44	134.5	861	0.014	22
61	18/11/1999	196	196		8.81	92.1	589	0.010	21

Table D.1 (continued). Groundwater data for samples from boreholes in sodic breccia pipes – cations.

SODIC BRECCIA PIPES										
Name	Date sampled	Na (mg/L)	Na (meq/L)	K (mg/L)	K (meq/L)	Mg (mg/L)	Mg (meq/L)	Ca (mg/L)	Ca (meq/L)	Cations (meq/L)
58	19/11/1997	179	7.79	0.6	0.02	2	0.16	5	0.25	8.22
58	18/11/1999	143	6.22	0.71	0.02	1	0.08	1.2	0.05	6.38
60	07/05/1993	226	9.83	6	0.15	22	1.8	41	2.1	13.9
60	18/11/1999	133	5.79	0.65	0.02	1.7	0.14	23	1.2	7.10
60A	30/06/1993	119	5.18	2.2	0.06	1	0.08	8	0.40	5.72
61	30/06/1993	140	6.09	0.7	0.02	1	0.08	3	0.15	6.34
61	14/09/1994	151	6.57	0.6	0.02	0.3	0.02	1.6	0.08	6.69
61	17/09/1994	146	6.35	0.1	0.00	2	0.16	4	0.20	6.72
61	17/08/1998	180	7.83	0.7	0.02	2	0.16	4.6	0.23	8.28
61	07/07/1999	265	11.5	1	0.03	7.5	0.62	15	0.75	13.1
61	18/11/1999	190	8.26	1.3	0.03	2.4	0.20	30	1.5	10.0

Table D.1 (continued). Groundwater data for samples from boreholes in sodic breccia pipes – anions.

SODIC BRECCIA PIPES									
Name	Date sampled	Cl (mg/L)	Cl (meq/L)	SO ₄ (mg/L)	SO ₄ (meq/L)	HCO ₃ (mg/L)	HCO ₃ (meq/L)	Anions (meq/L)	Balance (%)
58	19/11/1997	130	3.67	18	0.37	271	4.44	8.60	-2.3
58	18/11/1999	63	1.78	3.3	0.07	233	3.82	5.93	3.7
60	07/05/1993	244	6.88	97	2.0	284	4.66	13.7	0.60
60	18/11/1999	62	1.75	8.8	0.18	235	3.85	5.90	9.2
60A	30/06/1993	49	1.38	9	0.19	261	4.28	6.05	-2.8
61	30/06/1993	102	2.88	7	0.15	207	3.39	6.61	-2.1
61	14/09/1994	94	2.65	3	0.06	249	4.08	6.95	-1.9
61	17/09/1994	93	2.62	12	0.25	246	4.03	7.05	-2.4
61	17/08/1998	150	4.23	5.7	0.12	246	4.03	8.73	-2.7
61	07/07/1999	317	8.94	33	0.69	216	3.54	13.3	-0.73
61	18/11/1999	153	4.32	6.4	0.13	233	3.82	8.34	9.1

Table D.1 (continued). Groundwater data for samples from boreholes in sodic breccia pipes – minor species and ion ratios.

SODIC BRECCIA PIPES										
Name	Date sampled	NO ₃ (mg N/L)	NH ₄ (mg N/L)	F (mg/L)	Fe _T (mg/L)	Si (mg/L)	P (mg/L)	Na/Cl (wt)	Mg/Ca (wt)	SAR
58	19/11/1997	0.08		2.1		7.7	0.016	2.1	0.66	17.1
58	18/11/1999			2.2		9.6		3.5	0.16	7.99
60	07/05/1993	0.05	0.69	3		6.3	0.015	1.4	0.88	7.08
60	18/11/1999			2.3		10		3.3	0.12	7.21
60A	30/06/1993	0.06	0.13	3.7		6.3	0.08	3.7	0.21	10.6
61	30/06/1993			3.6		0.8	0.017	2.1	0.55	17.9
61	14/09/1994	0.1		2.8	0.55	7.2		2.5	0.31	28.7
61	17/09/1994			2.7		6.2	0.009	2.4	0.82	14.9
61	17/08/1998			2.7	0.05	5.7		1.9	0.72	17.6
61	07/07/1999		2.1	2.3	0.06	9.1		1.3	0.82	14.0
61	18/11/1999			1.3		7.2		1.9	0.13	8.98

Table D.1 (continued). Groundwater data for samples from boreholes in sodic breccia pipes – saturation indices.

SODIC BRECCIA PIPES										
Name	Date sampled	Calcite	Dolomite	Gypsum	Anhydrite	Fluorite	Chalcedony	Quartz	log pCO ₂	Data source
58	19/11/1997	-0.07	-0.18	-3.44	-3.66	-1.51	-0.02	0.41	-2.89	NWQDB
58	18/11/1999	1.07	1.45	-3.56	-3.80	-0.82	0.06	0.50	-3.72	This study
60	07/05/1993	0.59	1.27	-1.95	-2.17	-0.40	-0.10	0.32	-2.69	Woodford, 1994
60	18/11/1999	0.48	0.14	-3.06	-3.29	-0.70	0.13	0.57	-2.93	This study
60A	30/06/1993	-0.13	-0.82	-3.48	-3.70	-0.78	-0.10	0.33	-2.59	Woodford, 1994
61	30/06/1993	-0.37	-0.86	-4.02	-4.24	-1.23	-1.01	-0.58	-3.00	Woodford, 1994
61	14/09/1994	-1.84	-4.06	-4.65	-4.87	-1.71	-0.04	0.39	-1.61	Woodford, 1994
61	17/09/1994	0.00	0.06	-3.69	-3.91	-1.37	-0.13	0.30	-3.13	CSIR
61	17/08/1998	0.23	0.43	-3.99	-4.21	-1.31	-0.14	0.29	-3.39	Cavé, 1999
61	07/07/1999	0.36	0.73	-2.78	-3.01	-0.98	0.08	0.52	-3.17	This study
61	18/11/1999	1.04	1.29	-3.16	-3.39	-1.13	-0.03	0.41	-3.53	This study

Table D.2. Groundwater data for samples from boreholes in calcic breccia pipes – borehole information.

CALCIC BRECCIA PIPES									
Name	DWAF No.	Date sampled	Farm	Location	Lithology	Use	Latitude	Longitude	Elevation (m)
48	G39848	06/05/1992	Enkelde Wilgenboom	Platberg/Airfield	breccia -Ca	Stock	31.49333	19.72444	
49	G39849	06/02/1992	Enkelde Wilgenboom	Platberg/Airfield	breccia -Ca	Stock	31.49306	19.72444	
49	G39849	06/02/1992	Enkelde Wilgenboom	Platberg/Airfield	breccia -Ca	Stock	31.49306	19.72444	
49	G39849	06/02/1992	Enkelde Wilgenboom	Platberg/Airfield	breccia -Ca	Stock	31.49306	19.72444	
49	G39849	03/03/1992	Enkelde Wilgenboom	Platberg/Airfield	breccia -Ca	Stock	31.49306	19.72444	
49	G39849	05/03/1992	Enkelde Wilgenboom	Platberg/Airfield	breccia -Ca	Stock	31.49306	19.72444	
49	G39849	18/03/1992	Enkelde Wilgenboom	Platberg/Airfield	breccia -Ca	Stock	31.49306	19.72444	
49	G39849	19/03/1992	Enkelde Wilgenboom	Platberg/Airfield	breccia -Ca	Stock	31.49306	19.72444	
35	G39635	14/05/1991	Calvinia Allotment	Bakenskop	breccia - Ca	Domestic	31.48556	19.85667	
57	G39857	17/03/1993	Calvinia Allotment	Bakenskop	breccia -Ca	Domestic	31.48583	19.85444	1015
57	G39857	18/03/1993	Calvinia Allotment	Bakenskop	breccia -Ca	Domestic	31.48583	19.85444	1015
57	G39857	22/04/1993	Calvinia Allotment	Bakenskop	breccia -Ca	Domestic	31.48583	19.85444	1015
57	G39857	22/04/1993	Calvinia Allotment	Bakenskop	breccia -Ca	Domestic	31.48583	19.85444	1015
57	G39857	15/04/1994	Calvinia Allotment	Bakenskop	breccia -Ca	Domestic	31.48583	19.85444	1015
57	G39857	18/11/1999	Calvinia Allotment	Bakenskop	breccia -Ca	Domestic	31.45444	19.81083	
59	G39859	03/08/1993	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	03/08/1993	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	04/08/1993	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	04/08/1993	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	05/08/1993	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	12/08/1993	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	12/08/1993	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	21/08/1993	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	20/09/1994	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	20/09/1994	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	20/09/1994	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	26/09/1994	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	26/09/1994	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	10/05/1996	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048
59	G39859	07/07/1999	Calvinia Allotment	Golf course	breccia -Ca	Domestic	31.48306	19.76417	1048

Table D.2 (continued). Groundwater data for samples from boreholes in calcic breccia pipes – macro variables.

CALCIC BRECCIA PIPES									
Name	Date sampled	Borehole Depth (m)	Sample Depth (m)	Preservation	Lab. pH	EC (mS/m)	TDS (mg/L)	Ionic strength	Temp. (°C)
48	06/05/1992	91	91	HgCl ₂	7.9	108	729	0.013	
49	06/02/1992	41	41	HgCl ₂	8.1	124	831	0.015	
49	06/02/1992	97	97	HgCl ₂	8.1	125	810	0.015	
49	06/02/1992	61	61	HgCl ₂	8.1	121	814	0.015	
49	03/03/1992	247	247	HgCl ₂	7.9	80.4	500	0.009	
49	05/03/1992	284	284	HgCl ₂	7.9	121	831	0.016	
49	18/03/1992	241	241	HgCl ₂	8.1	115	843	0.016	
49	19/03/1992	301	301	HgCl ₂	8.1	120	821	0.015	
35	14/05/1991	187	187	HgCl ₂	7.9	262	1675	0.034	
57	17/03/1993	48	48	HgCl ₂	7.4	168	1068	0.019	
57	18/03/1993	64	64	HgCl ₂	7.4	147	959	0.016	
57	22/04/1993	114	114	HgCl ₂	7.4	112	771	0.013	
57	22/04/1993	150	150	HgCl ₂	7.4	108	752	0.012	
57	15/04/1994	84	84		7.6	123	715	0.012	
57	18/11/1999	84	9.4		7.55	335	2144	0.037	
59	03/08/1993	194	12		7.8	361	2094	0.044	
59	03/08/1993	194	45		7.9	447	2785	0.059	
59	04/08/1993	194	70		8.2	395	2489	0.053	
59	04/08/1993	194	88		8.1	282	1695	0.035	
59	05/08/1993	194	103		8.1	228	1330	0.027	
59	12/08/1993	194	162		8.3	217	1297	0.026	
59	12/08/1993	194	164		8.2	311	1920	0.040	
59	21/08/1993	217	217		8.2	250	1550	0.031	
59	20/09/1994	194	150		7.6	297	1900	0.039	
59	20/09/1994	194	150		7.6	297	1856	0.039	
59	20/09/1994	194	150		7.6	299	1759	0.037	
59	26/09/1994	194	150		8.2	171	1083	0.021	
59	26/09/1994	194	150		8.4	174	1081	0.021	
59	10/05/1996	217	150	HgCl ₂	8.3	186	1161	0.023	
59	07/07/1999	194	150		7.57	167	1069	0.021	23.8

Table D.2 (continued). Groundwater data for samples from boreholes in calcic breccia pipes – cations.

CALCIC BRECCIA PIPES										
Name	Date sampled	Na (mg/L)	Na (meq/L)	K (mg/L)	K (meq/L)	Mg (mg/L)	Mg (meq/L)	Ca (mg/L)	Ca (meq/L)	Cations (meq/L)
48	06/05/1992	166	7.22	39	1.0	12	0.99	30	1.50	11.0
49	06/02/1992	129	5.61	5.6	0.14	32	2.63	76	3.79	12.2
49	06/02/1992	138	6.00	18	0.45	27	2.22	61	3.04	12.0
49	06/02/1992	130	5.65	11	0.28	32	2.63	69	3.44	12.0
49	03/03/1992	116	5.05	4.2	0.11	8	0.66	39	1.95	7.77
49	05/03/1992	143	6.22	4.5	0.12	29	2.39	77	3.84	12.6
49	18/03/1992	132	5.74	3.1	0.08	36	2.96	77	3.84	12.6
49	19/03/1992	143	6.22	2.9	0.07	27	2.22	78	3.89	12.4
35	14/05/1991	333	14.5	4.8	0.12	80	6.58	134	6.69	27.9
57	17/03/1993	246	10.7	24	0.61	33	2.71	37	1.85	16.1
57	18/03/1993	245	10.7	23	0.59	24	1.97	28	1.40	14.7
57	22/04/1993	199	8.66	9.2	0.24	16	1.32	24	1.20	11.5
57	22/04/1993	195	8.48	15	0.38	15	1.23	22	1.10	11.3
57	15/04/1994	208	9.05	31	0.79	3	0.25	10	0.50	10.9
57	18/11/1999	505	22.0	3.2	0.08	67	5.51	116	5.79	33.4
59	03/08/1993	306	13.3	46	1.2	153	12.6	145	7.24	34.6
59	03/08/1993	322	14.0	7.9	0.20	199	16.4	322	16.1	46.7
59	04/08/1993	277	12.1	13	0.32	175	14.4	283	14.1	41.0
59	04/08/1993	227	9.87	7	0.18	106	8.72	174	8.68	27.5
59	05/08/1993	186	8.09	3.4	0.09	82	6.75	123	6.14	21.1
59	12/08/1993	186	8.09	4.5	0.12	78	6.42	119	5.94	20.6
59	12/08/1993	246	10.7	3.9	0.10	122	10.0	203	10.1	31.0
59	21/08/1993	219	9.53	3.7	0.09	98	8.06	137	6.84	24.5
59	20/09/1994	234	10.2	7.3	0.19	117	9.63	203	10.1	30.1
59	20/09/1994	234	10.2	7.3	0.19	117	9.63	203	10.1	30.1
59	20/09/1994	225	9.79	6.2	0.16	112	9.21	197	9.83	29.0
59	26/09/1994	165	7.18	3.4	0.09	56	4.61	96	4.79	16.7
59	26/09/1994	165	7.18	3.4	0.09	55	4.52	99	4.94	16.7
59	10/05/1996	182	7.92	4.2	0.11	65	5.35	108	5.39	18.8
59	07/07/1999	167	7.26	2.5	0.06	57	4.69	98	4.89	16.9

Table D.2 (continued). Groundwater data for samples from boreholes in calcic breccia pipes – anions.

CALCIC BRECCIA PIPES									
Name	Date sampled	Cl (mg/L)	Cl (meq/L)	SO ₄ (mg/L)	SO ₄ (meq/L)	HCO ₃ (mg/L)	HCO ₃ (meq/L)	Anions (meq/L)	Balance (%)
48	06/05/1992	231	6.52	105	2.19	138	2.26	11.1	-0.12
49	06/02/1992	197	5.56	99	2.06	293	4.80	12.5	-1.1
49	06/02/1992	210	5.92	102	2.12	250	4.10	12.2	-0.94
49	06/02/1992	204	5.75	98	2.04	270	4.42	12.3	-0.93
49	03/03/1992	189	5.33	25	0.52	115	1.88	7.93	-1.1
49	05/03/1992	216	6.09	110	2.29	250	4.10	12.6	0.04
49	18/03/1992	214	6.04	106	2.21	273	4.47	12.8	-0.55
49	19/03/1992	218	6.15	104	2.17	246	4.03	12.4	-0.04
35	14/05/1991	739	20.9	183	3.81	200	3.28	28.0	-0.21
57	17/03/1993	348	9.82	88	1.83	286	4.68	16.5	-1.1
57	18/03/1993	278	7.84	76	1.58	281	4.60	14.2	2.0
57	22/04/1993	211	5.95	51	1.06	256	4.20	11.4	0.44
57	22/04/1993	192	5.42	55	1.15	255	4.18	10.9	1.2
57	15/04/1994	266	7.50	51	1.06	131	2.14	11.3	-2.1
57	18/11/1999	465	13.1	411	8.56	486	7.96	30.0	5.4
59	03/08/1993	917	25.9	337	7.02	124	2.04	35.9	-1.9
59	03/08/1993	1104	31.1	464	9.66	310	5.08	46.8	-0.16
59	04/08/1993	1026	28.9	387	8.06	286	4.68	42.4	-1.7
59	04/08/1993	672	19.0	213	4.43	261	4.28	28.3	-1.5
59	05/08/1993	508	14.3	155	3.23	262	4.30	22.0	-2.3
59	12/08/1993	485	13.7	152	3.16	255	4.18	21.3	-1.8
59	12/08/1993	720	20.3	297	6.18	298	4.88	31.9	-1.4
59	21/08/1993	585	16.5	188	3.91	271	4.44	25.6	-2.2
59	20/09/1994	706	19.9	228	4.75	339	5.56	31.1	-1.5
59	20/09/1994	706	19.9	228	4.75	311	5.10	30.6	-0.78
59	20/09/1994	651	18.4	211	4.39	307	5.03	28.7	0.60
59	26/09/1994	374	10.6	112	2.33	277	4.54	17.6	-2.6
59	26/09/1994	370	10.4	104	2.17	277	4.54	17.3	-1.7
59	10/05/1996	380	10.7	121	2.52	295	4.83	18.2	1.5
59	07/07/1999	332	9.37	103	2.14	270	4.42	16.0	2.8

Table D.2 (continued). Groundwater data for samples from boreholes in calcic breccia pipes – minor species and ion ratios.

CALCIC BRECCIA PIPES										
Name	Date sampled	NO ₃ (mg N/L)	NH ₄ (mg N/L)	F (mg/L)	Fe _T (mg/L)	Si (mg/L)	P (mg/L)	Na/Cl (wt)	Mg/Ca (wt)	SAR
48	06/05/1992	0.06	4.5	1.6		3.5	0.021	1.1	0.66	6.48
49	06/02/1992			0.62		8.1	0.018	1.0	0.69	3.13
49	06/02/1992		3.2	0.53		7.8	0.015	1.0	0.73	3.70
49	06/02/1992	0.04	0.29	0.58		7.6	0.017	0.98	0.76	3.24
49	03/03/1992		0.17	3.7		10.1	0.02	0.95	0.34	4.42
49	05/03/1992			1.4		10.8	0.01	1.0	0.62	3.52
49	18/03/1992			0.87		9.7	0.012	0.95	0.77	3.11
49	19/03/1992	0.05		1.3		10.7	0.013	1.0	0.57	3.56
35	14/05/1991			1.1		7.2	0.012	0.69	0.98	5.62
57	17/03/1993	0.05	3.0	2.3		5.2	0.016	1.1	1.5	7.09
57	18/03/1993	0.06	1.6	2.4		4.7	0.056	1.4	1.4	8.21
57	22/04/1993	0.05	0.84	2.8		5	0.021	1.5	1.1	7.72
57	22/04/1993	0.08	0.76	3.1		4.3	0.02	1.6	1.1	7.86
57	15/04/1994		3.8	12.1		3.6	0.026	1.2	0.49	14.8
57	18/11/1999	4.4		0.1		8		1.7	0.95	9.24
59	03/08/1993	13.8	4.1	0.41		6.8	0.029	0.51	1.7	4.23
59	03/08/1993	12.8	0.39	0.43		10.4	0.012	0.45	1.0	3.48
59	04/08/1993	9.7	0.81	0.47		10	0.009	0.42	1.0	3.19
59	04/08/1993	8.1	0.1	0.43		10.2	0.007	0.52	1.0	3.35
59	05/08/1993	2.2	0.09	0.4		10	0.006	0.56	1.1	3.19
59	12/08/1993	3.9	0.08	0.39		9.7	0.009	0.59	1.1	3.26
59	12/08/1993	6.8	0.1	0.39		10.7	0.009	0.53	0.99	3.37
59	21/08/1993	10.7	0.09	0.41		9.9	0.008	0.58	1.2	3.49
59	20/09/1994	11.2		0.6	0.47	8.9	0.012	0.51	0.95	3.24
59	20/09/1994	11.2		0.57		8.9	0.008	0.51	0.95	3.24
59	20/09/1994	11.1	0.12	1.3		10.8	0.012	0.53	0.94	3.17
59	26/09/1994	1.7		0.43	0.06	7.2	0.01	0.68	0.96	3.31
59	26/09/1994	1.8	0.11	0.59	0.06	8.7	0.006	0.69	0.92	3.30
59	10/05/1996	1.8	0.05	0.38		8.9	0.009	0.74	0.99	3.42
59	07/07/1999			1.0	0.18	9.1		0.78	0.96	3.32

Table D.2 (continued). Groundwater data for samples from boreholes in calcic breccia pipes – saturation indices.

CALCIC BRECCIA PIPES										
Name	Date sampled	Calcite	Dolomite	Gypsum	Anhydrite	Fluorite	Chalcedony	Quartz	log $p\text{CO}_2$	Data source
48	06/05/1992	-0.02	-0.09	-1.99	-2.21	-1.03	-0.36	0.07	-2.79	NWQDB
49	06/02/1992	0.87	1.72	-1.69	-1.91	-1.51	0.00	0.43	-2.68	NWQDB
49	06/02/1992	0.72	1.43	-1.76	-1.98	-1.73	-0.01	0.42	-2.75	NWQDB
49	06/02/1992	0.80	1.62	-1.73	-1.95	-1.61	-0.02	0.41	-2.71	NWQDB
49	03/03/1992	0.07	-0.20	-2.43	-2.65	-0.12	0.10	0.53	-2.86	NWQDB
49	05/03/1992	0.62	1.16	-1.64	-1.86	-0.82	0.13	0.56	-2.54	NWQDB
49	18/03/1992	0.84	1.71	-1.67	-1.89	-1.22	0.08	0.51	-2.71	NWQDB
49	19/03/1992	0.81	1.51	-1.66	-1.88	-0.88	0.13	0.55	-2.76	NWQDB
35	14/05/1991	0.66	1.45	-1.37	-1.59	-0.95	-0.04	0.39	-2.67	NWQDB
57	17/03/1993	-0.14	0.01	-2.06	-2.28	-0.71	-0.18	0.25	-1.98	NWQDB
57	18/03/1993	-0.25	-0.23	-2.21	-2.43	-0.75	-0.22	0.20	-1.98	NWQDB
57	22/04/1993	-0.33	-0.49	-2.39	-2.61	-0.65	-0.20	0.23	-2.01	NWQDB
57	22/04/1993	-0.37	-0.55	-2.39	-2.61	-0.59	-0.26	0.17	-2.01	NWQDB
57	15/04/1994	-0.79	-1.76	-2.73	-2.95	0.28	-0.34	0.09	-2.50	NWQDB
57	18/11/1999	0.59	1.29	-1.12	-1.34	-3.11	0.01	0.44	-1.92	This study
59	03/08/1993	0.34	1.05	-1.17	-1.39	-1.86	-0.06	0.37	-2.79	Woodford, 1994
59	03/08/1993	1.11	2.36	-0.81	-1.02	-1.57	0.12	0.55	-2.52	Woodford, 1994
59	04/08/1993	1.32	2.78	-0.90	-1.12	-1.51	0.10	0.53	-2.87	Woodford, 1994
59	04/08/1993	1.06	2.26	-1.23	-1.45	-1.67	0.11	0.54	-2.77	Woodford, 1994
59	05/08/1993	0.96	2.09	-1.44	-1.66	-1.82	0.10	0.53	-2.76	Woodford, 1994
59	12/08/1993	1.12	2.41	-1.46	-1.68	-1.85	0.08	0.51	-2.98	Woodford, 1994
59	12/08/1993	1.25	2.62	-1.07	-1.29	-1.73	0.13	0.55	-2.83	Woodford, 1994
59	21/08/1993	1.09	2.38	-1.35	-1.57	-1.79	0.09	0.52	-2.85	Woodford, 1994
59	20/09/1994	0.75	1.60	-1.17	-1.38	-1.34	0.05	0.48	-2.14	Woodford, 1994
59	20/09/1994	0.71	1.53	-1.16	-1.38	-1.38	0.05	0.48	-2.18	NWQDB
59	20/09/1994	0.70	1.51	-1.20	-1.42	-0.65	0.14	0.57	-2.19	NWQDB
59	26/09/1994	1.00	2.13	-1.62	-1.84	-1.80	-0.05	0.38	-2.82	NWQDB
59	26/09/1994	1.20	2.50	-1.64	-1.86	-1.51	0.03	0.46	-3.04	NWQDB
59	10/05/1996	1.16	2.45	-1.56	-1.78	-1.88	0.04	0.47	-2.91	NWQDB
59	07/07/1999	0.39	0.87	-1.64	-1.86	-1.03	0.08	0.51	-2.19	This study

Table D.2 (continued). Groundwater data for samples from boreholes in calcic breccia pipes – borehole information.

CALCIC BRECCIA PIPES									
Name	DWAF No.	Date sampled	Farm	Location	Lithology	Use	Latitude	Longitude	Elevation (m)
59	G39859	18/11/1999	Calvinia Allotment	Golf course	breccia -Ca		31.48306	19.76417	1048
62	G39862	30/06/1993	Calvinia Allotment	Golf Course	breccia -Ca	Domestic	31.48306	19.76417	
62	G39862	30/06/1993	Calvinia Allotment	Golf Course	breccia -Ca	Domestic	31.48306	19.76417	
62	G39862	18/11/1999	Calvinia Allotment	Golf Course	breccia -Ca		31.48306	19.76417	
646	G39646	14/08/1991	Gytjes Gat	Witkop	breccia -Ca		31.50889	19.84944	
646	G39646	14/08/1991	Gytjes Gat	Witkop	breccia -Ca		31.50889	19.84944	
646	G39646	14/08/1991	Gytjes Gat	Witkop	breccia -Ca		31.50889	19.84944	
646	G39646	15/08/1991	Gytjes Gat	Witkop	breccia -Ca		31.50889	19.84944	
646	G39646	21/09/1994	Gytjes Gat	Witkop	breccia -Ca	Domestic	31.50889	19.84944	
646	G39646	23/09/1994	Gytjes Gat	Witkop	breccia -Ca	Domestic	31.50889	19.84944	
646 2	G39646	21/09/1994	Gytjes Gat	Witkop	breccia -Ca	Domestic	31.50889	19.84944	
646 2	G39646	21/09/1994	Gytjes Gat	Witkop	breccia -Ca	Domestic	31.50889	19.84944	
648	G39648	11/09/1991	Gytjes Gat	Witkop	breccia -Ca		31.50917	19.85111	1000
648	G39648	11/09/1991	Gytjes Gat	Witkop	breccia -Ca		31.50917	19.85111	1000
648	G39648	11/09/1991	Gytjes Gat	Witkop	breccia -Ca		31.50917	19.85111	1000
648	G39648	01/10/1993	Gytjes Gat	Witkop	breccia -Ca	Stock	31.50917	19.85111	1000
648	G39648	09/11/1993	Gytjes Gat	Witkop	breccia -Ca		31.50917	19.85111	1000
648	G39648	09/11/1993	Gytjes Gat	Witkop	breccia -Ca		31.50917	19.85111	1000
648	G39648	09/11/1993	Gytjes Gat	Witkop	breccia -Ca		31.50917	19.85111	1000
648	G39648	12/11/1997	Gytjes Gat	Witkop	breccia -Ca		31.50917	19.85111	1000
648	G39648	17/08/1998	Gytjes Gat	Witkop	breccia -Ca		31.50917	19.85111	1000
649	G39649	12/09/1991	Gytjes Gat		shale		31.50806	19.85139	

Table D.2 (continued). Groundwater data for samples from boreholes in calcic breccia pipes – macro variables.

CALCIC BRECCIA PIPES									
Name	Date sampled	Borehole Depth (m)	Sample Depth (m)	Preservation	Lab. pH	EC (mS/m)	TDS (mg/L)	Ionic strength	Temp. (°C)
59	18/11/1999	217	150		7.29	252	1613	0.033	21.5
62	30/06/1993	193	193		7.6	228	1165	0.021	
62	30/06/1993	151	151		7.9	284	1712	0.034	
62	18/11/1999	194	11.8		7.25	224	1433	0.022	24
646	14/08/1991	75	75	HgCl ₂	8.2	571	3384	0.074	
646	14/08/1991	60	60	HgCl ₂	8.1	554	3403	0.073	
646	14/08/1991	54	54	HgCl ₂	8.1	558	3298	0.070	
646	15/08/1991	103	103	HgCl ₂	7.9	544	3352	0.072	
646	21/09/1994	103	100		7.6	506	3130	0.067	
646	23/09/1994	103	100	HgCl ₂	7.6	540	2990	0.065	
646 2	21/09/1994				7.6	496	2997	0.065	
646 2	21/09/1994			HgCl ₂	7.6	528	2910	0.063	
648	11/09/1991	65	65	HgCl ₂	8	486	2791	0.057	
648	11/09/1991	30	30	HgCl ₂	7.7	491	2776	0.056	
648	11/09/1991	15	15	HgCl ₂	7.9	370	2155	0.047	
648	01/10/1993	200	200	HgCl ₂	8.1	513	2888	0.060	
648	09/11/1993	200	65			486	3110	0.057	
648	09/11/1993	200	30			491	3142	0.056	
648	09/11/1993	200	15			370	2368	0.047	
648	12/11/1997	200	150		7.5	443	2835	0.051	22
648	17/08/1998	200	150		7.27	404	2586	0.067	
649	12/09/1991	85	85	HgCl ₂	8	323	1835	0.038	

Table D.2 (continued). Groundwater data for samples from boreholes in calcic breccia pipes – cations.

CALCIC BRECCIA PIPES										
Name	Date sampled	Na (mg/L)	Na (meq/L)	K (mg/L)	K (meq/L)	Mg (mg/L)	Mg (meq/L)	Ca (mg/L)	Ca (meq/L)	Cations (meq/L)
59	18/11/1999	214	9.31	3.3	0.08	82	6.75	212	10.6	26.7
62	30/06/1993	406	17.7	1.9	0.05	5	0.41	25	1.25	19.4
62	30/06/1993	261	11.4	6.1	0.16	94	7.73	161	8.03	27.3
62	18/11/1999	412	17.9	1.8	0.05	4.2	0.35	49	2.45	20.8
646	14/08/1991	598	26.0	8.1	0.21	210	17.3	287	14.3	57.8
646	14/08/1991	605	26.3	6.8	0.17	213	17.5	290	14.5	58.5
646	14/08/1991	594	25.8	27	0.70	197	16.2	273	13.6	56.4
646	15/08/1991	592	25.8	17	0.45	208	17.1	283	14.1	57.5
646	21/09/1994	528	23.0	5.2	0.13	192	15.8	283	14.1	53.0
646	23/09/1994	512	22.3	4.4	0.11	190	15.6	272	13.6	51.6
646_2	21/09/1994	516	22.4	4.2	0.11	187	15.4	275	13.7	51.7
646_2	21/09/1994	501	21.8	3.7	0.09	184	15.1	268	13.4	50.4
648	11/09/1991	593	25.8	6.7	0.17	145	11.9	166	8.28	46.2
648	11/09/1991	638	27.8	4.5	0.12	133	10.9	146	7.29	46.1
648	11/09/1991	355	15.4	8.5	0.22	133	10.9	217	10.8	37.4
648	01/10/1993	582	25.3	7.8	0.20	170	14.0	198	9.88	49.4
648	09/11/1993	593	25.8	6.7	0.17	145	11.9	166	8.28	46.2
648	09/11/1993	638	27.8	4.5	0.12	133	10.9	146	7.29	46.1
648	09/11/1993	355	15.4	8.5	0.22	133	10.9	217	10.8	37.4
648	12/11/1997	577	25.1	3.6	0.09	121	9.95	145	7.24	42.4
648	17/08/1998	590	25.7	5.8	0.15	210	17.3	220	11.0	54.3
649	12/09/1991	384	16.7	7.7	0.20	104	8.56	115	5.74	31.2

Table D.2 (continued). Groundwater data for samples from boreholes in calcic breccia pipes – anions.

CALCIC BRECCIA PIPES									
Name	Date sampled	Cl (mg/L)	Cl (meq/L)	SO ₄ (mg/L)	SO ₄ (meq/L)	HCO ₃ (mg/L)	HCO ₃ (meq/L)	Anions (meq/L)	Balance (%)
59	18/11/1999	544	15.4	149	3.10	349	5.72	24.2	5.0
62	30/06/1993	656	18.5	11	0.23	57.3	0.94	19.9	-1.3
62	30/06/1993	619	17.5	201	4.18	317	5.20	27.7	-0.76
62	18/11/1999	663	18.7	4.4	0.09	50	0.82	19.7	2.7
646	14/08/1991	1723	48.6	315	6.56	229	3.75	59.2	-1.2
646	14/08/1991	1732	48.9	309	6.43	235	3.85	59.4	-0.77
646	14/08/1991	1666	47.0	299	6.23	227	3.72	57.2	-0.74
646	15/08/1991	1705	48.1	301	6.27	233	3.82	58.4	-0.84
646	21/09/1994	1585	44.7	272	5.66	254	4.16	54.8	-1.6
646	23/09/1994	1515	42.7	238	4.96	246	4.03	51.9	-0.34
646_2	21/09/1994	1497	42.2	260	5.41	249	4.08	51.9	-0.25
646_2	21/09/1994	1465	41.3	231	4.81	244	4.00	50.5	-0.13
648	11/09/1991	1425	40.2	217	4.52	233	3.82	48.7	-2.6
648	11/09/1991	1457	41.1	160	3.33	237	3.88	48.4	-2.4
648	11/09/1991	1079	30.4	143	2.98	195	3.20	37.0	0.53
648	01/10/1993	1463	41.3	242	5.04	222	3.64	50.0	-0.59
648	09/11/1993	1425	40.2	217	4.52	284	4.66	49.5	-3.5
648	09/11/1993	1457	41.1	160	3.33	289	4.74	49.2	-3.3
648	09/11/1993	1079	30.4	143	2.98	238	3.90	37.7	-0.41
648	12/11/1997	1272	35.9	106	2.21	388	6.36	44.5	-2.4
648	17/08/1998	1570	44.3	150	3.12	388	6.36	53.8	0.40
649	12/09/1991	900	25.4	83	1.73	239	3.92	31.1	0.22

Table D.2 (continued). Groundwater data for samples from boreholes in calcic breccia pipes – minor species and ion ratios.

CALCIC BRECCIA PIPES										
Name	Date sampled	NO ₃ (mg N/L)	NH ₄ (mg N/L)	F (mg/L)	Fe _T (mg/L)	Si (mg/L)	P (mg/L)	Na/Cl (wt)	Mg/Ca (wt)	SAR
59	18/11/1999					9.8		0.61	0.64	3.16
62	30/06/1993	0.24		3.1		6.7	0.017	0.95	0.33	19.4
62	30/06/1993	11.5		0.82		9.1	0.02	0.65	0.96	4.04
62	18/11/1999		0.23	1.5		5		0.96	0.14	15.2
646	14/08/1991	2.9		0.85		7.3	0.022	0.54	1.2	6.54
646	14/08/1991	2.9	0.05	0.88		7.7	0.022	0.54	1.2	6.58
646	14/08/1991	3.4	0.07	0.79		5	0.016	0.55	1.2	6.69
646	15/08/1991	2.6	0.19	0.86		7.2	0.02	0.54	1.2	6.52
646	21/09/1994	2.4	0.23	1.1		6.5	0.023	0.51	1.1	5.94
646	23/09/1994	2.5	0.15	0.85		7.8	0.005	0.52	1.1	5.83
646 2	21/09/1994	2.0		1.1		6.4	0.011	0.53	1.1	5.88
646 2	21/09/1994	2.0		4.9		7.9		0.53	1.1	5.77
648	11/09/1991	0.88		1.2		6	0.006	0.64	1.4	8.11
648	11/09/1991			1.2		6.2	0.006	0.68	1.5	9.19
648	11/09/1991	5.3	0.49	0.87		7.2	0.005	0.51	1.0	4.68
648	01/10/1993	0.46		0.91		7	0.012	0.61	1.4	7.33
648	09/11/1993	0.9	0.83	1.2		6		0.64	1.4	8.11
648	09/11/1993			1.2		6.2		0.68	1.5	9.19
648	09/11/1993	5.3		0.9		7.2		0.51	1.0	4.68
648	12/11/1997			1.4	0.13	7.58	0.2	0.70	1.4	8.56
648	17/08/1998		0.7	1.1	0.07	5		0.58	1.6	6.83
649	12/09/1991	0.05	0.58	1.2		5.9	0.008	0.66	1.5	6.25

Table D.2 (continued). Groundwater data for samples from boreholes in calcic breccia pipes – saturation indices.

CALCIC BRECCIA PIPES										
Name	Date sampled	Calcite	Dolomite	Gypsum	Anhydrite	Fluorite	Chalcedony	Quartz	log $p\text{CO}_2$	Data source
59	18/11/1999	0.46	0.81	-1.27	-1.50		0.14	0.58	-1.83	This study
62	30/06/1993	-0.79	-1.93	-3.09	-3.31	-0.55	-0.07	0.36	-2.88	NWQDB
62	30/06/1993	0.93	1.98	-1.27	-1.49	-1.13	0.06	0.49	-2.47	NWQDB
62	18/11/1999	-0.92	-2.57	-3.21	-3.44	-0.89	-0.18	0.25	-2.59	This study
646	14/08/1991	1.19	2.60	-1.05	-1.27	-1.06	-0.04	0.39	-2.98	NWQDB
646	14/08/1991	1.12	2.46	-1.05	-1.27	-1.03	-0.01	0.42	-2.86	NWQDB
646	14/08/1991	1.09	2.39	-1.08	-1.29	-1.13	-0.20	0.23	-2.87	NWQDB
646	15/08/1991	0.93	2.07	-1.07	-1.29	-1.05	-0.04	0.39	-2.65	NWQDB
646	21/09/1994	0.69	1.56	-1.09	-1.31	-0.81	-0.08	0.35	-2.30	NWQDB
646	23/09/1994	0.67	1.53	-1.15	-1.37	-1.04	0.00	0.43	-2.31	NWQDB
646 2	21/09/1994	0.67	1.53	-1.11	-1.33	-0.81	-0.09	0.34	-2.30	NWQDB
646 2	21/09/1994	0.66	1.51	-1.17	-1.38	0.47	0.01	0.44	-2.31	NWQDB
648	11/09/1991	0.84	1.97	-1.34	-1.56	-0.92	-0.12	0.31	-2.73	NWQDB
648	11/09/1991	0.51	1.34	-1.51	-1.73	-0.96	-0.10	0.33	-2.41	NWQDB
648	11/09/1991	0.81	1.77	-1.37	-1.59	-1.02	-0.04	0.39	-2.70	NWQDB
648	01/10/1993	0.97	2.23	-1.25	-1.47	-1.09	-0.05	0.38	-2.87	NWQDB
648	09/11/1993	-0.05	0.19	-1.34	-1.56	-0.90	-0.11	0.32	-1.62	Woodford, 1994
648	09/11/1993	-0.09	0.13	-1.51	-1.73	-0.94	-0.10	0.33	-1.61	Woodford, 1994
648	09/11/1993	0.02	0.18	-1.37	-1.59	-0.99	-0.03	0.40	-1.70	Woodford, 1994
648	12/11/1997	0.50	1.24	-1.66	-1.89	-0.74	0.02	0.46	-2.01	CSIR
648	17/08/1998	0.45	1.23	-1.45	-1.67	-0.93	-0.19	0.24	-1.78	Cavé, 1999
649	12/09/1991	0.77	1.84	-1.80	-2.02	-0.93	-0.13	0.30	-2.70	NWQDB

Table D.3. Groundwater data for samples from other boreholes yielding sodic waters – borehole information.

OTHER SODIC GROUNDWATERS									
Name	DWAF No.	Date sampled	Farm	Location	Lithology	Use	Latitude	Longitude	Elevation (m)
CT58		26/03/1980	Calvinia Allotment	Akkerendam	?	Domestic	31.43417	19.78333	
DW12		01/07/1980	Downes Wes		?	Stock	31.54806	19.8775	
JV1		07/08/1999	Calvinia Allotment	Jaagvlakte	?	Domestic	31.47297	19.87634	1030
80	G39580	31/10/1990	Onwetende Fontein		?	Domestic	31.50944	19.91917	
93	G39593	21/11/1990	Albertfontein Ruggens		dolerite/shale	Domestic	31.48722	19.96722	
50	G39850	12/05/1992	Albertfontein Ruggens		dolerite/shale	Domestic/Stock	31.48194	19.96361	

Table D.3 (continued). Groundwater data for samples from other boreholes yielding sodic waters – macro variables.

Name	Date sampled	Borehole Depth (m)	Sample Depth (m)	Preservation	Lab. pH	EC (mS/m)	TDS (mg/L)	Ionic strength	Temp. (°C)
CT58	26/03/1980	104	100		7.6	52.1	416	0.006	
DW12	01/07/1980	30	30		7.6	83.4	610	0.008	
JV1	07/08/1999				9.09	78	499	0.007	16.4
80	31/10/1990	64.5	64.5	HgCl ₂	9.1	121	924	0.014	
93	21/11/1990	42	42	HgCl ₂	7.8	94.3	756	0.012	
50	12/05/1992	79	79	HgCl ₂	8.2	65.7	455	0.007	

Table D.3 (continued). Groundwater data for samples from other boreholes yielding sodic waters – cations.

Name	Date sampled	Na (mg/L)	Na (meq/L)	K (mg/L)	K (meq/L)	Mg (mg/L)	Mg (meq/L)	Ca (mg/L)	Ca (meq/L)	Cations (meq/L)
CT58	26/03/1980	92	4.0	0.55	0.01	2.9	0.24	25	1.3	5.51
DW12	01/07/1980	188	8.2	1	0.03	0.6	0.05	1.3	0.06	8.32
JV1	07/08/1999	144	6.3	0.7	0.02	0.15	0.01	2	0.10	6.42
80	31/10/1990	285	12.4	12	0.31	2	0.16	2	0.10	13.0
93	21/11/1990	210	9.1	18	0.45	7	0.58	13	0.65	10.8
50	12/05/1992	136	5.9	4.9	0.13	3	0.25	9	0.45	6.75

Table D.3 (continued). Groundwater data for samples from other boreholes yielding sodic waters – anions.

OTHER SODIC GROUNDWATERS									
Name	Date sampled	Cl (mg/L)	Cl (meq/L)	SO ₄ (mg/L)	SO ₄ (meq/L)	HCO ₃ (mg/L)	HCO ₃ (meq/L)	Anions (meq/L)	Balance (%)
CT58	26/03/1980	36	1.02	1.7	0.04	256	4.20	5.33	1.7
DW12	01/07/1980	121	3.41	4.3	0.09	287	4.70	8.43	-0.65
JV1	07/08/1999	93	2.62	18	0.37	233	3.82	6.93	-5.7
80	31/10/1990	221	6.23	17	0.35	382	6.26	13.1	-0.29
93	21/11/1990	172	4.85	66	1.37	266	4.36	10.7	0.60
50	12/05/1992	139	3.92	20	0.42	135	2.21	6.93	-1.4

Table D.3 (continued). Groundwater data for samples from other boreholes yielding sodic waters – minor species and ion ratios.

Name	Date sampled	NO ₃ (mg N/L)	NH ₄ (mg N/L)	F (mg/L)	Fe _T (mg/L)	Si (mg/L)	P (mg/L)	Na/Cl (wt)	Mg/Ca (wt)	SAR
CT58	26/03/1980	0.15	0.15	1.4		9.9		3.9	0.19	4.64
DW12	01/07/1980	0.92	0.03	3.0		7.2		2.4	0.76	34.2
JV1	07/08/1999			3.7	0.09	6.7		2.4	0.12	26.5
80	31/10/1990	0.1	0.67	4.5		6.1	0.01	2.0	1.7	34.1
93	21/11/1990	0.35	0.1	1.4		6	0.039	1.9	0.89	11.7
50	12/05/1992	0.06	0.12	7		6	0.087	1.5	0.55	10.0

Table D.3 (continued). Groundwater data for samples from other boreholes yielding sodic waters – saturation indices.

Name	Date sampled	Calcite	Dolomite	Gypsum	Anhydrite	Fluorite	Chalcedony	Quartz	log pCO ₂	Data source
CT58	26/03/1980	-0.03	-0.65	-3.72	-3.94	-1.12	0.10	0.53	-2.20	Van Wyk, 1980
DW12	01/07/1980	-1.29	-2.57	-4.62	-4.84	-1.78	-0.04	0.39	-2.15	Seward, 1983
JV1	07/08/1999	0.09	-0.70	-3.84	-4.08	-1.32	-0.03	0.43	-3.82	This study
80	31/10/1990	0.29	0.96	-4.02	-4.24	-1.40	-0.19	0.24	-3.62	NWQDB
93	21/11/1990	-0.18	-0.28	-2.52	-2.74	-1.49	-0.12	0.31	-2.40	NWQDB
50	12/05/1992	-0.18	-0.49	-3.10	-3.32	-0.18	-0.13	0.30	-3.09	NWQDB

Table D.4. Groundwater data for samples from boreholes in alluvial aquifers – borehole information.

ALLUVIUM									
Name	DWAF No.	Date sampled	Farm	Location	Lithology	Use	Latitude	Longitude	Elevation (m)
22	G29622	28/01/1991	Downes Wes		alluvium	Domestic	31.51	19.8944	
23	G29623	28/01/1991	Downes Wes		alluvium	Domestic	31.50778	19.895	
23	G29623	29/01/1991	Downes Wes		alluvium/shale	Domestic	31.50778	19.895	
24	G39624	30/01/1991	Onwetende Fontein		alluvium	Domestic	31.50806	19.92417	
24	G39624	07/02/1991	Onwetende Fontein		alluvium	Domestic	31.50806	19.92417	
24	G39624	08/02/1991	Onwetende Fontein		alluvium/shale	Domestic	31.50806	19.92417	
24A	G39624A	24/05/1992	Onwetende Fontein		alluvium	Domestic/Stock	31.50778	19.92194	1015
24A	G39624A	25/05/1992	Onwetende Fontein		alluvium/shale	Domestic/Stock	31.50778	19.92194	1015
25	G29625	20/02/1991	Onwetende Fontein		alluvium/shale	Domestic	31.50861	19.92333	
26	G39626	11/02/1991	Onwetende Fontein		alluvium	Domestic	31.50861	19.92333	
26	G39626	12/02/1991	Onwetende Fontein		alluvium/shale	Domestic	31.50861	19.92333	
26A	G39626A	14/05/1991	Onwetende Fontein		alluvium		31.50889	19.92083	
26A	G39626A	14/05/1991	Onwetende Fontein		alluvium/shale		31.50889	19.92194	
27	G39627	14/02/1991	Downes Wes		alluvium	Domestic	31.51667	19.93472	
27A	G39627A	17/03/1992	Downes Wes		alluvium	Domestic/Stock	31.51083	19.89389	
27A	G39627A	17/08/1998	Downes Wes		alluvium		31.51083	19.89389	
32	G39632	23/04/1991	Downes Wes		alluvium		31.49944	19.87472	
32	G39632	23/04/1991	Downes Wes		alluvium/shale		31.49944	19.87472	
32	G39632	23/04/1991	Downes Wes		alluvium/shale		31.49944	19.87472	
33	G39633	26/04/1991	Downes Wes		alluvium		31.50111	19.87361	
33	G39633	19/02/1992	Downes Wes		alluvium	Domestic/Stock	31.50111	19.87361	
34	G39634	07/05/1991	Downes Wes		alluvium		31.50333	19.87306	
37	G39637	13/06/1991	Downes Wes		alluvium		31.49694	19.87528	
38	G39638	17/06/1991	Downes Wes		alluvium		31.49778	19.87444	990
38	G39638	25/07/1991	Downes Wes		alluvium		31.49778	19.87444	990
38	G39638	16/02/1992	Downes Wes		alluvium		31.49778	19.87444	990
38	G39638	12/11/1997	Downes Wes		alluvium		31.49778	19.87444	990
38	G39638	17/08/1998	Downes Wes		alluvium		31.49778	19.87444	990
39	G39639	26/06/1991	Downes Wes		alluvium		31.49833	19.875	
43	G39843	03/12/1991	Enkelde Wilgenboom		alluvium/shale		31.49028	19.70861	940

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – macro variables.

ALLUVIUM									
Name	Date sampled	Borehole Depth (m)	Sample Depth (m)	Preservation	Lab. pH	EC (mS/m)	TDS (mg/L)	Ionic strength	Temp. (°C)
22	28/01/1991	13	13	HgCl ₂	8	711	5247	0.105	
23	28/01/1991	60	13	HgCl ₂	8.1	492	3248	0.064	
23	29/01/1991	60	60	HgCl ₂	7.6	496	3255	0.063	
24	30/01/1991	66	12	HgCl ₂	8	630	4576	0.089	
24	07/02/1991	66	18	HgCl ₂	7.8	616	4520	0.085	
24	08/02/1991	66	66	HgCl ₂	8	623	4506	0.087	
24A	24/05/1992	73	11	HgCl ₂	8.3	430	3023	0.056	
24A	25/05/1992	73	73	HgCl ₂	8.3	449	3081	0.057	
25	20/02/1991	44	44	HgCl ₂	7.9	614	4354	0.083	
26	11/02/1991	73	9	HgCl ₂	8.1	641	4609	0.088	
26	12/02/1991	73	73	HgCl ₂	8.1	326	1965	0.037	
26A	14/05/1991	102	18	HgCl ₂	7.6	518	3729	0.072	
26A	14/05/1991	102	102	HgCl ₂	7.5	513	3694	0.071	
27	14/02/1991	12	12	HgCl ₂	8.3	725	5275	0.103	
27A	17/03/1992	15	15	HgCl ₂	8.0	706	5212	0.102	
27A	17/08/1998				8.3	774	4954	0.127	19
32	23/04/1991	72	9.5	HgCl ₂	7.9	441	3295	0.063	
32	23/04/1991	72	72	HgCl ₂	7.8	426	3197	0.061	
32	23/04/1991	72	42	HgCl ₂	7.8	488	3239	0.062	
33	26/04/1991	18	11	HgCl ₂	8	588	4232	0.082	
33	19/02/1992	18	18	HgCl ₂	8.2	645	4150	0.079	
34	07/05/1991	18	18	HgCl ₂	7.6	1029	6808	0.132	
37	13/06/1991	10.5	10.5	HgCl ₂	8	306	2252	0.042	
38	17/06/1991	10.5	10.5	HgCl ₂	8.1	268	2016	0.037	
38	25/07/1991	10	10	HgCl ₂	8.2	269	1995	0.035	
38	16/02/1992	17	17	HgCl ₂	8.1	232	1784	0.032	
38	12/11/1997	17	17		7.5	560	3584	0.073	18.6
38	17/08/1998	17	17		7.37	516	3302	0.092	19
39	26/06/1991	11.5	11.5	HgCl ₂	8.1	258	1923	0.035	
43	03/12/1991	25	25	HgCl ₂	7.7	994	7200	0.143	

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – cations.

ALLUVIUM										
Name	Date sampled	Na (mg/L)	Na (meq/L)	K (mg/L)	K (meq/L)	Mg (mg/L)	Mg (meq/L)	Ca (mg/L)	Ca (meq/L)	Cations (meq/L)
22	28/01/1991	1052	45.8	4.3	0.11	368	30.3	238	11.9	88.0
23	28/01/1991	720	31.3	6.1	0.16	164	13.5	163	8.13	53.1
23	29/01/1991	913	39.7	4.1	0.10	285	23.5	208	10.4	73.6
24	30/01/1991	923	40.1	3.8	0.10	297	24.4	216	10.8	75.5
24	07/02/1991	925	40.2	9.8	0.25	255	21.0	197	9.83	72.7
24	08/02/1991	958	41.7	9.3	0.24	232	19.1	193	9.63	70.6
24A	24/05/1992	683	29.7	3.8	0.10	156	12.8	122	6.09	48.7
24A	25/05/1992	852	37.1	4.3	0.11	184	15.1	173	8.63	60.9
25	20/02/1991	517	22.5	13	0.33	68	5.59	69	3.44	31.9
26	11/02/1991	1092	47.5	5.7	0.15	238	19.6	171	8.53	75.8
26	12/02/1991	675	29.4	3.4	0.09	178	14.6	157	7.83	51.9
26A	14/05/1991	454	19.8	2.6	0.07	207	17.0	334	16.7	53.5
26A	14/05/1991	832	36.2	5.7	0.15	200	16.5	184	9.18	62.0
27	14/02/1991	1104	48.0	12	0.31	352	29.0	227	11.3	88.6
27A	17/03/1992	1100	47.9	4.7	0.12	322	26.5	272	13.6	88.0
27A	17/08/1998	1270	55.2	5.3	0.14	480	39.5	260	13.0	108
32	23/04/1991	699	30.4	3.5	0.09	185	15.2	174	8.68	54.4
32	23/04/1991	723	31.5	13	0.34	164	13.5	162	8.08	53.4
32	23/04/1991	1247	54.2	7.1	0.18	251	20.7	187	9.33	84.4
33	26/04/1991	939	40.8	3.9	0.10	270	22.2	160	7.98	71.1
33	19/02/1992	919	40.0	3.3	0.08	248	20.4	128	6.39	66.9
34	07/05/1991	1526	66.4	43	1.1	379	31.2	314	15.7	114
37	13/06/1991	453	19.7	4.5	0.12	109	8.97	134	6.69	35.5
38	17/06/1991	416	18.1	2.7	0.07	94	7.73	105	5.24	31.1
38	25/07/1991	423	18.4	3.1	0.08	80	6.58	101	5.04	30.1
38	16/02/1992	377	16.4	0.5	0.01	72	5.92	91	4.54	26.9
38	12/11/1997	612	26.6	2.0	0.05	218	17.9	278	13.9	58.5
38	17/08/1998	645	28.1	3.9	0.10	340	28.0	340	17.0	73.2
39	26/06/1991	402	17.5	1.7	0.04	80	6.58	98	4.89	29.0
43	03/12/1991	1504	65.4	8.9	0.23	377	31.0	487	24.3	121

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – anions.

ALLUVIUM									
Name	Date sampled	Cl (mg/L)	Cl (meq/L)	SO ₄ (mg/L)	SO ₄ (meq/L)	HCO ₃ (mg/L)	HCO ₃ (meq/L)	Anions (meq/L)	Balance (%)
22	28/01/1991	2264	63.9	951	19.8	359	5.88	89.8	-0.99
23	28/01/1991	1401	39.5	581	12.1	204	3.34	55.1	-1.9
23	29/01/1991	1362	38.4	521	10.9	314	5.15	54.5	-1.4
24	30/01/1991	1791	50.5	910	19.0	419	6.86	76.7	-0.79
24	07/02/1991	1669	47.1	900	18.7	538	8.82	74.7	-1.4
24	08/02/1991	1715	48.4	934	19.5	429	7.03	75.2	-1.0
24A	25/05/1992	919	25.9	686	14.3	488	8.00	48.4	1.3
24A	24/05/1992	921	26.0	648	13.5	478	7.83	47.6	1.2
26	11/02/1991	1863	52.6	852	17.7	386	6.32	76.7	-0.60
25	20/02/1991	1739	49.1	826	17.2	395	6.47	72.8	-1.5
26	12/02/1991	895	25.3	172	3.58	228	3.74	32.6	-1.1
26A	14/05/1991	1481	41.8	684	14.2	315	5.16	61.2	-0.23
26A	14/05/1991	1452	41.0	638	13.3	417	6.83	61.1	0.69
27	14/02/1991	2166	61.1	1027	21.4	381	6.24	89.0	-0.21
27A	17/03/1992	2118	59.8	977	20.3	405	6.64	87.0	0.60
27A	17/08/1998	2585	72.9	1200	25.0	595	9.76	108	0.11
32	23/04/1991	1108	31.3	693	14.4	426	6.98	52.8	1.5
32	23/04/1991	1078	30.4	683	14.2	417	6.83	51.6	0.32
32	23/04/1991	1091	30.8	684	14.2	390	6.40	51.6	1.7
33	26/04/1991	1610	45.4	814	17.0	432	7.08	69.5	1.2
33	19/02/1992	1622	45.8	762	15.9	466	7.64	69.3	-1.8
34	07/05/1991	2862	80.7	1396	29.1	281	4.61	115	-0.05
37	13/06/1991	648	18.3	481	10.0	420	6.88	35.3	0.31
38	17/06/1991	513	14.5	407	8.47	476	7.80	30.8	0.53
38	25/07/1991	467	13.2	396	8.24	510	8.36	30.1	0.07
38	16/02/1992	415	11.7	332	6.91	487	7.98	26.8	0.17
38	12/11/1997	1515	42.7	413	8.60	527	8.64	60.0	-1.3
38	17/08/1998	1970	55.6	480	9.99	561	9.20	74.8	-1.1
39	26/06/1991	508	14.3	384	8.00	449	7.36	29.7	-1.3
43	03/12/1991	3256	91.9	1312	27.3	251	4.11	123	-0.98

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – minor species and ion ratios.

ALLUVIUM										
Name	Date sampled	NO ₃ (mg N/L)	NH ₄ (mg N/L)	F (mg/L)	Fe _T (mg/L)	Si (mg/L)	P (mg/L)	Na/Cl (wt)	Mg/Ca (wt)	SAR
22	28/01/1991	2.37	0.05	1.32		11.5	0.009	0.72	2.55	9.97
23	28/01/1991	1.87	0.19	0.6		6.8	0.014	0.79	1.66	9.52
23	29/01/1991	0.67	0.07	0.7		9.6	0.007	0.82	1.5	9.57
24	30/01/1991	3.94	0.05	1.14		13.3		0.79	2.27	9.57
24	07/02/1991	0.16	19.5	1.21		12.7	0.061	0.85	2.13	10.25
24	08/02/1991	3.7		1.2		14.2	0.01	0.82	2.3	9.66
24A	24/05/1992	2.16	0.09	2.03		14.4	0.021	1.14	2.11	9.66
24A	25/05/1992	1.9	0.11	1.2		13.7	0.005	1.1	1.8	9.08
25	20/02/1991	0.15	0.04	0.95		7	0.006	0.85	2.0	11.0
26	11/02/1991	0.19	0.09	1.1		8.3		0.90	2.29	12.67
26	12/02/1991	0.07	1.2	1.2		3.7	0.006	0.89	1.6	10.6
26A	14/05/1991	0.93	0.05	0.77		7	0.015	0.89	1.8	10.8
26A	14/05/1991			0.9		7.7	0.03	0.88	1.79	10.1
27	14/02/1991	2.87	0.06	1.15		12.1	0.007	0.79	2.56	10.70
27A	17/03/1992	2.5		1.3		13.3	0.01	0.80	1.95	10.7
27A	17/08/1998			0.8	0.1	7		0.76	3.04	10.8
32	23/04/1991	1.37		0.72		8.2	0.036	0.97	1.75	8.79
32	23/04/1991	1.4		0.58		8.9	0.019	0.97	1.9	8.76
32	23/04/1991	2.6	0.1	0.62		7.9	0.016	1.0	1.7	9.57
33	26/04/1991	0.53	0.07	0.95		9.1	0.024	0.90	2.78	10.51
33	19/02/1992	0.06	0.06	1.08		9.8	0.023	0.87	3.19	10.92
34	07/05/1991	1.08	1.79	1.24		4.3	0.018	0.82	1.99	13.71
37	13/06/1991	0.56		0.69		6.8	0.012	1.08	1.34	7.04
38	17/06/1991	0.4		0.59		10.9	0.022	1.25	1.48	7.10
38	25/07/1991	3.54	0.04	0.58		11.7	0.018	1.40	1.31	7.63
38	16/02/1992	2.16	0.09	0.61		11.2	0.02	1.40	1.30	7.17
38	12/11/1997	0.26		0.4	0.22	11.09		0.62	1.29	6.68
38	17/08/1998			0.4	0.13	7.7		0.50	1.65	5.92
39	26/06/1991	0.34		0.61		10.7	0.017	1.22	1.35	7.30
43	03/12/1991	0.88	0.04	0.53		10.3	0.018	0.71	1.28	12.4

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – saturation indices.

ALLUVIUM										
Name	Date sampled	Calcite	Dolomite	Gypsum	Anhydrite	Fluorite	Chalcedony	Quartz	log $p\text{CO}_2$	Data source
22	28/01/1991	1.03	2.60	-0.79	-1.01	-0.93	0.17	0.60	-2.58	NWQDB
23	28/01/1991	0.82	1.98	-0.98	-1.20	-1.56	-0.07	0.36	-2.90	NWQDB
23	29/01/1991	0.56	1.42	-0.99	-1.21	-1.39	0.09	0.52	-2.19	NWQDB
24	30/01/1991	1.07	2.64	-0.80	-1.02	-1.04	0.23	0.66	-2.51	NWQDB
24	07/02/1991	0.96	2.38	-0.83	-1.04	-1.00	0.21	0.64	-2.18	NWQDB
24	08/02/1991	1.07	2.63	-0.80	-1.02	-1.02	0.26	0.69	-2.49	NWQDB
24A	24/05/1992	1.24	2.93	-1.05	-1.26	-0.63	0.25	0.68	-2.73	Woodford, 1994
24A	25/05/1992	1.32	3.03	-0.95	-1.17	-1.05	0.23	0.66	-2.73	NWQDB
25	20/02/1991	0.93	2.28	-0.85	-1.07	-1.19	-0.05	0.38	-2.42	NWQDB
26	11/02/1991	1.04	2.58	-0.90	-1.12	-1.13	0.02	0.45	-2.64	NWQDB
26	12/02/1991	0.62	1.58	-1.67	-1.89	-1.14	-0.33	0.10	-2.82	NWQDB
26A	14/05/1991	0.43	1.23	-0.92	-1.14	-1.36	-0.04	0.38	-2.09	NWQDB
26A	14/05/1991	0.67	1.73	-0.94	-1.15	-1.21	0.00	0.43	-2.08	NWQDB
27	14/02/1991	1.30	3.14	-0.78	-1.00	-1.07	0.18	0.61	-2.89	Woodford, 1994
27A	17/03/1992	1.14	2.70	-0.71	-0.93	-0.84	0.23	0.66	-2.53	NWQDB
27A	17/08/1998	1.43	3.42	-0.70	-0.94	-1.32	0.02	0.47	-2.73	Cavé, 1999
32	23/04/1991	0.96	2.29	-0.90	-1.12	-1.40	0.02	0.45	-2.37	NWQDB
32	23/04/1991	0.81	2.03	-0.94	-1.16	-1.63	0.06	0.48	-2.27	NWQDB
32	23/04/1991	0.80	1.95	-0.92	-1.14	-1.55	0.00	0.43	-2.30	NWQDB
33	26/04/1991	0.98	2.53	-0.95	-1.16	-1.30	0.07	0.49	-2.48	NWQDB
33	19/02/1992	1.11	2.85	-1.05	-1.27	-1.26	0.09	0.52	-2.66	NWQDB
34	07/05/1991	0.61	1.65	-0.57	-0.79	-0.91	-0.25	0.18	-2.28	NWQDB
37	13/06/1991	1.00	2.26	-1.05	-1.27	-1.43	-0.07	0.36	-2.46	NWQDB
38	17/06/1991	1.07	2.43	-1.18	-1.40	-1.64	0.14	0.57	-2.50	Woodford, 1994
38	25/07/1991	1.18	2.60	-1.20	-1.42	-1.66	0.16	0.59	-2.57	NWQDB
38	16/02/1992	1.04	2.33	-1.29	-1.50	-1.63	0.15	0.58	-2.48	Woodford, 1994
38	12/11/1997	0.78	1.73	-0.93	-1.17	-1.64	0.23	0.68	-1.91	CSIR
38	17/08/1998	0.73	1.74	-0.87	-1.11	-1.67	0.07	0.52	-1.77	Cavé, 1999
39	26/06/1991	1.02	2.30	-1.22	-1.44	-1.62	0.13	0.56	-2.52	NWQDB
43	03/12/1991	0.84	1.92	-0.44	-0.65	-1.47	0.13	0.56	-2.45	Woodford, 1994

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – borehole information.

ALLUVIUM									
Name	DWAF No.	Date sampled	Farm	Location	Lithology	Use	Latitude	Longitude	Elevation (m)
43	G39843	03/12/1991	Enkelde Wilgenboom		alluvium/shale		31.49028	19.70861	940
43	G39843	03/12/1991	Enkelde Wilgenboom		alluvium/shale		31.49028	19.70861	940
43	G39843	03/12/1991	Enkelde Wilgenboom		alluvium/shale		31.49028	19.70861	940
43	G39843	04/12/1991	Enkelde Wilgenboom		alluvium/shale		31.49028	19.70861	940
43	G39843	27/08/1992	Enkelde Wilgenboom		alluvium/shale		31.49028	19.70861	940
43	G39843	27/08/1994	Enkelde Wilgenboom		alluvium/shale		31.49028	19.70861	940
75	G39575	22/10/1990	Onwetende Fontein		alluvium/shale	Domestic	31.50778	19.92361	
75	G39575	23/10/1990	Onwetende Fontein		alluvium/shale	Domestic	31.50778	19.92361	
76	G39576	24/10/1990	Onwetende Fontein		alluvium	Domestic	31.51444	19.93083	
76	G39576	25/10/1990	Onwetende Fontein		alluvium	Domestic	31.51444	19.93083	
77	G39577	26/10/1990	Onwetende Fontein	Downes Wes	alluvium/shale	Domestic	31.51778	19.93444	1025
78	G39578	30/10/1990	Downes Wes		alluvium	Domestic	31.50917	19.895	
86	G39586	08/11/1990	Witklip		alluvium	Domestic	31.5425	19.83694	
88	G38588	12/11/1990	Downes		alluvium	Domestic	31.565	19.95472	
89	G39589	13/11/1990	Boven Downes Ext		alluvium	Domestic	31.54639	19.95028	
92	G39592	20/11/1990	Onwetende Fontein		alluvium	Domestic	31.50944	19.91917	
92	G39592	20/11/1990	Onwetende Fontein		alluvium	Domestic	31.50944	19.91917	
641	G39641	29/07/1991	Calvinia Allotment		alluvium		31.47333	19.78389	
642	G39642	07/08/1991	Calvinia Allotment		alluvium		31.47778	19.78722	
644	G39644	12/08/1991	Calvinia Allotment		alluvium		31.46944	19.79639	
652	G39652	22/10/1991	Enkelde Wilgenboom		alluvium/shale		31.49583	19.69417	
652	G39652	22/10/1991	Enkelde Wilgenboom		alluvium/shale		31.49583	19.69417	
652	G39652	22/10/1991	Enkelde Wilgenboom		alluvium/shale		31.49583	19.69417	
653	G39653	23/10/1991	Enkelde Wilgenboom		alluvium/shale		31.49583	19.69417	
653	G39653	23/10/1991	Enkelde Wilgenboom		alluvium/shale		31.49583	19.69417	
654	G39654	17/11/1991	Enkelde Wilgenboom		alluvium		31.50583	19.68944	
655	G39655	17/11/1991	Enkelde Wilgenboom		alluvium/shale		31.50667	19.68861	
CT26		25/06/1980	Calvinia Allotment		alluvium	Irrigation	31.47556	19.78278	
CT50		27/06/1980	Calvinia Allotment		alluvium	Irrigation	31.47944	19.71667	
CT55		14/10/1980	Calvinia Allotment		alluvium/shale	Irrigation	31.47083	19.77361	

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – macro variables.

ALLUVIUM									
Name	Date sampled	Borehole Depth (m)	Sample Depth (m)	Preservation	Lab. pH	EC (mS/m)	TDS (mg/L)	Ionic strength	Temp. (°C)
43	03/12/1991	19	19	HgCl ₂	8	1095	7640	0.152	
43	03/12/1991	39	39	HgCl ₂	8	1015	6875	0.138	
43	03/12/1991	9	9	HgCl ₂	7.7	1222	8183	0.164	
43	04/12/1991	139	139	HgCl ₂	7.8	977	6638	0.134	
43	27/08/1992	139	100	HgCl ₂	9.7	863	5730	0.111	
43	27/08/1994								
75	22/10/1990	100	23	HgCl ₂	7.7	531	3754	0.071	
75	23/10/1990	100	100	HgCl ₂	7.8	470	3881	0.074	
76	24/10/1990	19	5	HgCl ₂	7.8	1201	9104	0.172	
76	25/10/1990	19	19	HgCl ₂	8	367	2523	0.046	
77	26/10/1990	85	85	HgCl ₂	8	754	5139	0.099	
78	30/10/1990	24	24	HgCl ₂	7.9	600	3951	0.079	
86	08/11/1990	16	16	HgCl ₂	7.5	925	6523	0.156	
88	12/11/1990	22	22	HgCl ₂	7.2	401	2775	0.050	
89	13/11/1990	6	6	HgCl ₂	7.5	159	1094	0.021	
92	20/11/1990	15	15	HgCl ₂	7.6	595	4049	0.078	
92	20/11/1990	15	6	HgCl ₂	7.6	775	4717	0.091	
641	29/07/1991	18	18	HgCl ₂	8.1	204	1301	0.026	
642	07/08/1991	18	18	HgCl ₂	8	1203	8098	0.163	
644	12/08/1991	17	17	HgCl ₂	8.1	165	1232	0.022	
652	22/10/1991	60	6	HgCl ₂	7.8	250	1654	0.031	
652	22/10/1991	60	60	HgCl ₂	8	259	1611	0.030	
652	22/10/1991	60	25	HgCl ₂	7.9	237	1607	0.029	
653	23/10/1991	37	16	HgCl ₂	7.6	252	1547	0.029	
653	23/10/1991	37	37	HgCl ₂	7	245	1433	0.025	
654	17/11/1991	5	5	HgCl ₂	8.1	401	2583	0.049	
655	17/11/1991	28	28	HgCl ₂	7.8	152	812	0.014	
CT26	25/06/1980	8	8		7.4	348	2199	0.047	
CT50	27/06/1980	30	30		7.5	314	1877	0.040	
CT55	14/10/1980	6	6		7.2	1055	6500	0.160	

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – cations.

ALLUVIUM										
Name	Date sampled	Na (mg/L)	Na (meq/L)	K (mg/L)	K (meq/L)	Mg (mg/L)	Mg (meq/L)	Ca (mg/L)	Ca (meq/L)	Cations (meq/L)
43	03/12/1991	1655	72.0	11	0.28	396	32.6	517	25.8	131
43	03/12/1991	1518	66.0	12	0.31	362	29.8	464	23.2	119
43	03/12/1991	1836	79.9	26	0.66	419	34.5	553	27.6	143
43	04/12/1991	1460	63.5	12	0.31	350	28.8	462	23.1	116
43	27/08/1992	1209	52.6	9.5	0.24	278	22.9	388	19.4	95.1
43	27/08/1994									
75	22/10/1990	813	35.4	4.3	0.11	214	17.6	144	7.19	60.3
75	23/10/1990	816	35.5	1.9	0.05	230	18.9	155	7.73	62.2
76	24/10/1990	2119	92.2	23	0.59	490	40.3	348	17.4	151
76	25/10/1990	733	31.9	8.9	0.23	54	4.44	72	3.59	40.2
77	26/10/1990	668	29.1	5.3	0.14	160	13.2	147	7.34	49.7
78	30/10/1990	840	36.5	5.4	0.14	268	22.0	159	7.93	66.7
86	08/11/1990	253	11.0	23	0.59	855	70.3	701	35.0	117
88	12/11/1990	705	30.7	5.6	0.14	93	7.65	96	4.79	43.3
89	13/11/1990	197	8.57	3.8	0.10	50	4.11	74	3.69	16.5
92	20/11/1990	920	40.0	6.6	0.17	220	18.1	166	8.28	66.6
92	20/11/1990	1079	46.9	12	0.31	244	20.1	225	11.2	78.6
641	29/07/1991	130	5.65	0.9	0.02	74	6.09	153	7.63	19.4
642	07/08/1991	1403	61.0	11	0.29	534	43.9	640	31.9	137
644	12/08/1991	214	9.31	5.3	0.14	49	4.03	89	4.44	18.0
652	22/10/1991	309	13.4	7.8	0.20	70	5.76	122	6.09	25.5
652	22/10/1991	346	15.1	38	0.97	51	4.20	87	4.34	25.1
652	22/10/1991	349	15.2	31	0.79	51	4.20	83	4.14	24.7
653	23/10/1991	332	14.4	27	0.70	50	4.11	109	5.44	24.7
653	23/10/1991	387	16.8	56	1.4	22	1.81	49	2.45	22.7
654	17/11/1991	572	24.9	4.7	0.12	122	10.0	126	6.29	41.3
655	17/11/1991	249	10.8	46	1.2	2	0.16	17	0.85	13.1
CT26	25/06/1980	240	10.4	1.6	0.04	165	13.6	256	12.8	36.8
CT50	27/06/1980	257	11.2	2.6	0.07	116	9.54	203	10.1	30.9
CT55	14/10/1980	665	28.9	26	0.65	527	43.4	1008	50.3	123

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – anions.

ALLUVIUM									
Name	Date sampled	Cl (mg/L)	Cl (meq/L)	SO ₄ (mg/L)	SO ₄ (meq/L)	HCO ₃ (mg/L)	HCO ₃ (meq/L)	Anions (meq/L)	Balance (%)
43	03/12/1991	3469	97.9	1343	28.0	245	4.02	130	0.28
43	03/12/1991	3135	88.4	1136	23.7	243	3.98	116	1.3
43	03/12/1991	3721	105	1399	29.1	226	3.70	138	1.7
43	04/12/1991	2997	84.5	1157	24.1	194	3.18	112	1.7
43	27/08/1992	2566	72.4	988	20.6	277	4.54	97.8	-1.4
43	27/08/1994								
75	22/10/1990	1349	38.1	825	17.2	387	6.34	61.9	-1.3
75	23/10/1990	1391	39.2	838	17.5	434	7.11	64.1	-1.5
76	24/10/1990	3803	107	1784	37.1	434	7.11	153	-0.91
76	25/10/1990	1092	30.8	338	7.04	224	3.67	41.6	-1.7
77	26/10/1990	2190	61.8	1047	21.8	209	3.42	87.0	-1.5
78	30/10/1990	1697	47.9	743	15.5	232	3.80	67.3	-0.45
86	08/11/1990	3201	90.3	1367	28.5	99	1.62	121	-1.6
88	12/11/1990	947	26.7	402	8.37	517	8.47	43.7	-0.55
89	13/11/1990	329	9.28	113	2.35	326	5.34	17.0	-1.6
92	20/11/1990	1571	44.3	808	16.8	349	5.72	67.1	-0.36
92	20/11/1990	1910	53.9	889	18.5	345	5.65	78.3	0.16
641	29/07/1991	353	9.96	257	5.35	298	4.88	20.8	-3.4
642	07/08/1991	3463	97.7	1686	35.1	361	5.92	139	-0.56
644	12/08/1991	241	6.80	235	4.89	390	6.40	18.2	-0.59
652	22/10/1991	424	12.0	373	7.77	343	5.62	25.5	0.11
652	22/10/1991	488	13.8	347	7.22	239	3.92	25.0	0.19
652	22/10/1991	411	11.6	385	8.02	289	4.74	24.4	0.59
653	23/10/1991	514	14.5	270	5.62	217	3.56	24.2	1.1
653	23/10/1991	522	14.7	218	4.54	139	2.28	22.2	1.3
654	17/11/1991	833	23.5	524	10.9	401	6.57	41.0	0.34
655	17/11/1991	373	10.5	52	1.08	68.3	1.12	12.8	1.4
CT26	25/06/1980	804	22.7	423	8.81	304	4.98	36.6	0.37
CT50	27/06/1980	756	21.3	236	4.91	278	4.56	31.3	-0.58
CT55	14/10/1980	3591	101	520	10.8	138	2.26	115	3.5

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – minor species and ion ratios.

ALLUVIUM										
Name	Date sampled	NO ₃ (mg N/L)	NH ₄ (mg N/L)	F (mg/L)	Fe _T (mg/L)	Si (mg/L)	P (mg/L)	Na/Cl (wt)	Mg/Ca (wt)	SAR
43	03/12/1991	0.76		0.52		10.7	0.006	0.74	1.26	13.3
43	03/12/1991	0.93	0.75	0.50		11.1		0.75	1.29	12.8
43	03/12/1991	0.73	0.14	0.67		9.5		0.76	1.25	14.3
43	04/12/1991	1.1	1.4	0.47		11	0.013	0.75	1.25	12.5
43	27/08/1992	3.1	0.13	0.65		10.6	0.015	0.73	1.18	11.4
43	27/08/1994				1.27					
75	22/10/1990	3.8	0.15	1.3		12.8	0.007	0.93	2.5	10.0
75	23/10/1990	3.1	0.15	1.4		14.4	0.007	0.90	2.5	9.72
76	24/10/1990	22.64	0.42	1.32		11.6	0.26	0.86	2.32	17.16
76	25/10/1990	0.06	0.17	1.24		6	0.016	1.04	1.24	15.91
77	26/10/1990	0.06	0.16	0.74		8.5	0.1	0.88	2.2	14.0
78	30/10/1990	1.2	0.23	0.96		8.1	0.009	0.76	2.78	9.44
86	08/11/1990	5.23	1.87	0.43		11.7	0.009	0.12	2.01	1.52
88	12/11/1990	1.63	0.27	1.32		9.6	0.039	1.15	1.60	12.29
89	13/11/1990		0.06	0.65		6.2	0.01	0.92	1.11	4.34
92	20/11/1990	1.83	0.04	1.27		12.8	0.015	0.90	2.19	11.02
92	20/11/1990	2.89	0.14	1.23		12.7	0.009	0.87	1.79	11.86
641	29/07/1991	7.92	0.06	0.34		14.6	0.014	0.57	0.80	2.16
642	07/08/1991		0.07	0.3		11.8	0.035	0.62	1.38	9.91
644	12/08/1991	1.37	1.22	0.46		10.4	0.07	1.37	0.91	4.52
652	22/10/1991	1.3	0.52	0.5		9.4		1.1	0.95	5.52
652	22/10/1991	1.1	7.7	0.57		7.3		1.1	0.97	7.28
652	22/10/1991	0.17	5.2	0.58		7.3		1.3	1.0	7.44
653	23/10/1991	6.2		0.82		5.2	0.005	1.0	0.76	6.61
653	23/10/1991	7.8	3.2	1.3		3.5	0.009	1.1	0.74	11.5
654	17/11/1991	0.24		0.84		11.7	0.005	1.06	1.60	8.71
655	17/11/1991	0.06	1.5	0.93		8.2		1.0	0.19	15.2
CT26	25/06/1980	1.1		0.3		16		0.46	1.06	2.88
CT50	27/06/1980	6.3	0.04	0.73		10	0.005	0.52	0.94	3.56
CT55	14/10/1980	5.6	0.05	0.31		14.2	0.06	0.29	0.86	4.23

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – saturation indices.

ALLUVIUM										
Name	Date sampled	Calcite	Dolomite	Gypsum	Anhydrite	Fluorite	Chalcedony	Quartz	log $p\text{CO}_2$	Data source
43	03/12/1991	1.12	2.49	-0.42	-0.64	-1.49	0.15	0.57	-2.78	Woodford, 1994
43	03/12/1991	1.10	2.44	-0.50	-0.72	-1.53	0.16	0.59	-2.78	Woodford, 1994
43	03/12/1991	0.83	1.89	-0.40	-0.61	-1.26	0.10	0.53	-2.50	Woodford, 1994
43	04/12/1991	0.82	1.87	-0.49	-0.71	-1.57	0.16	0.59	-2.66	Woodford, 1994
43	27/08/1992	2.10	4.42	-0.59	-0.80	-1.31	-0.15	0.28	-5.09	Woodford, 1994
43	27/08/1994									Woodford, 1994
75	22/10/1990	0.62	1.76	-0.94	-1.16	-0.99	0.22	0.65	-2.21	NWQDB
75	23/10/1990	0.79	2.10	-0.91	-1.13	-0.92	0.27	0.70	-2.26	NWQDB
76	24/10/1990	0.98	2.46	-0.51	-0.73	-0.92	0.19	0.62	-2.32	NWQDB
76	25/10/1990	0.48	1.19	-1.42	-1.64	-1.13	-0.12	0.31	-2.72	NWQDB
77	26/10/1990	0.70	1.88	-0.81	-1.03	-1.47	0.04	0.47	-2.81	Woodford, 1994
78	30/10/1990	0.63	1.83	-0.97	-1.19	-1.27	0.02	0.45	-2.65	NWQDB
86	08/11/1990	0.37	1.19	-0.37	-0.58	-1.72	0.19	0.62	-2.68	NWQDB
88	12/11/1990	0.16	0.65	-1.27	-1.49	-1.01	0.09	0.52	-1.55	NWQDB
89	13/11/1990	0.29	0.77	-1.70	-1.92	-1.54	-0.10	0.32	-2.03	NWQDB
92	20/11/1990	0.53	1.53	-0.90	-1.12	-0.99	0.22	0.65	-2.15	NWQDB
92	20/11/1990	0.63	1.65	-0.78	-1.00	-0.92	0.22	0.65	-2.17	NWQDB
641	29/07/1991	1.09	2.22	-1.14	-1.36	-1.87	0.26	0.69	-2.70	NWQDB
642	07/08/1991	1.35	2.98	-0.29	-0.50	-1.95	0.19	0.62	-2.63	NWQDB
644	12/08/1991	0.99	2.08	-1.35	-1.57	-1.80	0.11	0.54	-2.57	NWQDB
652	22/10/1991	0.73	1.57	-1.11	-1.33	-1.66	0.08	0.50	-2.33	NWQDB
652	22/10/1991	0.64	1.38	-1.25	-1.47	-1.67	-0.04	0.39	-2.68	NWQDB
652	22/10/1991	0.60	1.32	-1.23	-1.45	-1.68	-0.04	0.39	-2.50	NWQDB
653	23/10/1991	0.32	0.65	-1.25	-1.47	-1.24	-0.18	0.25	-2.32	NWQDB
653	23/10/1991	-0.78	-1.57	-1.61	-1.83	-1.10	-0.35	0.08	-1.89	NWQDB
654	17/11/1991	1.03	2.39	-1.07	-1.29	-1.32	0.17	0.60	-2.59	NWQDB
655	17/11/1991	-0.65	-1.89	-2.51	-2.73	-1.73	0.01	0.44	-2.99	NWQDB
CT26	25/06/1980	0.56	1.27	-0.88	-1.10	-1.92	0.31	0.74	-2.00	Seward, 1983
CT50	27/06/1980	0.56	1.23	-1.15	-1.37	-1.17	0.11	0.53	-2.13	Seward, 1983
CT55	14/10/1980	0.41	0.91	-0.59	-0.81	-1.71	0.28	0.70	-2.23	NWQDB

Table D.4. Groundwater data for samples from boreholes in alluvial aquifers – borehole information.

ALLUVIUM									
Name	DWAF No.	Date sampled	Farm	Location	Lithology	Use	Latitude	Longitude	Elevation (m)
CT56		14/10/1980	Calvinia Allotment		alluvium/shale	Irrigation	31.47083	19.77361	
CT59		10/11/1980	Calvinia Allotment		alluvium/shale	Domestic/Irrigation	31.47611	19.77667	
CT60		10/11/1980	Calvinia Allotment		alluvium/shale	Irrigation	31.47472	19.77917	
CT61		10/11/1980	Calvinia Allotment		alluvium/shale	Irrigation	31.47556	19.78	
CT62		12/11/1980	Calvinia Allotment		alluvium/shale	Domestic/Irrigation	31.46972	19.77889	
CT63		26/11/1980	Calvinia Allotment		alluvium/shale	Irrigation	31.47694	19.7725	
CT65		28/11/1980	Calvinia Allotment		alluvium/shale	Irrigation	31.47056	19.77889	
DW10		01/07/1980	Downes Wes		alluvium	Stock	31.51889	19.88917	
EW14		30/06/1980	Enkelde Wilgenboom		alluvium	Stock	31.50083	19.695	
EW37		01/07/1980	Enkelde Wilgenboom		alluvium	Stock	31.51111	19.68306	
PS26	G32626	28/07/1980	Calvinia Allotment	Akkerendam	alluvium/shale		31.48167	19.79167	981.62
PS26	G32626	28/07/1980	Calvinia Allotment	Akkerendam	alluvium/shale		31.48167	19.79167	981.62
PS26	G32626	30/07/1980	Calvinia Allotment	Akkerendam	alluvium/shale		31.48167	19.79167	981.62
PS26	G32626	25/07/1980	Calvinia Allotment	Akkerendam	alluvium		31.48167	19.79167	981.62
PS30	G32630	03/09/1980	Calvinia Allotment		alluvium/shale	Domestic/Stock/Irrig.	31.485	19.79833	
T2		30/06/1980	Tygerhoek		alluvium/shale	Stock	31.46972	19.69083	

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – macro variables.

ALLUVIUM									
Name	Date sampled	Borehole Depth (m)	Sample Depth (m)	Preservation	Lab. pH	EC (mS/m)	TDS (mg/L)	Ionic strength	Temp. (°C)
CT56	14/10/1980	33	33		7.2	857	5007	0.122	
CT59	10/11/1980	50	50		7.5	291	1694	0.039	
CT60	10/11/1980	7.6	7		7.4	336	1930	0.045	
CT61	10/11/1980	7.6	7.6		7.5	245	1455	0.033	
CT62	12/11/1980	40	40		7.3	1150	7099	0.174	
CT63	26/11/1980	7	7		7.5	608	3789	0.079	
CT65	28/11/1980	12.1	12		7.7	496	3008	0.065	
DW10	01/07/1980	24	24		7.5	518	2995	0.064	
EW14	30/06/1980	10	10		7.5	231	1510	0.029	
EW37	01/07/1980	7.6	7.6		7.6	562	3577	0.068	
PS26	28/07/1980	117	91		7.3	313	1714	0.032	
PS26	28/07/1980	117	91		7.3	351	1886	0.034	
PS26	30/07/1980	117	91		6.8	352	1885	0.033	
PS26	25/07/1980	117	6.5		7.4	626	3886	0.076	
PS30	03/09/1980	30	30		7.1	411	2226	0.046	
T2	30/06/1980	24.2	24		7.4	690	4384	0.087	

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – cations.

ALLUVIUM										
Name	Date sampled	Na (mg/L)	Na (meq/L)	K (mg/L)	K (meq/L)	Mg (mg/L)	Mg (meq/L)	Ca (mg/L)	Ca (meq/L)	Cations (meq/L)
CT56	14/10/1980	495	21.5	5.0	0.13	421	34.6	721	36.0	92.3
CT59	10/11/1980	170	7.39	5.1	0.13	144	11.9	222	11.1	30.5
CT60	10/11/1980	173	7.53	1.8	0.05	180	14.8	259	12.9	35.3
CT61	10/11/1980	136	5.92	0.5	0.01	114	9.38	196	9.78	25.1
CT62	12/11/1980	766	33.3	14	0.35	619	50.9	1008	50.3	135
CT63	26/11/1980	454	19.8	2.6	0.07	207	17.0	334	16.7	53.5
CT65	28/11/1980	217	9.44	3.3	0.08	67	5.51	139	6.94	22.0
DW10	01/07/1980	507	22.1	4.2	0.11	175	14.4	286	14.3	50.8
EW14	30/06/1980	253	11.0	0.55	0.01	63	5.18	144	7.19	23.4
EW37	01/07/1980	823	35.8	1.7	0.04	166	13.7	166	8.28	57.8
PS26	28/07/1980	479	20.8	13	0.34	38	3.13	65	3.24	27.5
PS26	28/07/1980	603	26.2	4.0	0.10	19	1.56	65	3.24	31.1
PS26	30/07/1980	630	27.4	4.4	0.11	12	0.99	45	2.25	30.8
PS26	25/07/1980	867	37.7	28	0.71	197	16.2	184	9.18	63.8
PS30	03/09/1980	435	18.9	72	1.8	69	5.68	243	12.1	38.6
T2	30/06/1980	76	3.31	0.28	0.01	33	2.71	48	2.40	8.4

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – anions.

ALLUVIUM									
Name	Date sampled	Cl (mg/L)	Cl (meq/L)	SO ₄ (mg/L)	SO ₄ (meq/L)	HCO ₃ (mg/L)	HCO ₃ (meq/L)	Anions (meq/L)	Balance (%)
CT56	14/10/1980	2784	78.5	413	8.60	148	2.43	89.9	1.3
CT59	10/11/1980	640	18.1	232	4.83	276	4.52	27.5	5.1
CT60	10/11/1980	791	22.3	289	6.02	227	3.72	32.2	4.6
CT61	10/11/1980	535	15.1	231	4.81	240	3.94	23.9	2.5
CT62	12/11/1980	3878	109	624	13.0	168	2.76	126	3.6
CT63	26/11/1980	1527	43.1	688	14.3	325	5.33	62.8	2.6
CT65	28/11/1980	1187	33.5	489	10.2	316	5.18	49.1	4.3
DW10	01/07/1980	1516	42.8	218	4.54	255	4.18	52.1	-1.2
EW14	30/06/1980	454	12.8	237	4.93	353	5.78	23.6	-0.53
EW37	01/07/1980	1418	40.0	666	13.9	337	5.52	59.4	-1.4
PS26	28/07/1980	828	23.4	139	2.89	149	2.44	28.8	-2.2
PS26	28/07/1980	997	28.1	93	1.94	100	1.64	31.9	-1.2
PS26	30/07/1980	1072	30.2	34	0.71	83	1.36	32.4	-2.7
PS26	25/07/1980	1680	47.4	703	14.6	216	3.54	65.8	-1.5
PS30	03/09/1980	1076	30.4	247	5.14	62	1.02	36.9	2.2
T2	30/06/1980	1807	51.0	972	20.2	211	3.46	74.8	-1.3

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – minor species and ion ratios.

ALLUVIUM										
Name	Date sampled	NO ₃ (mg N/L)	NH ₄ (mg N/L)	F (mg/L)	Fe _T (mg/L)	Si (mg/L)	P (mg/L)	Na/Cl (wt)	Mg/Ca (wt)	SAR
CT56	14/10/1980	4.6	0.05	0.15		13.9	0.006	0.27	0.96	3.62
CT59	10/11/1980	1.2	0.05	0.51		16.4	0.009	0.41	1.1	2.18
CT60	10/11/1980	2.0	0.04	0.31		16.3	0.011	0.34	1.1	2.02
CT61	10/11/1980	0.43		0.32		14	0.005	0.39	0.96	1.91
CT62	12/11/1980	4.9	0.05	0.15		13.3	0.006	0.30	1.0	4.68
CT63	26/11/1980	0.93	0.05	0.57		15.1	0.01	0.65	1.3	6.42
CT65	28/11/1980	3.9	0.06	0.25		13.2	0.015	0.59	1.0	4.81
DW10	01/07/1980	7.9	0.06	0.7		9.1		0.52	1.01	5.82
EW14	30/06/1980	1.2		0.63		11.7		0.86	0.72	4.43
EW37	01/07/1980	0.08		0.84		13.9		0.89	1.65	10.8
PS26	28/07/1980	0.38		1.5		3.9		0.89	0.96	11.7
PS26	28/07/1980	0.69		2.2		5.1	0.007	0.93	0.48	16.9
PS26	30/07/1980	0.32	0.04	2.2		6.4		0.91	0.44	21.6
PS26	25/07/1980	2.5		1.0		4.5		0.80	1.77	10.6
PS30	03/09/1980	5.0	0.05	1.0		5.9	0.044	0.62	0.47	6.34
T2	30/06/1980	0.4		1.3		3.5	0.008	0.76	2.2	9.38

Table D.4 (continued). Groundwater data for samples from boreholes in alluvial aquifers – saturation indices.

ALLUVIUM										
Name	Date sampled	Calcite	Dolomite	Gypsum	Anhydrite	Fluorite	Chalcedony	Quartz	log $p\text{CO}_2$	Data source
CT56	14/10/1980	0.35	0.83	-0.74	-0.96	-2.39	0.26	0.69	-2.18	NWQDB
CT59	10/11/1980	0.60	1.36	-1.14	-1.36	-1.46	0.32	0.75	-2.14	Seward, 1983
CT60	10/11/1980	0.46	1.10	-1.03	-1.25	-1.88	0.32	0.75	-2.13	NWQDB
CT61	10/11/1980	0.51	1.13	-1.14	-1.36	-1.87	0.25	0.68	-2.19	NWQDB
CT62	12/11/1980	0.58	1.31	-0.54	-0.76	-2.40	0.25	0.68	-2.25	NWQDB
CT63	26/11/1980	0.71	1.66	-0.70	-0.92	-1.40	0.29	0.72	-2.10	NWQDB
CT65	28/11/1980	0.93	2.01	-0.79	-1.01	-2.05	0.23	0.66	-2.31	NWQDB
DW10	01/07/1980	0.61	1.36	-1.16	-1.38	-1.18	0.07	0.50	-2.19	Seward, 1983
EW14	30/06/1980	0.55	1.09	-1.20	-1.42	-1.36	0.17	0.60	-2.01	Seward, 1983
EW37	01/07/1980	0.54	1.44	-0.94	-1.16	-1.28	0.25	0.68	-2.16	Seward, 1983
PS26	28/07/1980	-0.34	-0.57	-1.73	-1.95	-0.89	-0.30	0.13	-2.18	Seward, 1983
PS26	28/07/1980	-0.51	-1.21	-1.90	-2.12	-0.55	-0.19	0.24	-2.35	Seward, 1983
PS26	30/07/1980	-1.24	-2.69	-2.46	-2.68	-0.69	-0.09	0.34	-1.93	Seward, 1983
PS26	25/07/1980	0.19	0.75	-0.90	-1.12	-1.11	-0.24	0.19	-2.16	Seward, 1983
PS30	03/09/1980	-0.42	-1.03	-1.06	-1.28	-0.77	-0.12	0.31	-2.38	NWQDB
T2	30/06/1980	0.21	0.88	-0.76	-0.98	-0.90	-0.34	0.09	-2.18	Seward, 1983

Table D.5. Groundwater data for samples from boreholes in fractured rock aquifers – borehole information.

FRACTURED ROCK									
Name	DWAF No.	Date sampled	Farm	Location	Lithology	Use	Latitude	Longitude	Elevation (m)
29	G39629	11/03/1991	Albertfontein Ruggens		dolerite/shale	Domestic	31.48139	19.96917	1078
29	G39629	11/03/1991	Albertfontein Ruggens		dolerite/shale	Domestic	31.48139	19.96917	1078
36	G39636	23/05/1991	Albertfontein Ruggens		dolerite/shale	Domestic	31.48111	19.96889	1070
36	G39636	23/05/1991	Albertfontein Ruggens		dolerite/shale	Domestic	31.48111	19.96889	1070
36	G39636	23/05/1991	Albertfontein Ruggens		dolerite/shale	Domestic	31.48111	19.96889	1070
36	G39636	27/05/1991	Albertfontein Ruggens		dolerite/shale	Domestic	31.48111	19.96889	1070
36	G39636	28/05/1991	Albertfontein Ruggens		dolerite/shale	Domestic	31.48111	19.96889	1070
44	G39844	05/12/1991	Vlakkefontein		shale		31.58278	19.74583	
44	G39844	05/12/1991	Vlakkefontein		shale		31.58278	19.74583	
44	G39844	05/12/1991	Vlakkefontein		shale		31.58278	19.74583	
44	G39844	05/12/1991	Vlakkefontein		shale		31.58278	19.74583	
44	G39844	09/12/1991	Vlakkefontein		shale		31.58278	19.74583	
72	G39972	21/02/1994	Albertfontein Ruggens		dolerite/shale	Domestic	31.48111	19.96889	1078
72	G39972	21/02/1994	Albertfontein Ruggens		dolerite/shale	Domestic	31.48111	19.96889	1078
72	G39972	21/02/1994	Albertfontein Ruggens		dolerite/shale	Domestic	31.48111	19.96889	1078
72	G39972	03/03/1994	Albertfontein Ruggens		dolerite/shale	Domestic	31.48111	19.96889	1078
72	G39972	05/03/1994	Albertfontein Ruggens		dolerite/shale	Domestic	31.48111	19.96889	1078
72	G39972	06/03/1994	Albertfontein Ruggens		dolerite/shale	Domestic	31.48111	19.96889	1078
72	G39972	10/09/1994	Albertfontein Ruggens		dolerite/shale		31.48111	19.96889	1070
72	G39972	16/09/1994	Albertfontein Ruggens		dolerite/shale	Domestic	31.48111	19.96889	1078
94	G39594	24/11/1990	Albertfontein Ruggens		dolerite/shale	Domestic	31.48139	19.96917	1078
94	G39594	15/05/1991	Albertfontein Ruggens		dolerite/shale		31.48139	19.96917	1078
94	G39594	16/05/1991	Albertfontein Ruggens		dolerite/shale		31.48139	19.96917	1078
94	G39594	21/05/1991	Albertfontein Ruggens		dolerite/shale		31.48139	19.96917	1078
95	G39595	27/11/1990	Albertfontein Ruggens		dolerite/shale	Domestic	31.48306	19.96806	
98	G39598	03/12/1990	Albertfontein Ruggens		dolerite/shale	Domestic	31.48167	19.96472	
99	G39599	03/12/1990	Ronde Rug		dolerite/shale	Domestic	31.475	19.97472	
650	G39650	23/09/1991	Enkelde Wilgenboom		dolerite/shale		31.49222	19.72556	
BN1		21/07/1982	Buffelsfontein		dolerite/shale	Stock	31.57333	19.67583	
CA1		31/03/1993	Calvinia Allotment		shale	Irrigation	31.46083	19.78	

Table D.5 (continued). Groundwater data for samples from boreholes in fractured rock aquifers – macro parameters.

FRACTURED ROCK									
Name	Date sampled	Borehole Depth (m)	Sample Depth (m)	Preservation	Lab. pH	EC (mS/m)	TDS (mg/L)	Ionic strength	Temp. (°C)
29	11/03/1991	54	54		7.8	166	1154	0.023	
29	11/03/1991	54	40		8	140	935	0.019	
36	23/05/1991	53.5	31	HgCl ₂	8	191	1198	0.023	
36	23/05/1991	53.5	18	HgCl ₂	8.2	194	1230	0.024	
36	23/05/1991	53.5	34	HgCl ₂	8	185	1149	0.023	
36	27/05/1991	53.5	52	HgCl ₂	8.1	162	1078	0.022	
36	28/05/1991	53.5	53.5	HgCl ₂	8.3	186	1206	0.023	
44	05/12/1991	58	58	HgCl ₂	8.3	152	946	0.018	
44	05/12/1991	15	15	HgCl ₂	8	137	974	0.018	
44	05/12/1991	96	96	HgCl ₂	8.3	146	904	0.018	
44	05/12/1991	31	31	HgCl ₂	8.3	152	949	0.019	
44	09/12/1991	146	146	HgCl ₂	8.2	148	915	0.019	
72	21/02/1994	54	54		8.1	145	998	0.019	
72	21/02/1994	37	37		7.8	114	823	0.016	
72	21/02/1994	63	63		8.2	163	1093	0.022	
72	03/03/1994	127	127		8.1	163	1094	0.021	
72	05/03/1994	194	194		8	151	1054	0.021	
72	06/03/1994	250	250		8.2	150	1031	0.020	
72	10/09/1994					165	1056	0.023	
72	16/09/1994	250	250		8.1	152	1067	0.021	
94	24/11/1990	63	63	HgCl ₂	7.9	181	1173	0.023	
94	15/05/1991	42	42	HgCl ₂	8.1	128	957	0.019	
94	16/05/1991	56	56	HgCl ₂	8	156	1163	0.023	
94	21/05/1991	90	90	HgCl ₂	8.1	145	1169	0.023	
95	27/11/1990	53	53	HgCl ₂	7.9	138	879	0.018	
98	03/12/1990	99	99	HgCl ₂	7.6	102	726	0.013	
99	03/12/1990	38	38	HgCl ₂	8	145	1049	0.020	
650	23/09/1991	85	85	HgCl ₂	8.1	127	862	0.016	
BN1	21/07/1982				8.4	190	1065	0.020	
CA1	31/03/1993	4	4	HgCl ₂	7.8	198	1209	0.025	

Table D.5 (continued). Groundwater data for samples from boreholes in fractured rock aquifers – cations.

FRACTURED ROCK										
Name	Date sampled	Na (mg/L)	Na (meq/L)	K (mg/L)	K (meq/L)	Mg (mg/L)	Mg (meq/L)	Ca (mg/L)	Ca (meq/L)	Cations (meq/L)
29	11/03/1991	142	6.18	6.4	0.16	80	6.58	100	4.99	17.9
29	11/03/1991	129	5.61	3.0	0.08	70	5.76	66	3.29	14.7
36	23/05/1991	171	7.44	22	0.57	74	6.09	85	4.24	18.3
36	23/05/1991	182	7.92	35	0.89	80	6.58	76	3.79	19.2
36	23/05/1991	164	7.13	17	0.42	74	6.09	85	4.24	17.9
36	27/05/1991	144	6.26	2.6	0.07	75	6.17	86	4.29	16.8
36	28/05/1991	167	7.26	14	0.35	75	6.17	90	4.49	18.3
44	05/12/1991	121	5.26	46	1.2	44	3.62	87	4.34	14.5
44	05/12/1991	130	5.65	73	1.9	35	2.88	80	3.99	14.7
44	05/12/1991	121	5.26	17	0.43	46	3.78	93	4.64	14.2
44	05/12/1991	118	5.13	8.9	0.23	51	4.20	109	5.44	15.0
44	09/12/1991	116	5.05	13	0.34	48	3.95	102	5.09	14.5
72	21/02/1994	132	5.74	3.8	0.10	62	5.10	87	4.34	15.3
72	21/02/1994	110	4.78	7.4	0.19	47	3.87	68	3.39	12.3
72	21/02/1994	143	6.22	5.0	0.13	72	5.92	98	4.89	17.2
72	03/03/1994	139	6.05	3.2	0.08	71	5.84	97	4.84	16.8
72	05/03/1994	131	5.70	3.1	0.08	67	5.51	99	4.94	16.2
72	06/03/1994	130	5.65	2.7	0.07	67	5.51	97	4.84	16.1
72	10/09/1994	142	6.18	2.1	0.05	76	6.25	110	5.49	18.0
72	16/09/1994	130	5.65	2.8	0.07	69	5.68	96	4.79	16.2
94	24/11/1990	156	6.79	2.9	0.07	74	6.09	110	5.49	18.4
94	15/05/1991	109	4.74	2.8	0.07	66	5.43	88	4.39	14.6
94	16/05/1991	142	6.18	5.2	0.13	80	6.58	103	5.14	18.0
94	21/05/1991	146	6.35	2.8	0.07	81	6.66	105	5.24	18.3
95	27/11/1990	111	4.83	2.8	0.07	66	5.43	62	3.09	13.4
98	03/12/1990	109	4.74	5.7	0.15	24	1.97	71	3.54	10.4
99	03/12/1990	151	6.57	17	0.45	64	5.27	73	3.64	16.0
650	23/09/1991	136	5.92	3.7	0.09	34	2.80	84	4.19	13.0
BN1	21/07/1982	248	10.8	0.9	0.02	48	3.95	39	1.95	16.7
CA1	31/03/1993	113	4.92	0.8	0.02	87	7.16	145	7.24	19.3

Table D.5 (continued). Groundwater data for samples from boreholes in fractured rock aquifers – anions.

FRACTURED ROCK									
Name	Date sampled	Cl (mg/L)	Cl (meq/L)	SO ₄ (mg/L)	SO ₄ (meq/L)	HCO ₃ (mg/L)	HCO ₃ (meq/L)	Anions (meq/L)	Balance (%)
29	11/03/1991	295	8.32	193	4.02	337	5.52	17.9	0.04
29	11/03/1991	246	6.94	165	3.44	255	4.18	14.6	0.43
36	23/05/1991	315	8.89	239	4.98	282	4.62	18.7	-0.84
36	23/05/1991	342	9.65	251	5.23	260	4.26	19.2	-0.15
36	23/05/1991	304	8.58	215	4.48	285	4.67	17.8	0.14
36	27/05/1991	281	7.93	187	3.89	301	4.93	16.8	-0.04
36	28/05/1991	312	8.80	220	4.58	320	5.24	18.8	-1.4
44	05/12/1991	278	7.84	136	2.83	221	3.62	14.5	-0.08
44	05/12/1991	288	8.12	140	2.91	210	3.44	14.7	0.03
44	05/12/1991	275	7.76	140	2.91	203	3.33	14.2	0.08
44	05/12/1991	282	7.95	145	3.02	221	3.62	14.8	0.63
44	09/12/1991	271	7.64	136	2.83	221	3.62	14.3	0.77
72	21/02/1994	224	6.32	150	3.12	338	5.54	15.0	0.88
72	21/02/1994	154	4.34	100	2.08	333	5.46	12.0	1.2
72	21/02/1994	269	7.59	173	3.60	331	5.42	16.7	1.5
72	03/03/1994	265	7.48	164	3.41	353	5.78	16.7	0.25
72	05/03/1994	244	6.88	154	3.21	356	5.83	16.0	0.86
72	06/03/1994	236	6.66	143	2.98	355	5.82	15.5	1.9
72	10/09/1994	272	7.67	183	3.81	377	6.18	17.7	0.69
72	16/09/1994	263	7.42	156	3.25	350	5.74	16.5	-0.80
94	24/11/1990	283	7.98	214	4.46	331	5.42	17.9	1.4
94	15/05/1991	206	5.81	135	2.81	351	5.76	14.4	0.77
94	16/05/1991	295	8.32	194	4.04	344	5.64	18.0	0.01
94	21/05/1991	296	8.35	195	4.06	343	5.62	18.1	0.72
95	27/11/1990	226	6.38	134	2.79	276	4.52	13.7	-1.1
98	03/12/1990	162	4.57	73	1.52	281	4.61	10.7	-1.4
99	03/12/1990	226	6.38	196	4.08	315	5.16	15.8	0.67
650	23/09/1991	225	6.35	102	2.12	277	4.54	13.0	-0.17
BN1	21/07/1982	362	10.2	109	2.27	253	4.14	16.7	-0.12
CA1	31/03/1993	294	8.29	231	4.81	310	5.08	18.7	1.8

Table D.5 (continued). Groundwater data for samples from boreholes in fractured rock aquifers – minor species and ion ratios.

FRACTURED ROCK										
Name	Date sampled	NO ₃ (mg N/L)	NH ₄ (mg N/L)	F (mg/L)	Fe _T (mg/L)	Si (mg/L)	P (mg/L)	Na/Cl (wt)	Mg/Ca (wt)	SAR
29	11/03/1991	0.12		0.46		11.5	0.014	0.74	1.32	2.57
29	11/03/1991	0.57	0.06	0.44		11.3	0.018	0.81	1.75	2.64
36	23/05/1991	1.96	0.05	0.54		5.4	0.015	0.84	1.44	3.27
36	23/05/1991	0.98	0.08	0.68		5.9	0.028	0.82	1.74	3.48
36	23/05/1991	1.2	0.07	0.58		6.0	0.027	0.83	1.44	3.14
36	27/05/1991	0.43	0.05	0.46		11.3	0.015	0.79	1.44	2.74
36	28/05/1991	2.0	0.08	0.50		8.9	0.013	0.83	1.37	3.15
44	05/12/1991	2.6	1.2	0.53		5.1	0.005	0.67	0.83	2.64
44	05/12/1991	2.9	4.8	0.65		3.8		0.70	0.72	3.05
44	05/12/1991	2.2	1.1	0.38		8.9	0.006	0.68	0.82	2.56
44	05/12/1991	3.0	0.34	0.45		9.7	0.005	0.65	0.77	2.34
44	09/12/1991	1.9	0.70	0.42		9.3	0.008	0.66	0.78	2.37
72	21/02/1994			0.59		10.1	0.009	0.91	1.17	2.64
72	21/02/1994	0.78	0.36	0.78		9.3	0.013	1.10	1.14	2.51
72	21/02/1994	0.36		0.60		10.5	0.009	0.82	1.21	2.68
72	03/03/1994	0.29		0.55		10.5	0.008	0.81	1.21	2.62
72	05/03/1994			0.57		10.5	0.008	0.83	1.12	2.49
72	06/03/1994			0.56		10.6	0.007	0.85	1.14	2.49
72	10/09/1994	0.6		0.40	0.63	10.6		0.81	1.14	2.55
72	16/09/1994			0.95		9.1	0.012	0.76	1.19	2.47
94	24/11/1990	0.43		0.64		11.2	0.007	0.85	1.11	2.82
94	15/05/1991	0.06		0.48		10.1	0.008	0.82	1.24	2.14
94	16/05/1991	0.05		0.46		10.9	0.011	0.74	1.28	2.55
94	21/05/1991	0.06		0.50		11.1	0.013	0.76	1.27	2.60
95	27/11/1990	0.05		0.56		11.7	0.005	0.76	1.76	2.34
98	03/12/1990	0.06	0.50	0.66		7.7	0.007	1.04	0.56	2.85
99	03/12/1990	1.4	0.75	0.74		8.3	0.014	1.03	1.45	3.11
650	23/09/1991		0.04	0.67		8.6	0.013	0.93	0.67	3.16
BN1	21/07/1982	0.85	0.04	1.3		10.3	0.008	1.1	2.0	6.28
CA1	31/03/1993	6.4	0.05	0.3		15	0.015	0.59	0.99	1.83

Table D.5 (continued). Groundwater data for samples from boreholes in fractured rock aquifers – saturation indices.

FRACTURED ROCK										
Name	Date sampled	Calcite	Dolomite	Gypsum	Anhydrite	Fluorite	Chalcedony	Quartz	log $p\text{CO}_2$	Data source
29	11/03/1991	0.70	1.65	-1.41	-1.63	-1.77	0.16	0.59	-2.33	NWQDB
29	11/03/1991	0.62	1.62	-1.60	-1.82	-1.95	0.15	0.58	-2.64	NWQDB
36	23/05/1991	0.74	1.76	-1.38	-1.60	-1.70	-0.17	0.26	-2.61	NWQDB
36	23/05/1991	0.84	2.05	-1.42	-1.64	-1.56	-0.13	0.29	-2.85	NWQDB
36	23/05/1991	0.75	1.79	-1.42	-1.64	-1.63	-0.12	0.31	-2.60	NWQDB
36	27/05/1991	0.88	2.05	-1.47	-1.69	-1.82	0.15	0.58	-2.68	NWQDB
36	28/05/1991	1.10	2.46	-1.40	-1.62	-1.75	0.04	0.47	-2.87	NWQDB
44	05/12/1991	0.97	2.00	-1.54	-1.76	-1.63	-0.20	0.23	-3.02	NWQDB
44	05/12/1991	0.63	1.26	-1.55	-1.77	-1.47	-0.32	0.11	-2.73	NWQDB
44	05/12/1991	0.96	1.97	-1.50	-1.72	-1.89	0.04	0.47	-3.06	NWQDB
44	05/12/1991	1.06	2.14	-1.44	-1.66	-1.69	0.08	0.51	-3.03	NWQDB
44	09/12/1991	0.94	1.91	-1.48	-1.70	-1.77	0.06	0.49	-2.92	NWQDB
72	21/02/1994	0.95	2.11	-1.53	-1.75	-1.57	0.10	0.53	-2.63	NWQDB
72	21/02/1994	0.59	1.37	-1.75	-1.97	-1.38	0.07	0.50	-2.32	NWQDB
72	21/02/1994	1.07	2.36	-1.45	-1.67	-1.53	0.12	0.54	-2.75	NWQDB
72	03/03/1994	1.00	2.22	-1.47	-1.69	-1.61	0.12	0.55	-2.61	NWQDB
72	05/03/1994	0.93	2.04	-1.48	-1.70	-1.56	0.12	0.55	-2.51	NWQDB
72	06/03/1994	1.11	2.41	-1.52	-1.74	-1.58	0.12	0.55	-2.72	NWQDB
72	10/09/1994	0.00	0.19	-1.39	-1.61	-1.84	-0.13	0.56	-1.47	Woodford, 1994
72	16/09/1994	1.00	2.21	-1.49	-1.71	-1.13	0.06	0.48	-2.62	CSIR
94	24/11/1990	0.82	1.83	-1.33	-1.55	-1.44	0.15	0.58	-2.44	NWQDB
94	15/05/1991	0.98	2.18	-1.57	-1.79	-1.74	0.10	0.53	-2.61	NWQDB
94	16/05/1991	0.91	2.06	-1.40	-1.62	-1.76	0.14	0.57	-2.52	NWQDB
94	21/05/1991	1.01	2.26	-1.39	-1.61	-1.68	0.14	0.57	-2.63	NWQDB
95	27/11/1990	0.55	1.47	-1.70	-1.92	-1.74	0.17	0.60	-2.50	NWQDB
98	03/12/1990	0.36	0.61	-1.81	-2.03	-1.45	-0.01	0.42	-2.18	NWQDB
99	03/12/1990	0.74	1.78	-1.50	-1.72	-1.46	0.02	0.45	-2.55	NWQDB
650	23/09/1991	0.88	1.73	-1.65	-1.87	-1.41	0.03	0.46	-2.71	NWQDB
BN1	21/07/1982	0.77	1.99	-1.98	-2.20	-1.23	0.10	0.53	-3.06	NWQDB
CA1	31/03/1993	0.81	1.74	-1.20	-1.42	-2.00	0.28	0.71	-2.37	NWQDB

Table D.5 (continued). Groundwater data for samples from boreholes in fractured rock aquifers – borehole information.

FRACTURED ROCK									
Name	DWAF No.	Date sampled	Farm	Location	Lithology	Use	Latitude	Longitude	Elevation (m)
CT45		30/06/1980	Calvinia Allotment		shale	Stock			
DW6		01/07/1980	Downes Wes		shale	Stock	31.52	19.88917	
EW29		30/06/1980	Enkelde Wilgenboom		shale	Stock	31.49028	19.69	
K35		06/05/1991	Kreitsberg		shale		31.5656	19.83194	
KF1		07/08/1999	Kopoasfontein		dolerite/shale	Stock	31.48964	19.90833	1050
Oil1		17/11/1980	Muisvlakte		shale	Domestic	31.48694	19.895	
PS22	G32622	15/07/1980	Calvinia Allotment	Akkerendam	dolerite/shale	Domestic	31.45056	19.77111	1019.31
PS22	G32622	01/08/1980	Calvinia Allotment	Akkerendam	dolerite/shale		31.45056	19.77111	1019.31
PS25	G32625	24/07/1980	Calvinia Allotment	Akkerendam	shale		31.435	19.76528	1103.54
PS27	G32627	01/08/1980	Calvinia Allotment	Akkerendam	shale		31.45056	19.77111	1019.59
T8		03/07/1980	Tygerhoek		alluvium	Irrigation/Stock	31.43833	19.69139	
T9		03/07/1980	Tygerhoek		shale	Stock	31.42583	19.7	
TK5		18/05/1982	Tygerhoek		shale	Stock	31.44639	19.72722	
TK6		18/05/1982	Tygerhoek		shale	Stock	31.46467	19.695	
VW68	G31268	21/03/1980	Calvinia Allotment	Karee Dam	dolerite/shale	Domestic	31.42139	19.78639	1038.38
VW68	G31268	01/08/1980	Calvinia Allotment	Karee Dam	dolerite/shale	Domestic			1038.38

Table D.5 (continued). Groundwater data for samples from boreholes in fractured rock aquifers – macro parameters.

FRACTURED ROCK									
Name	Date sampled	Borehole Depth (m)	Sample Depth (m)	Preservation	Lab. pH	EC (mS/m)	TDS (mg/L)	Ionic strength	Temp. (°C)
CT45	30/06/1980	24.2	24		7.7	241	1456	0.029	
DW6	01/07/1980	24.2	24		7.7	233	1348	0.028	
EW29	30/06/1980	30	30		7.5	383	2404	0.048	
K35	06/05/1991			HgCl ₂	7.8	250	1568	0.031	
KF1	07/08/1999				7.32	120	768	0.016	20
Oil1	17/11/1980	454.5	400		7.2	174	1119	0.020	
PS22	15/07/1980	50	50		7.7	62.3	437	0.008	
PS22	01/08/1980	50	50		7.6	59.6	424	0.008	
PS25	24/07/1980	30	30		7.5	59	434	0.007	
PS27	01/08/1980	34	34		7.5	60	428	0.008	
T8	03/07/1980	6	6		7.9	80.2	589	0.011	
T9	03/07/1980	27	27		7.8	81	599	0.011	
TK5	18/05/1982				8.2	78	647	0.011	
TK6	18/05/1982				8.1	113	879	0.014	
VW68	21/03/1980	36	36		7.6	60	385	0.007	
VW68	01/08/1980	60	60		7.7	48.1	308	0.007	

Table D.5 (continued). Groundwater data for samples from boreholes in fractured rock aquifers – cations.

FRACTURED ROCK										
Name	Date sampled	Na (mg/L)	Na (meq/L)	K (mg/L)	K (meq/L)	Mg (mg/L)	Mg (meq/L)	Ca (mg/L)	Ca (meq/L)	Cations (meq/L)
CT45	30/06/1980	221	9.61	0.57	0.01	71	5.84	152	7.58	23.1
DW6	01/07/1980	434	18.9	3.4	0.09	106	8.72	219	10.9	38.6
EW29	30/06/1980	302	13.1	2.2	0.06	66	5.43	140	6.99	25.6
K35	06/05/1991	325	14.1	13	0.34	4	0.33	38	1.90	16.7
KF1	07/08/1999	94	4.09	1.2	0.03	47	3.87	90	4.49	12.5
Oil1	17/11/1980	60	2.61	16	0.41	14	1.15	35	1.75	5.9
PS22	15/07/1980	49	2.13	2.8	0.07	21	1.73	42	2.10	6.0
PS22	01/08/1980	45	1.96	0.5	0.01	23	1.89	42	2.10	6.0
PS25	24/07/1980	46	2.00	4.1	0.10	22	1.81	42	2.10	6.0
PS27	01/08/1980	890	38.7	3.1	0.08	283	23.3	216	10.8	72.9
T8	03/07/1980	57	2.48	0.04	0.001	29	2.39	66	3.29	8.16
T9	03/07/1980	75	3.26	1.3	0.03	19	1.56	75	3.74	8.6
TK5	18/05/1982	157	6.83	0.3	0.01	32	2.63	48	2.40	11.9
TK6	18/05/1982	722	31.4	4.4	0.11	156	12.8	174	8.68	53.0
VW68	21/03/1980	32	1.39	0.82	0.02	20	1.65	42	2.10	5.2
VW68	01/08/1980	31	1.35	1.2	0.03	20	1.65	42	2.10	5.1

Table D.5 (continued). Groundwater data for samples from boreholes in fractured rock aquifers – anions.

FRACTURED ROCK									
Name	Date sampled	Cl (mg/L)	Cl (meq/L)	SO ₄ (mg/L)	SO ₄ (meq/L)	HCO ₃ (mg/L)	HCO ₃ (meq/L)	Anions (meq/L)	Balance (%)
CT45	30/06/1980	567	16.0	141	2.94	260	4.26	23.9	-1.8
DW6	01/07/1980	567	16.0	104	2.17	225	3.68	22.3	-0.73
EW29	30/06/1980	903	25.5	446	9.29	278	4.56	39.6	-1.3
K35	06/05/1991	575	16.2	166	3.46	311	5.10	24.9	1.4
KF1	07/08/1999	175	4.94	78	1.62	319	5.23	12.5	-0.22
Oil1	17/11/1980	178	5.02	396	8.24	160	2.62	16.0	2.2
PS22	15/07/1980	58	1.64	28	0.58	233	3.82	6.1	-0.96
PS22	01/08/1980	48	1.35	28	0.58	237	3.88	5.9	0.79
PS25	24/07/1980	47	1.33	20	0.42	240	3.94	5.8	1.4
PS27	01/08/1980	50	1.41	28	0.58	235	3.86	5.9	0.91
T8	03/07/1980	65	1.83	37	0.77	334	5.48	8.12	0.22
T9	03/07/1980	77	2.17	24	0.50	339	5.56	8.3	0.97
TK5	18/05/1982	47	1.33	57	1.19	366	6.00	8.7	-0.28
TK6	18/05/1982	114	3.22	75	1.56	431	7.06	12.3	-1.7
VW68	21/03/1980	29	0.82	14	0.29	245	4.02	5.2	-0.06
VW68	01/08/1980	25	0.71	13	0.27	244	4.00	5.0	1.0

Table D.5 (continued). Groundwater data for samples from boreholes in alluvial aquifers – minor species and ion ratios.

FRACTURED ROCK										
Name	Date sampled	NO ₃ (mg N/L)	NH ₄ (mg N/L)	F (mg/L)	Fe _T (mg/L)	Si (mg/L)	P (mg/L)	Na/Cl (wt)	Mg/Ca (wt)	SAR
CT45	30/06/1980	9.8		0.49		13.2		0.60	0.77	3.71
DW6	01/07/1980	5.8		0.81		9		0.59	0.79	3.78
EW29	30/06/1980	3.2		1.1		10.8		0.74	0.80	6.02
K35	06/05/1991	1.2		0.59		7.8	0.008	0.81	0.78	5.27
KF1	07/08/1999	9.4		1.4	0.41	12.7	0.01	0.83	0.86	2.00
Oil1	17/11/1980	0.28	0.51	2.2		4.4	0.12	2.8	0.17	13.4
PS22	15/07/1980	0.67		1.1		12.6		1.3	0.82	1.54
PS22	01/08/1980		0.04	0.98		14		1.5	0.90	1.39
PS25	24/07/1980	0.36	0.09	0.98		7.7		2.0	0.66	2.17
PS27	01/08/1980		0.04	1.0		11		1.4	0.86	1.43
T8	03/07/1980	0.11		0.64		11	0.03	1.35	0.72	1.47
T9	03/07/1980		0.06	0.68		15		1.5	1.1	2.07
TK5	18/05/1982	1.5	0.05	0.67		8.3	0.009	2.5	0.42	2.00
TK6	18/05/1982	4.9	0.04	1.5		14.3	0.11	2.1	1.1	4.31
VW68	21/03/1980		0.05	0.68		11.6		1.7	0.79	1.02
VW68	01/08/1980	0.02	0.04	0.8		11	0.015	1.9	0.79	0.99

Table D.5 (continued). Groundwater data for samples from boreholes in fractured rock aquifers – saturation indices.

FRACTURED ROCK										
Name	Date sampled	Calcite	Dolomite	Gypsum	Anhydrite	Fluorite	Chalcedony	Quartz	log $p\text{CO}_2$	Data source
CT45	30/06/1980	0.66	1.33	-1.40	-1.62	-1.54	0.22	0.65	-2.35	Seward, 1983
DW6	01/07/1980	0.57	1.17	-1.55	-1.77	-1.13	0.06	0.49	-2.41	Seward, 1983
EW29	30/06/1980	0.55	1.13	-0.89	-1.11	-0.79	0.14	0.57	-2.13	Seward, 1983
K35	06/05/1991	0.78	1.59	-1.37	-1.59	-1.43	-0.01	0.42	-2.37	NWQDB
KF1	07/08/1999	0.15	0.31	-1.73	-1.97	-0.68	0.27	0.71	-1.88	This study
Oil1	17/11/1980	-0.66	-1.95	-1.44	-1.66	-0.79	-0.25	0.18	-2.03	NWQDB
PS22	15/07/1980	0.22	0.48	-2.35	-2.57	-1.15	0.20	0.63	-2.35	Seward, 1983
PS22	01/08/1980	0.13	0.34	-2.36	-2.58	-1.26	0.25	0.68	-2.24	Seward, 1983
PS25	24/07/1980	-0.04	-0.12	-2.55	-2.77	-1.32	-0.01	0.42	-2.13	Seward, 1983
PS27	01/08/1980	0.02	0.12	-2.35	-2.57	-1.22	0.14	0.57	-2.14	Seward, 1983
T8	03/07/1980	0.72	1.44	-2.11	-2.33	-1.49	0.14	0.57	-2.41	Van Wyk, 1980
T9	03/07/1980	0.50	1.19	-2.43	-2.65	-1.57	0.28	0.71	-2.30	Van Wyk, 1980
TK5	18/05/1982	1.09	1.94	-1.88	-2.10	-1.40	0.01	0.44	-2.68	NWQDB
TK6	18/05/1982	0.84	1.87	-1.99	-2.21	-0.95	0.25	0.68	-2.51	NWQDB
VW68	21/03/1980	0.16	0.34	-2.63	-2.85	-1.56	0.17	0.59	-2.22	Van Wyk, 1980
VW68	01/08/1980	0.25	0.53	-2.67	-2.89	-1.42	0.14	0.57	-2.33	Van Wyk, 1980

Table D.6. Surface water data for samples from Calvinia – sample location.

SURFACE WATER							
Name	Date sampled	Farm	Location	Use	Latitude	Longitude	Elevation (m)
Dam	11/01/1994	Calvinia Allotment	Karee Dam	Domestic	31.42833	19.78708	1050
Dam	12/11/1997	Calvinia Allotment	Karee Dam	Domestic	31.42833	19.78708	1050
Dam	17/08/1998	Calvinia Allotment	Karee Dam – western shore	Domestic	31.42833	19.78708	1050
Plant	17/08/1998	Calvinia Allotment	Municipal waterworks	Domestic	31.43603	19.78548	1040
Town	09/08/1999	Calvinia Allotment	Tap outside municipality offices	Domestic	31.47433	19.775	990

Table D.6 (continued). Surface water data for samples from Calvinia – macro variables.

Name	Date sampled	Sample Depth (m)	Preservation	Lab. pH	EC (mS/m)	TDS (mg/L)	Ionic strength	Temp. (°C)
Dam	11/01/1994	surface			21	134	0.003	
Dam	12/11/1997	surface					0.002	
Dam	17/08/1998	surface		7.34	17.8	114	0.003	
Plant	17/08/1998	surface		7.08	18.6	119	0.003	9.5
Town	09/08/1999	surface		7.01	26	166	0.003	12.5

Table D.6 (continued). Surface water data for samples from Calvinia – cations.

Name	Date sampled	Na (mg/L)	Na (meq/L)	K (mg/L)	K (meq/L)	Mg (mg/L)	Mg (meq/L)	Ca (mg/L)	Ca (meq/L)	Cations (meq/L)
Dam	11/01/1994	12	0.52	1	0.03	10	0.82	18	0.90	2.27
Dam	12/11/1997	12	0.52	1	0.03	10	0.82	18	0.90	2.27
Dam	17/08/1998	12	0.52	0.7	0.02	12	0.99	18	0.90	2.43
Plant	17/08/1998	13	0.57	0.8	0.02	12	0.99	17	0.85	2.42
Town	09/08/1999	11	0.48	0.8	0.02	6.7	0.55	19	0.95	2.01

Table D.6 (continued). Surface water data for samples from Calvinia – anions.

OTHER SODIC GROUNDWATERS									
Name	Date sampled	Cl (mg/L)	Cl (meq/L)	SO ₄ (mg/L)	SO ₄ (meq/L)	HCO ₃ (mg/L)	HCO ₃ (meq/L)	Anions (meq/L)	Balance (%)
Dam	11/01/1994	13	0.37	9	0.19	124	2.04	2.59	-6.7
Dam	12/11/1997	13	0.37	9	0.19				
Dam	17/08/1998	16	0.45	6.5	0.14	107	1.76	2.37	1.2
Plant	17/08/1998	16	0.45	20	0.42	89.1	1.46	2.36	1.3
Town	09/08/1999	7.4	0.21	45	0.94	43.9	0.72	2.08	-1.7

Table D.6 (continued). Surface water data for samples from Calvinia – minor species and ion ratios.

Name	Date sampled	NO ₃ (mg N/L)	NH ₄ (mg N/L)	F (mg/L)	Fe _T (mg/L)	Si (mg/L)	P (mg/L)	Na/Cl (wt)	Mg/Ca (wt)	SAR
Dam	11/01/1994							1.4	0.92	0.56
Dam	12/11/1997							1.4	0.92	0.56
Dam	17/08/1998	0.3		0.1		4.5		1.2	1.1	0.54
Plant	17/08/1998	0.4		0.1	0.08	3.7		1.3	1.2	0.59
Town	09/08/1999	3				11.6		2.3	0.58	0.55

Table D.6 (continued). Surface water data for samples from Calvinia – saturation indices.

Name	Date sampled	Calcite	Dolomite	Gypsum	Anhydrite	Fluorite	Chalcedony	Quartz	log pCO ₂	Data source
Dam	11/01/1994	-1.04	-1.98	-3.07	-3.29				-1.90	Woodford, 1994
Dam	12/11/1997			-3.03	-3.25					CSIR
Dam	17/08/1998	-1.00	-2.06	-3.18	-3.44	-3.29	-0.05	0.43	-2.40	Cavé, 1999
Plant	17/08/1998	-1.35	-2.68	-2.73	-2.98	-3.41	-0.18	0.29	-2.23	Cavé, 1999
Town	09/08/1999	-1.47	-3.04	-2.34	-2.56		0.17	0.60	-2.36	This study

APPENDIX E
X-RAY DIFFRACTION DATA FOR CLAY MINERALS IN
KOPOASFONTEIN BRECCIATED SHALES

Sample KF1

Mineral	Reflection	K saturation		Heat 550°C		Mg saturation		Glycerol	
		d ¹ (Å)	RI ² (%)	d (Å)	RI (%)	d (Å)	RI (%)	d (Å)	RI (%)
chlorite (C)	001	14.2	22.0	13.9	25.4	14.6	16.9	14.4	25.6
	002(+K)	7.10	96.2*	7.05	5.37	7.16	72.9*	7.08	81.3*
	003	4.74	21.3	?	-	4.74	15.5	4.72	19.0
	004(+K)	3.55	87.7*	3.48	9.59	3.56	73.1*	3.54	76.8*
	005	2.83	13.7	?	-	2.84	13.2	-	-
	006 (+Q)	1.54	8.81*	1.54	3.74*	1.54	8.14*	-	-
illite (I)	001	10.1	95.3	10.0	74.9	10.2	61.7	10.1	56.5
	002	5.00	32.8	5.00	22.9	5.00	26.8	5.01	27.8
	003 (+Q)	3.33?	72.4 [#]	3.33?	80.3 [#]	3.33?	65.8 [#]	3.33?	67.4 [#]
	004	2.50	7.56	2.50	8.90	2.50	7.21	-	-
	005	2.00	43.6	2.00	18.6	2.00	40.6	-	-
	006	1.51	4.53	1.50	1.58	1.51	2.72	-	-
kaolinite (K)	001(+C)	7.10	96.2*	-	-	7.16	72.9*	7.08	81.3*
	002(+C)	3.55	87.7*	-	-	3.56	73.1*	3.54	76.8*
quartz (Q)	100	4.27	6.41	4.25	4.58	4.28	7.96	4.25	7.59
	101 (+I)	3.34	27.6 [#]	3.34	19.7 [#]	3.34	34.2 [#]	3.34	32.6 [#]
	110	2.46	6.26	2.46	4.06	2.47	7.83	-	-
	102	2.28	2.56	2.28	1.70	2.28	2.02	-	-
	111	2.24	3.34	?	-	?	-	-	-
	200	2.13	6.75	2.13	2.79	2.14	7.10	-	-
	112	1.82	6.70	1.82	5.03	1.82	7.87	-	-
	211 (+C)	1.54	8.81*	1.54	3.74	1.54	8.14*	-	-
plagio- clase		3.78	4.55	3.77	3.89	3.79	5.78	3.77	3.87
		3.68	5.26	3.68	2.18	3.68	5.61	3.66	3.22
		3.20	24.0	3.19	14.1	3.21	23.8	3.19	18.9
		2.99	6.86	2.99	3.62	3.00	6.89	-	-
vermic. smectite						not present		not present	

¹ d-spacing

² relative intensity of x-ray reflections

Symbols:

- no data

? uncertain or missing peak

* combined intensity of overlapping reflections.

intensities recalculated using the formulae RI (Q 101) = 4.3 × RI (Q 100) and

RI (I 003) = RI (Q+I) - RI (Q 101)

after Moore and Reynolds (1989) where RI is the relative intensity of the peaks, Q 101 and Q 100 are the first 2 quartz reflections, I 003 is the third order illite reflection and Q+I is the combined reflection at 26.7° 2θ.

Sample KF2

Mineral	Reflection	K saturation		Heat 550°C		Mg saturation		Glycerol	
		d ¹ (Å)	RI ² (%)	d (Å)	RI (%)	d (Å)	RI (%)	d (Å)	RI (%)
vermiculite (V)	001 (+I)	10.1	96.9*	10.1	72.1*	14.3	28.7	14.0	26.9
	002 (+K,I)	5.01	28.9*	5.00	23.9	7.08	19.3*	6.99	22.9*
	003 (+I,Q)	3.33?	100*	3.33?	100*	4.71	6.23	4.63	6.44
	004 (+K,I)	2.51	10.7*	2.51	9.88*	3.54	20.9*	3.54	23.8*
illite (I)	001 (+V)	10.1	96.9*	10.2	72.1*	9.98	56.8	10.1	63.3
	002 (+V)	5.01	28.9*	5.00	23.9*	5.00	26.9	5.00	34.4
	003 (+Q,V)	3.33?	73.6 [#]	3.33?	82.8 [#]	3.33?	76.0 [#]	3.33?	71.7 [#]
	004 (+V)	2.51	10.7*	2.51	9.88*	2.50	9.01	-	-
	005	2.01	30.1	2.00	25.1	2.00	36.5	-	-
	006	1.50	8.04	1.50	5.68	1.51	4.33	-	-
kaolinite (K)	001(+V)	7.08	23.7	-	-	7.08	19.3*	6.99	22.9*
	002(+V)	3.54	22.8	-	-	3.54	20.9*	3.54	23.8*
quartz (Q)	100	4.26	6.14	4.26	3.99	4.25	5.56	4.26	6.59
	101 (+I)	3.34	26.4 [#]	3.34	17.2 [#]	3.34	24.0 [#]	3.34	28.3 [#]
	110	2.45	8.23	2.46	3.76	2.46	4.85	-	-
	102	2.28	3.84	2.28	2.54	?	-	-	-
	111	2.25	4.00	?	-	?	-	-	-
	200	2.13	10.5	2.14	4.03	2.14	5.37	-	-
	112	1.82	4.35	1.82	4.34	1.82	4.78	-	-
	211 (+C)	1.55	4.48*	1.54	5.36	1.54	4.11*	-	-
plagioclase (P)		3.78	8.50	3.77	6.28	3.76	6.87	3.78	5.54
		3.67	7.40	3.66	5.58	3.66	5.14	3.67	3.60
		3.19	25.0	3.19	18.0	3.19	20.7	3.20	22.7
		3.00	17.3	2.99	9.19	3.00	11.8	-	-
chlorite smectite		trace quantity						not present	

¹ mineral d-spacing

² relative intensity of x-ray reflections

Symbols:

- no data

? uncertain or missing peak

* combined intensity of overlapping reflections

[#] intensities recalculated using the formulae $RI(Q\ 101) = 4.3 \times RI(Q\ 100)$ and

$RI(I\ 003) = RI(Q+I) - RI(Q\ 101)$

after Moore and Reynolds (1989) where RI is the relative intensity of the peaks, Q 101 and Q 100 are the first 2 quartz reflections, I 003 is the third order illite reflection and Q+I is the combined reflection at 26.7° 2θ.

Sample KF3

Mineral	Reflection	K saturation		Heat 550°C		Mg saturation		Glycerol	
		d ¹ (Å)	RI ² (%)	d (Å)	RI (%)	d (Å)	RI (%)	d (Å)	RI (%)
chlorite (C)	001 (+V)	14.1	17.3	13.9	18.3	14.6	40.8*	14.5	39.1*
	002 (+V,K)	7.06	84.1*	6.94	4.28	7.07	59.2*	7.10	62.0*
	003 (+V)	4.70	17.6	?	-	4.72	11.5*	4.72	16.1*
	004 (+V,K)	3.53	76.8*	3.46	11.5	3.54	65.2*	3.54	68.6*
	005 (+V)	2.83	13.9	?	-	2.83	11.5*	-	-
	006 (+Q)	1.55	5.04*	1.54	2.81*	1.54	6.85*	-	-
vermiculite (V)	001 (+I,C)	10.0	83.3*	10.0	90.4*	14.6	40.8*	14.5	39.1*
	002 (+I,K)	4.99	26.7*	5.00	23.2*	7.07	59.2*	7.10	62.0*
	003 (+I,Q)	3.33?	100*	3.33?	100*	4.72	11.5*	4.72	16.1*
	004 (+I, K)	2.50	11.4*	2.50	8.89*	3.54	65.2*	3.54	68.6*
illite (I)	001 (+V)	10.0	83.3*	10.0	90.4*	10.1	46.2	10.1	44.1
	002 (+V)	4.99	26.7*	5.00	23.2*	5.02	21.6	5.02	26.3
	003 (+Q,V)	3.33?	74.4 [#]	3.33?	77.4 [#]	3.33?	79.6 [#]	3.33?	73.0 [#]
	004 (+V)	2.50	11.4*	2.50	8.89*	2.50	9.76	-	-
	005 (+V)	2.00	23.9*	2.01	17.8*	2.00	34.1	-	-
	006 (+V)	1.50	3.99*	1.50	3.07*	1.50	3.90	-	-
kaolinite	001 (+C,V)	7.06	84.1*	-	-	7.07	59.2*	7.10	62.0*
	002 (+C,V)	3.53	76.8*	-	-	3.54	65.2*	3.54	68.6*
quartz (Q)	100	4.25	5.95	4.25	5.25	4.27	4.75	4.27	6.28
	101 (+I)	3.34	25.6 [#]	3.34	22.6 [#]	3.34	20.4 [#]	3.34	27 [#]
	110	2.45	9.27	2.45	4.12	2.46	7.82	-	-
	102	2.28	4.96	2.25	1.99	?	-	-	-
	200	2.13	8.33	2.13	3.37	2.13	7.80	-	-
	112	1.82	4.90	1.82	4.33	1.82	4.68	-	-
	211 (+C)	1.55	5.04*	1.54	2.81	1.54	6.85*	-	-
plagioclase (P)		3.77	8.07	3.77	6.28	3.76	6.84	3.78	7.21
		3.67	7.99	3.66	5.58	?	-	3.68	7.39
		3.19	32.4	3.19	18.0	3.19	33.2	3.20	31.1
		3.00	11.1	2.99	9.19	3.00	10.8	-	-
smectite								not present	

¹ mineral d-spacing

² relative intensity of x-ray reflections

Symbols:

- no data

? uncertain or missing peak

* combined intensity of overlapping reflections

intensities recalculated using the formulae $RI(Q\ 101) = 4.3 \times RI(Q\ 100)$ and $RI(I\ 003) = RI(Q+I) - RI(Q\ 101)$

after Moore and Reynolds (1989), where RI is the relative intensity of the peaks, Q 101 and Q 100 are the first 2 quartz reflections, I 003 is the third order illite reflection and Q+I is the combined reflection at 26.7° 2θ.

Sample KF4

Mineral	Reflection	K saturation		Heat 550°C		Mg saturation		Glycerol	
		d ¹ (Å)	RI ² (%)	d (Å)	RI (%)	d (Å)	RI (%)	d (Å)	RI (%)
chlorite (C)	001	14.1	18.8	13.8	57.7	14.1	20.9	14.1	21.4
	002 (+K)	7.06	100*	6.94	12.6	7.07	100*	7.07	100*
	003	4.71	21.4	?	-	4.71	23.0	4.71	26.1
	004 (+K)	3.53	92.8*	3.46?	42.1*	3.53	85.6*	3.54	83*
	005	2.83	20.3	?	-	2.83	21.1	-	-
	006 (+Q)	1.55	10.6*	?	-	1.55	9.00*	-	-
illite?	001	10.1?	2.69	10.0	3.71	10.0	3.31	10.1	2.64
kaolinite	001 (+C)	7.06	100*	-	-	7.07	100*	7.07	100*
	002 (+C)	3.53	19.6*	-	-	3.53	85.6*	3.54	83*
quartz (Q)	100	4.25	22.4	4.25	31.7	4.25	24.4	4.25	23.8
	101	3.34	57.8	3.34	91.4	3.34	57.2	3.34	57.7
	110	2.45	12.0	2.45	9.46	2.46	11.4	-	-
	102	2.28	8.42	2.28	5.68	2.28	7.92	-	-
	200	2.13	12.5	2.13	12.7	2.13	10.6	-	-
	112	1.82	11.4	1.82	13.4	1.82	14.5	-	-
	211 (+C)	1.54	10.4*	1.54	15.3	1.55	9.00*	-	-
plagio- clase (P)		3.78	24.2	3.78	37.6	3.77	26.7	3.77	27.6
		3.67	19.3	3.67	33.9	3.67	24.0	3.67	19.6
		3.19	55.6	3.19	100	3.19	62.3	3.19	67.4
		3.16	20.0	3.16	30.8	3.16	24.0	3.16	20.8
		3.00	16.2	3.00	20.9	3.00	17.5	-	-
vermic. smectite						trace quantity?		not present	

¹ mineral d-spacing

² relative intensity of x-ray reflections

Symbols:

- no data
- * combined intensity of overlapping reflections
- ? uncertain or missing peak

Reference

Moore, D.M. and Reynolds, R.C. Jr. (1989). *X-ray diffraction and the identification and analysis of clay minerals*. Oxford University Press Inc., New York, 332 p.

APPENDIX F
DOCUMENTED OCCURRENCES OF APOPHYLLITE AND
ASSOCIATED MINERAL ASSEMBLAGES

Table F.1. Occurrences of apophyllite, associated mineral assemblages and specimen numbers from published reports and museum specimens.

Location	Description	Associated Minerals	Literature Reference/ Mineral Collection	Samples ¹
AFRICA				
Kopoasfontein, Calvinia, South Africa	Fluorapophyllite in hydrothermal breccia pipe. Colourless, euhedral crystals in vugs, 1 - 5 mm size, 2 generations on baked shale, isotropic, twinned crystals	chlorite, calcite, quartz, sulphides (pyrrhotite, pyrite, chalcopyrite)	Council for Geoscience Cavé (1999)	LC13 (G39854B) Core G39856
De Beers Mine, Kimberley, South Africa	Hydroxyapophyllite. in kimberlites. Colourless, transparent crystals, tabular on 001.		Marriner <i>et al.</i> (1990) Dunn <i>et al.</i> (1978) Smithsonian Museum Dana (1966)	GM21, AP7 NMNH#93040
Wessels Mine, Kuruman, South Africa	Hydroxyapophyllite, tabular euhedral white to cream or colourless crystals up to 6 cm in altered wall rock near a dyke.	natrolite, inesite, datolite, tobermorite, rhodonite, thomsonite	Gutzmer & Cairncross (1993)	
Phalaborwa Quarry, South Africa		mesolite	Wilson (1983)	
Empangeni Quarry, South Africa	Apophyllite in basalts	babingtonite, calcite laumontite, natrolite, prehnite, pumpellyite, quartz, stilbite	Heron (1980)	

NORTH AMERICA				
New Almaden Mines, Santa Clara County, California	Large crystals, often brown stained	mercury, bitumen, gyrolite	Murdoch and Webb (1966) Dana (1966)	
NW of Inverness, Tomales Bay, Vonsen, Marin County, California	Clear glassy crystals (1-2 mm) in fissures of quartzite	wollastonite and calcite	Murdoch and Webb (1966) Pemberton (1983)	
Pacific Electric Quarry, Brush Canyon, Los Angeles County, California	Thin tabular crystals coating basalt joints	natrolite, analcime and prehnite	Murdoch and Webb (1966) Pemberton (1983)	
Buckeye mine, Onion Valley, Kunz, Plumas County, California	Basalt cavities		Murdoch and Webb (1966)	
Crestmore Quarry, Riverside County, California	Small, clear pyramidal crystals in limestone or wollastonite	wollastonite and calcite prehnite	Bailey (1941) Murdoch and Webb (1966) Pemberton (1983)	
City Quarry, Riverside, Riverside County, California	Skeletal crystals (≤ 3 mm)		Murdoch and Webb (1966) Pemberton (1983)	
Jensen Quarry, Riverside County, California	Clear, colourless crystals in hornfels lenses.		Pemberton (1983)	
Fort Point, San Francisco, California	Minute colourless crystals	gyrolite	Murdoch and Webb (1966) Pemberton (1983)	
Point Sal, Santa Barbara County, California	Basic intrusive rocks		Murdoch and Webb (1966)	
La Honda, San Mateo, California	Small quantities		Murdoch and Webb (1966)	

Coyote Peak, Orick, Humboldt County, California	Fluorapophyllite in diatreme		Pemberton (1983)	
Rosenhahnite locality, Mendocino County, California	Apophyllite veinlets		Pemberton (1983)	
Ash Creek, Mendocino County, California	Crystalline coating on metagreywacke		Pemberton (1983)	
Table Mountain, Golden, Colorado	Fluorapophyllite, opaque, altered crystals	zeolites	Kile and Modreski (1988) Cross and Hildebrand (1882)	
East Granby quarry, Connecticut	Pseudomorphic alteration to fine-grained chlorite in shear openings in basalt trap rock	datolite, prehnite, quartz, calcite	Wolfe and Vilks (1960)	
Morehouse Parish, Smackover Formation, Louisiana	Contact metamorphic assemblage along dike, ass. with hydrocarbons	calcite, feldspar, albite, diopside, hydrogrossular, pyrite, pectolite, fluorite	Heydari <i>et al.</i> (1997), Dutrow <i>et al.</i> (1997).	
Phoenix Mine, Keweenaw County, Michigan		copper minerals	Marriner <i>et al.</i> (1990) Colville & Anderson (1971) Dana (1966)	GM4
Snake Hill and Bergen Hill, Bergen, Hudson County, New Jersey	In trap rock	various zeolites	Marriner <i>et al.</i> (1990) Dana (1966)	GM3, GM7, AP8,
Great Notch 3, Passaic County, New Jersey	Hydroxyapophyllite, chalky white, slightly decomposed, hydrothermally altered		Marriner <i>et al.</i> (1990) Dunn <i>et al.</i> (1978)	GM5

Paterson and West Paterson, Passaic County, New Jersey	In trap rock	various zeolites	Stanford University Dana (1966)	#29820 = LC7
Ore Knob mine, Jefferson, Ashe County, North Carolina	Hydroxyapophyllite type locality, 1 cm coating of multiply-twinned white crystals	pyrrhotite and chalcopyrite ore	Dunn <i>et al.</i> (1978) Smithsonian Museum	MNNH#115268
Hyc0 Lake, Person County, North Carolina	Zoned crystals		Furbish (1976)	
Sweet Home Mines, Linn County, Oregon			Stanford University	#29960 = LC10
Polk County, Oregon	Green apophyllite	zeolites, quartz	Gladwell (1992)	
French Creek Mines, Chester County, Pennsylvania	Colourless, euhedral crystals		University of Colorado Denver Museum Colorado School of Mines Dana (1966)	LC3 DMNH# 12007 7796
Bingham Canyon, Utah		thaumasite, thomsonite, gyrolite, okenite, stilbite, tobermorite	Stephens and Bray (1973)	
Bull Run, Silver Bow County, Virginia			Denver Museum	

Centerville, Fairfax County, Virginia	Large crystals (up to 10 mm) on light green prehnite Occur in basalt cavities	prehnite, thaumasite	Colorado School of Mines Denver Museum Marriner <i>et al.</i> (1990) Prince (1971) Medici (1972)	TM 11116 = LC2 DMNH #7386 = LC4 GM6
Murdochville, Quebec, Canada	Opaque, white crystals		Colorado School of Mines	83.256 = LC1
Gaspé Mine, Quebec, Canada		copper minerals	Marriner <i>et al.</i> (1990)	GM2
Mont St. Hilaire, Quebec, Canada	Euhedral crystals - used to refine crystal structure		Chao (1971)	
Karatut, Disko Island, Godhaven Distr. W Greenland			Marriner <i>et al.</i> (1990)	GM25
Blomindon, Kings County, Novo Scotia	In basalts	zeolites, quartz, calcite	Marriner <i>et al.</i> (1990)	GM1

SOUTH AND CENTRAL AMERICA				
Guanajuato, Mexico	Colourless or pink crystals on amethyst, NH ₄ rich Hydroxy- have up to 1% Na ₂ O	quartz	Colorado School of Mines Stanford University Marriner <i>et al.</i> (1990) Dunn <i>et al.</i> (1978) Dana (1966)	435:1:3 = LC14, TM 9805 #4276 = LC6 GM13, GM11
Refugio Mine, Lahuz, Guanajuato State, Mexico			Marriner <i>et al.</i> (1990)	GM12
El Fenomena Mine, Baja-California, Mexico		prehnite	Sinkankas (1963)	
Juchipila, Zacatecas, Mexico	In basalt vesicles	heulandite, clinoptilolite, harmotome, laumontite	Merrick (1995)	
Herval and Laguna, Santa Catrina, Brazil	In basalt vesicles	heulandite, stilbite, chabazite, mordenite	Marriner <i>et al.</i> (1990) Mason and Greenberg (1954)	GM10
ASIA				
Poona, Maharastra District, India	Amygdules in Deccan trap lavas. Colourless, some v. large crystals.	zeolites, stilbnite	Wards Earth Science Denver Museum Rossman (1974) Ståhl (1993) Pande & Vadrabade (1990)	49-5856 = LC15 DMNH#13046 = LC9, DMNH#15147 = LC12,

Khadrakvasla, Poona, India	Green fluorapophyllite		Stanford Univeristy	#31222 = LC5
Jalgaon, India	Large (> 5 cm), colourless, gem quality tetragonal crystal points.	pink stilbite intergrowths	Kristall Ocean Export Pvt. Ltd, India	LC8
Nassik, India	Fluorapophyllite		Ståhl <i>et al.</i> (1987)	
Western Ghats, India (Thul Ghat, Bhore Ghat)			Dana (1966)	
Syhadree Mts., Bombay, India			Marriner <i>et al.</i> (1990) Dana (1966)	GM16, AP6, GM15
Parvati Hills, Bombay, India	Hydroxyapophyllite		Dunn <i>et al.</i> (1978) Belsare (1969)	BM # 1977,473
Tubaoshan, Liyang County, Jiangsu, China		phyllosilicates, talc and serpentine	Yaun <i>et al.</i> (1994)	
Maze, Niigata Prefecture, Japan	Measured $\delta^{18}\text{O}$		Noto <i>et al.</i> (1990)	
Sampo Mine, Okayama, Japan	Natroapophyllite in skarns. Contact metasomatic zone	zeophyllite, cuspidine, fluorapophyllite, calcite	Matsueda <i>et al.</i> (1981)	SA1 - 4
EUROPE AND RUSSIA				
Marienberg, Aussig, Bohemia, Czech Republic			Marriner <i>et al.</i> (1990) Dana (1966)	GM29
Ransko Massif, Bohemia, Czech Republic	Fissure mineral in basic massif	analcime, clinozoisite, grossular, gyrolite	Nemec (1982)	

Frumm Bach, Seiser Alpe, Rozen, Tyrrol, Austria			Marriner <i>et al.</i> (1990) Stanford University	GM20 #1074 = LC11
Mont da Sores, Seiser Alpe, Tretino, Italy			Dana (1966)	
San Venanzo and Cupaella, Umbria, Italy	In cavities in kalsilitite lava flows	goetzenite, khibinskite	Cundari and Ferguson (1994)	
Samson Mine, Andeasberg, Harz Mts., Germany	Pink coloured	Ag veins	Marriner <i>et al.</i> (1990) Dana (1966)	GM17, GM19
Niederrothweil, Kaiserstuhl, Baden, Germany			Marriner <i>et al.</i> (1990)	GM18
Korsnaes Lead Mine, Svartoren, Vaasa Prov. Finland	Honey yellow with complex twinning		Marriner <i>et al.</i> (1990) Sahama (1965)	GM23
Viipuri, Finland	In rapakivi granites		Vorma (1961)	
Gikenmine, Sulitjela, Nordland, Norway			Marriner <i>et al.</i> (1990)	GM24
Boliden deposit, Sweden			Ödman (1941)	
Berufjord, Iceland			Dana (1966)	
Faeroe Islands, Iceland	In hydrothermally altered basalt	gyrolite	Geptner and Petrova (1988)	
Hesto, Faeroe Islands			Marriner <i>et al.</i> (1990) Dana (1966)	GM26
Eide, Ostera, Faeroe Islands			Marriner <i>et al.</i> (1990)	GM27

Storr Mount, Isle of Skye, Inverness, Scotland			Marriner <i>et al.</i> (1990) Dana (1966)	GM30
Traprain Law, Haddingtonshire, Scotland	In a geode in phonolite	analcime, calcite, powellite	Bathey and Moss (1962)	
Collinward, near Belfast, Co. Antrim, Ireland			Dana (1966)	
Standzha- Planina, Bulgaria	In skarns, non-ore association		Kostov (1962)	
Hackman Ravine & Mt. Yukspor Khibiny Tundras, Kola Peninsula, Russia	In natrolite veins in aegerine-alkali amphibole-nepheline-syenite	lamprophyllite, arfvedsonite, microcline, apatite, eucolite, fluorite, calcite, catapleiite and opal.	Barabanov (1957)	
Transbaikalia, USSR	Alteration product of charoite		Lazebnik <i>et al.</i> (1977).	
Tyrny-Auz deposit, USSR	Late stage mineralisation, hydrothermal-metasomatic formations in skarnised marble	datolite & xonotlite with andradite, fluorite, calcite, sulphides, tellurides, native Bi, wollastonite	Kulikov <i>et al.</i> (1981)	
Uzbekistan, ore deposits	Skarns and veinlets and vugs in volcanic rocks K ₂ O content ranges from 0.92 - 4.36 wt %	xonotlite, thaumasite, stevensite, zeolites, calcite, anhydrite	Badalov and Protod'yakanova (1976)	

Kok-kai Ridge & Gyaurbakh Canyon, Karadag, Crimea	Pink β -apophyllite, Na-rich (1.17% Na ₂ O) fluorapophyllite (1.78% F)	quartz, zeolites, celadonite, chalcedony, calcite, mesolite, natrolite, datolite	Suprychev (1968).	
Korsun'Novomirgorodsk pluton, Ukraine	In granite pegmatites		Nazarenko (1963) Litvin <i>et al.</i> (1964)	
Northern Kazakhstan	In leucocratic quartz gabbro	quartz, prehnite	Spiridonov (1964)	
Enisei region, Siberian Platform	Contains liquid inclusions	zeolites, chalcedony, quartz, Iceland spar	Andrusenko and Vasil'eva (1968)	
Erachimsk syncline, NW Siberian Platform	Occurs in pillow lavas	zeolites, hydrated ca silicates, analcime, barite, aragonite, saponite, Fe, Pb & Zn sulphides	Anastasenko (1966)	
AUSTRALIA AND NEW ZEALAND				
Tertiary basalts, Tasmania	Amygdaloidal	gonnardite, tacharanite, tobermorite	Sutherland (1965)	
Holyoake Valley, Nelson, New Zealand	Late stage mineral in contact aureole of granodiorite	vesuviante, prehnite	Watters (1995)	

NOTE: 1. Sample numbers in *italics* are those for which chemical analyses are available,
 from this study: *LC1-15*;
 from Marriner *et al.* (1990): *GM1 - 31* and *AP1 - 8*;
 from Dunn *et al.* (1978): *NMNH#93040*, *MNNH#115268* and *BM # 1977,473* (hydroxyapophyllites).
 or from Matsueda *et al.* (1981): *SA1 - 4*

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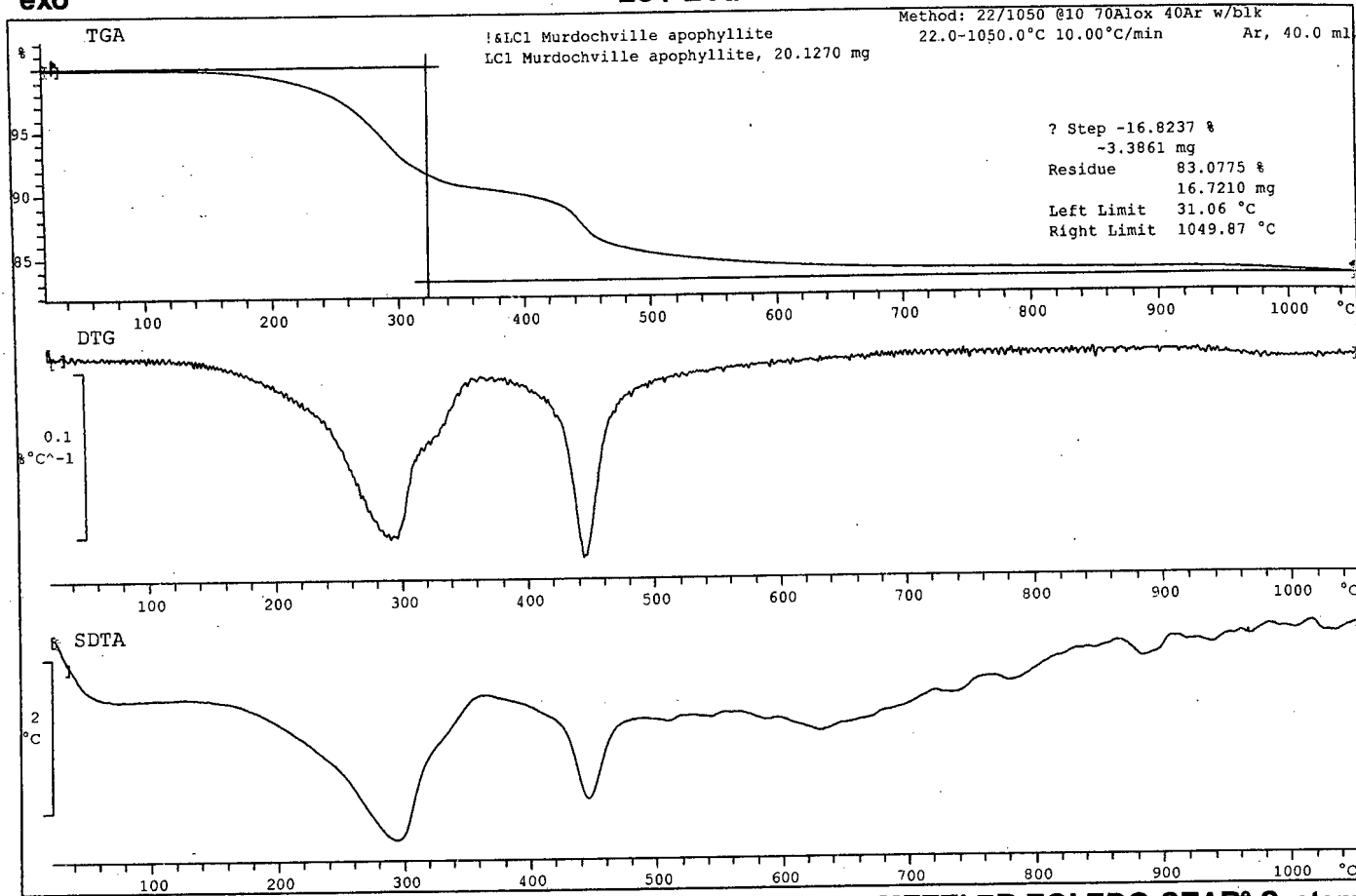
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APPENDIX G
COPIES OF THERMAL SPECTRA OF APOPHYLLITE SAMPLES
FROM USGS THERMOCHEMISTRY LABORATORY

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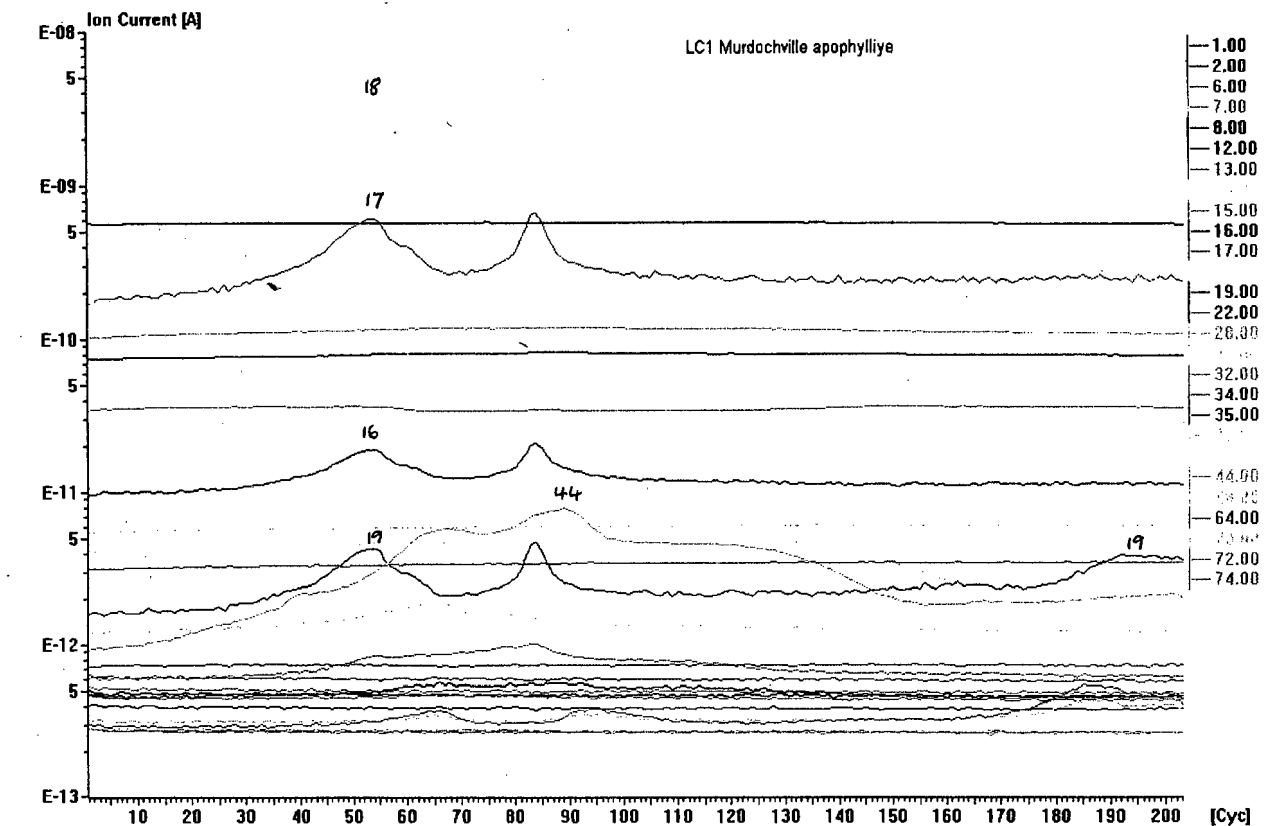
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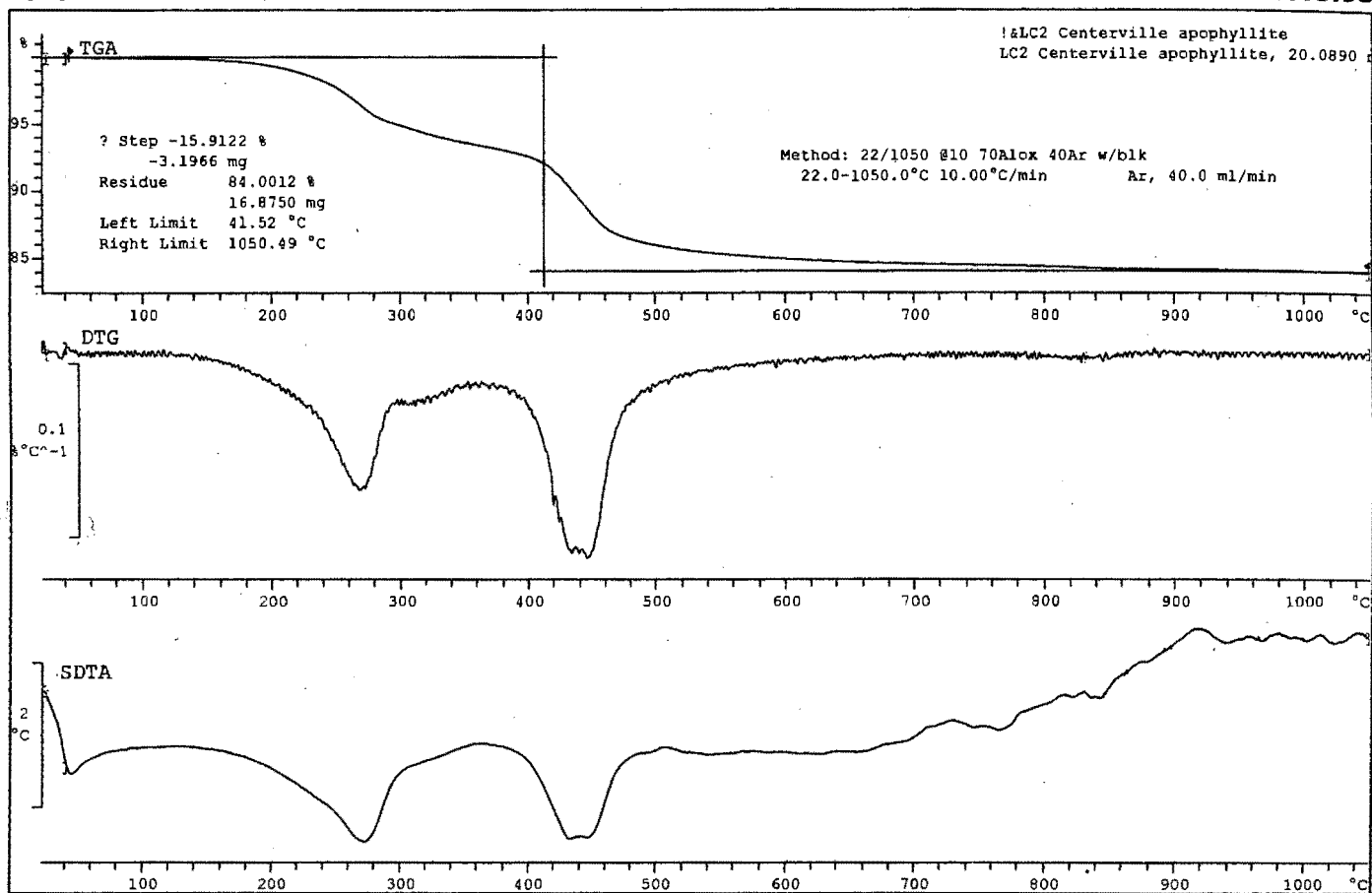
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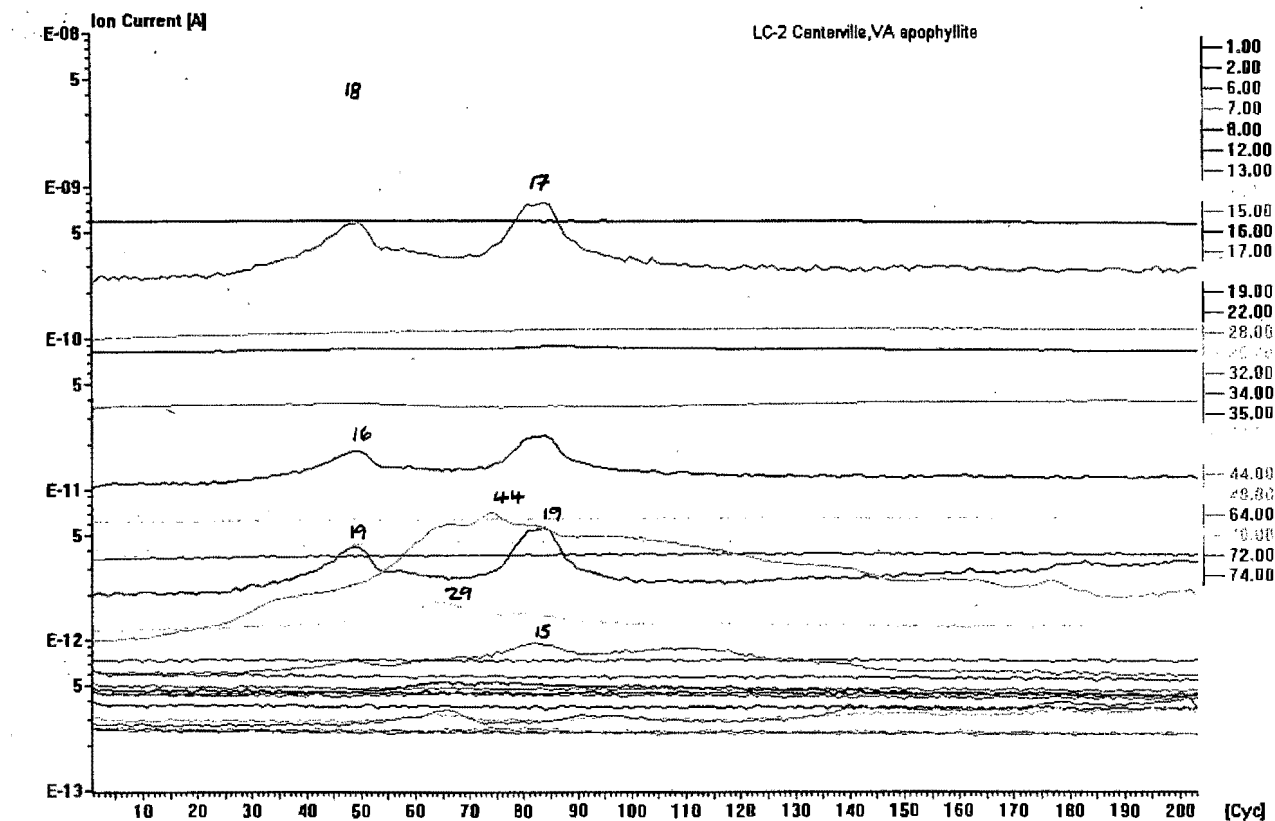
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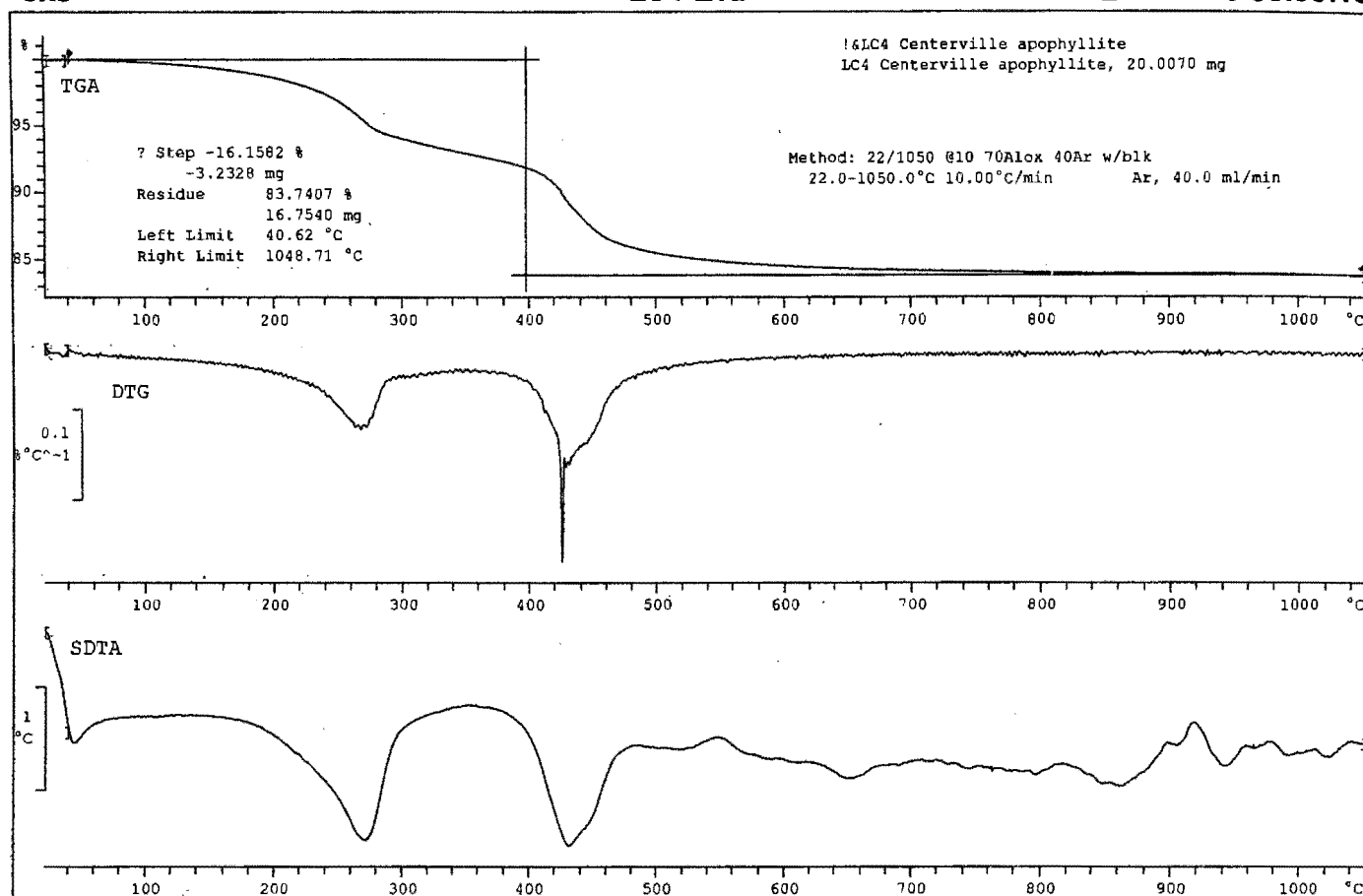
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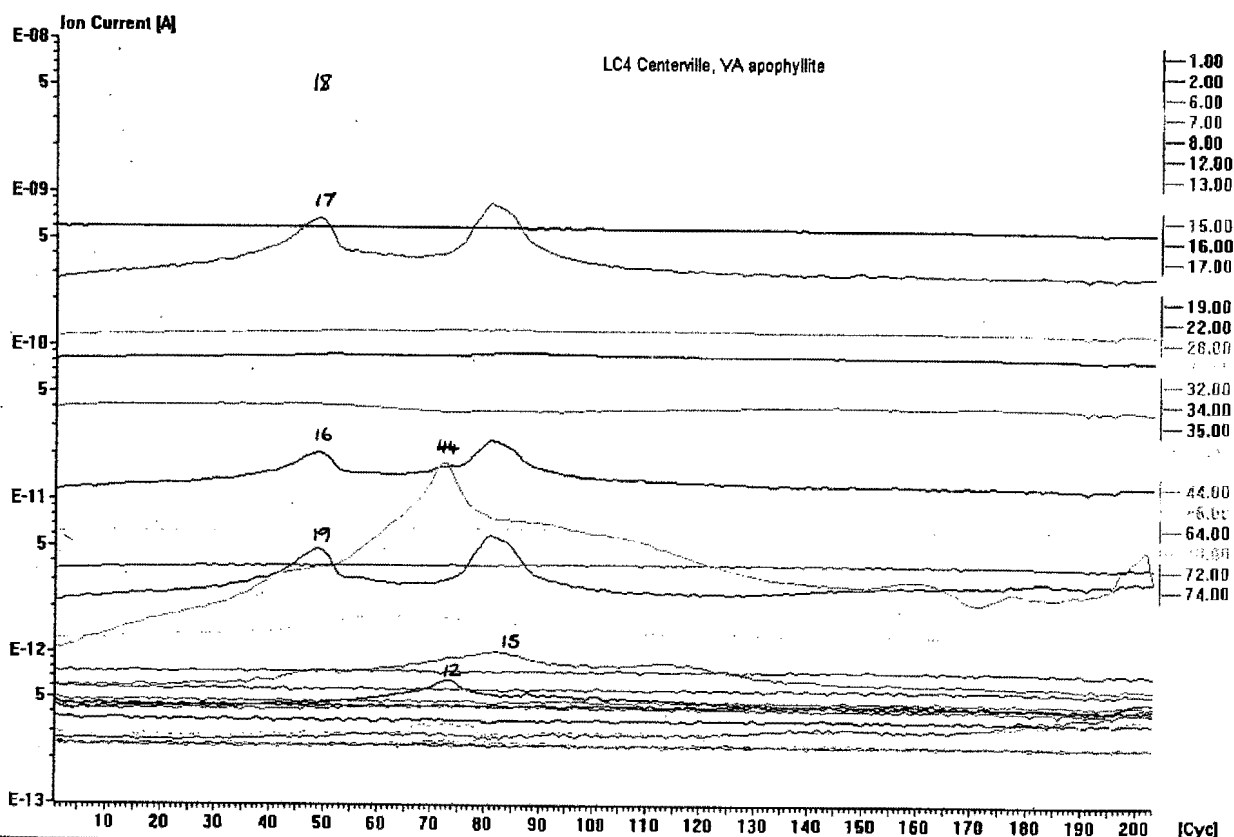
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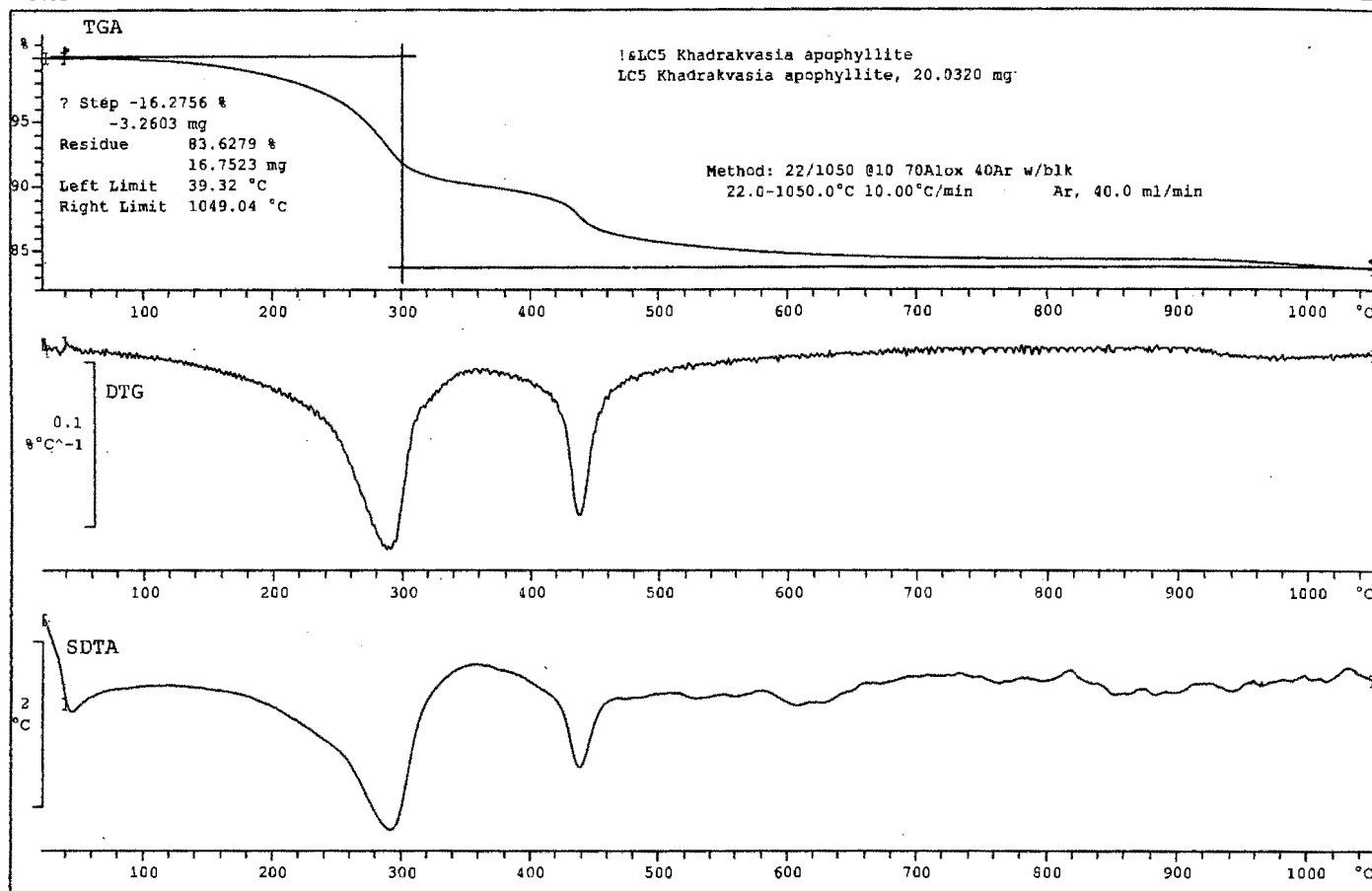
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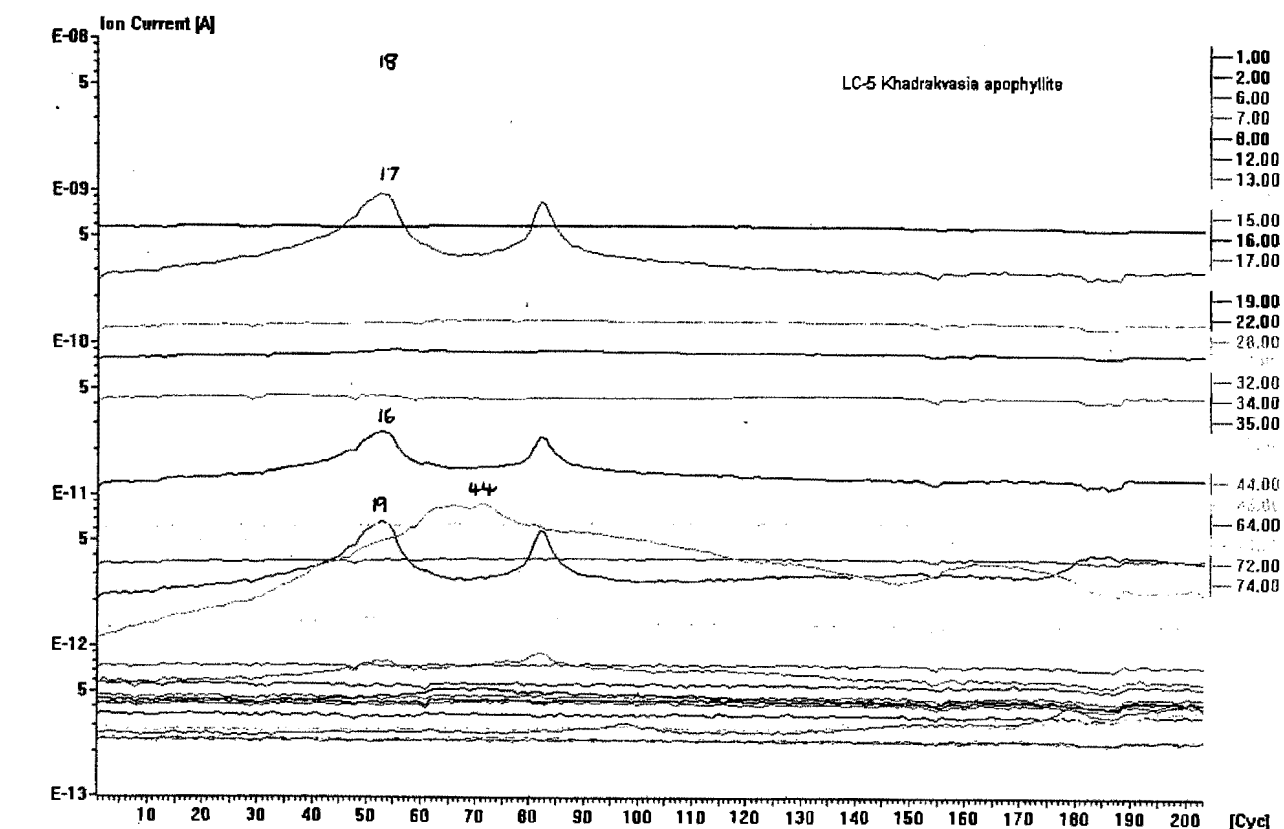
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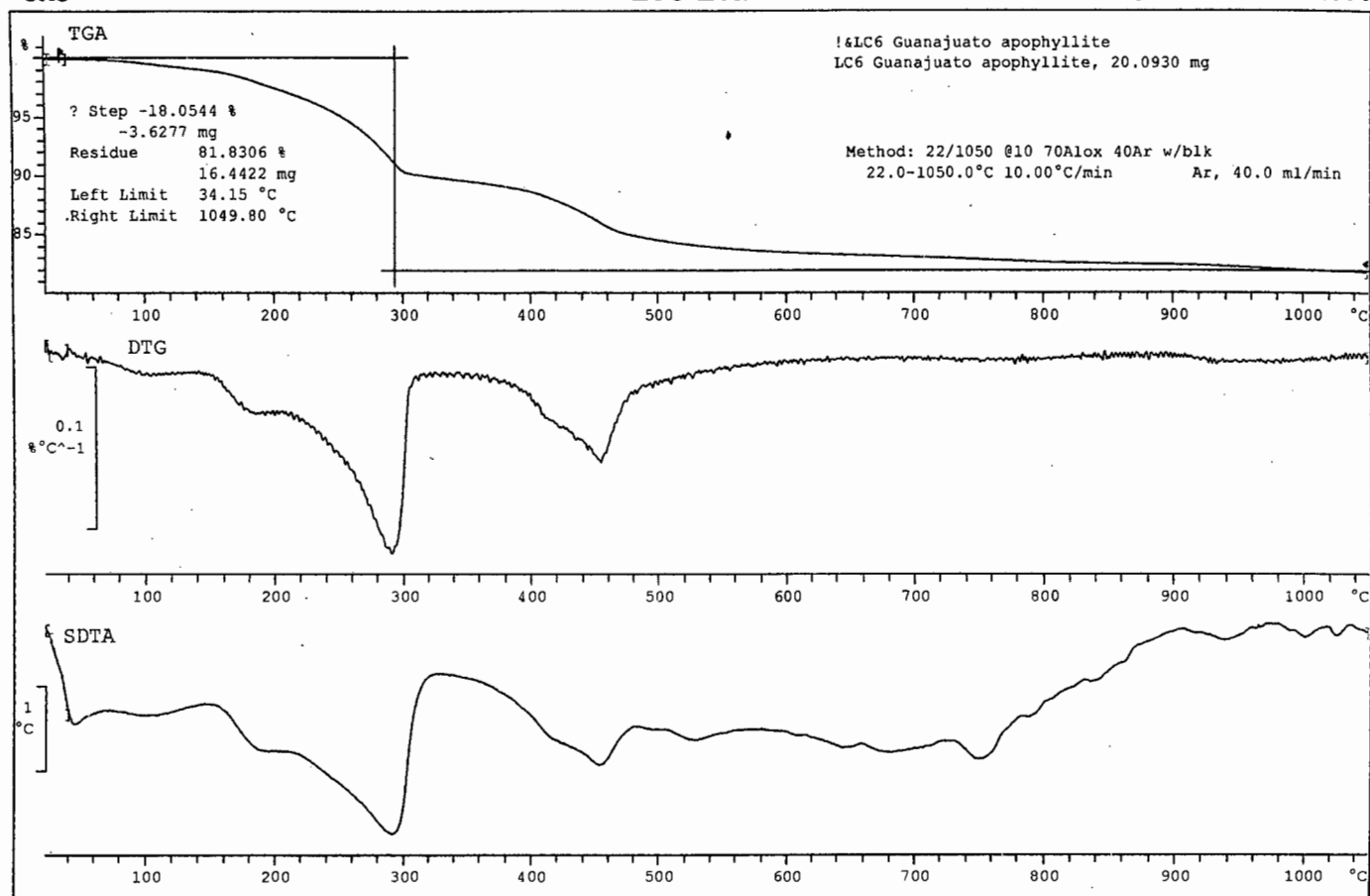
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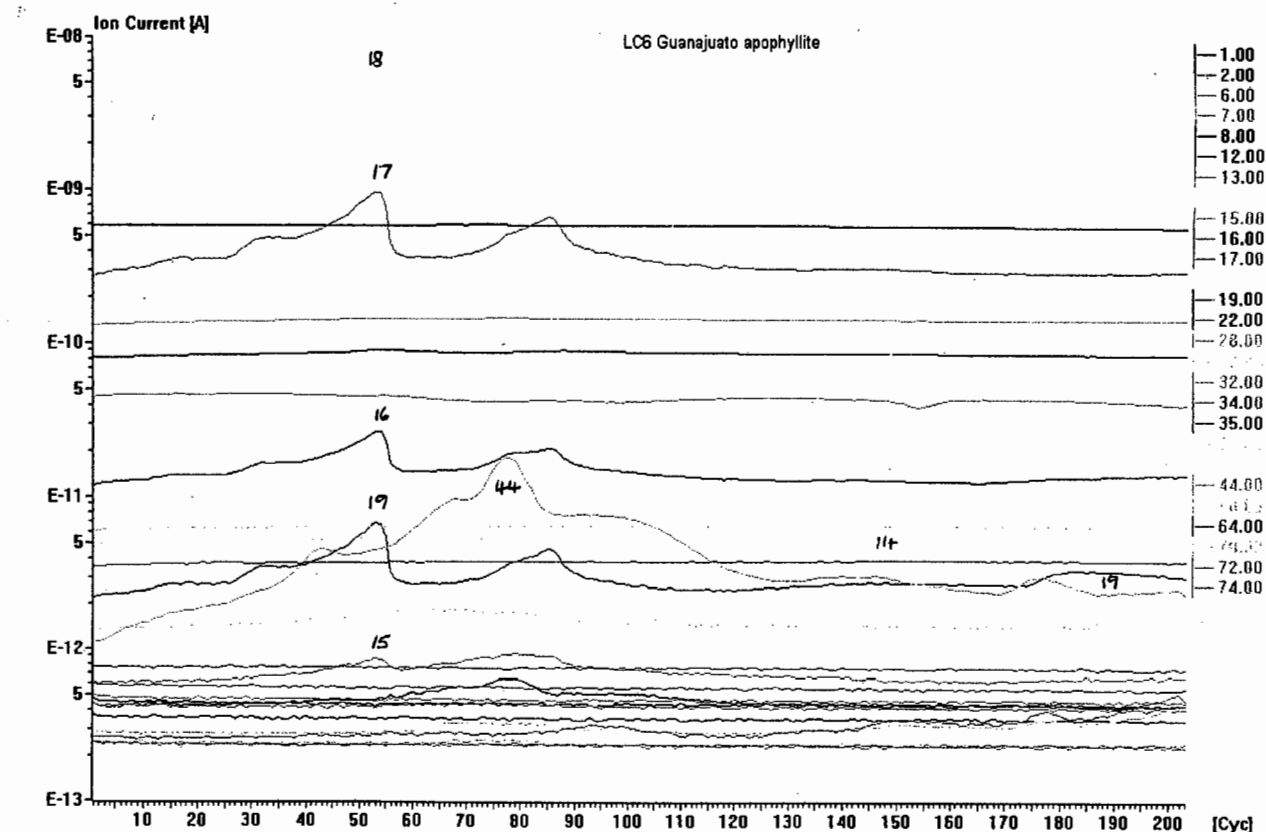
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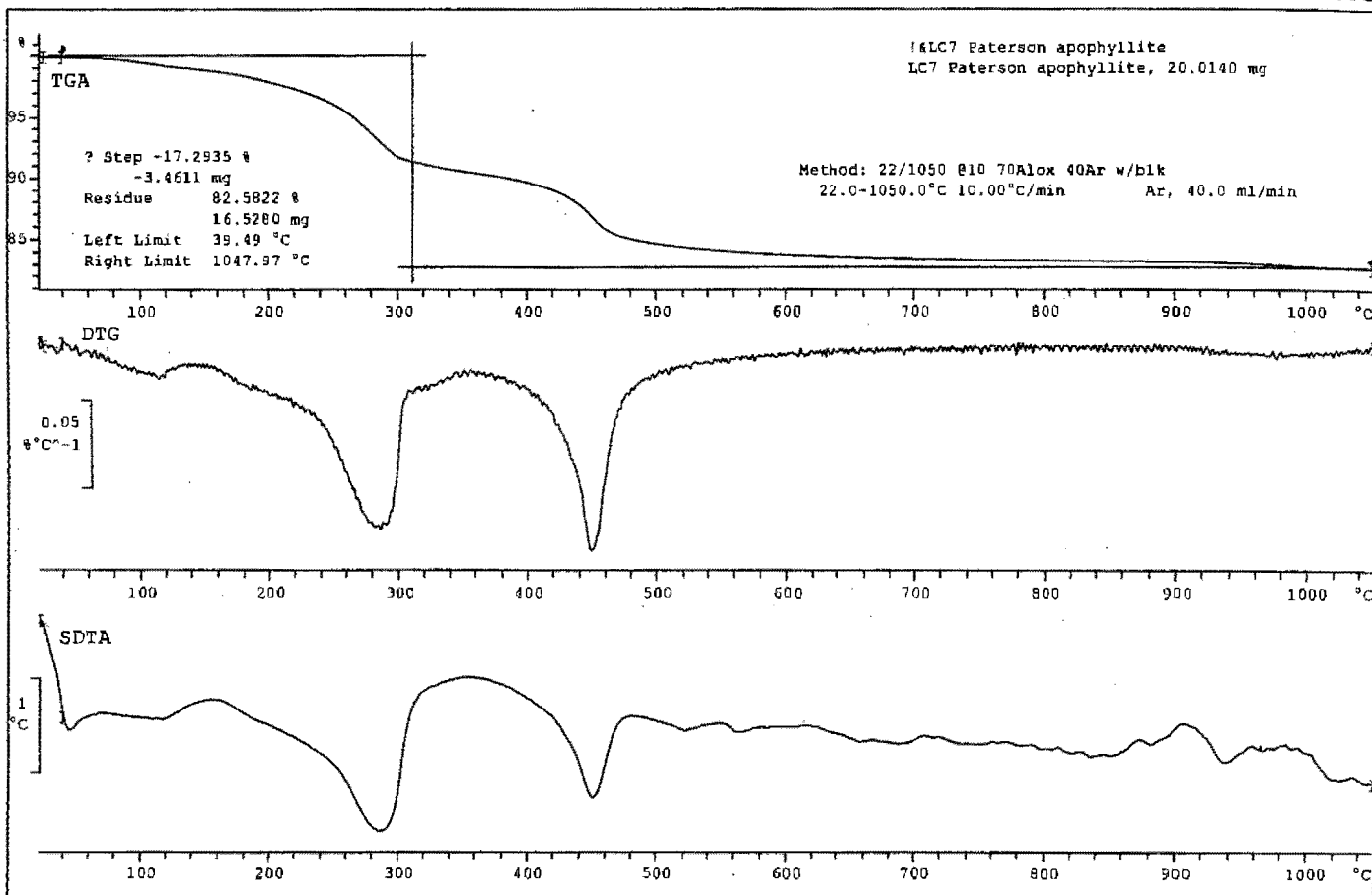
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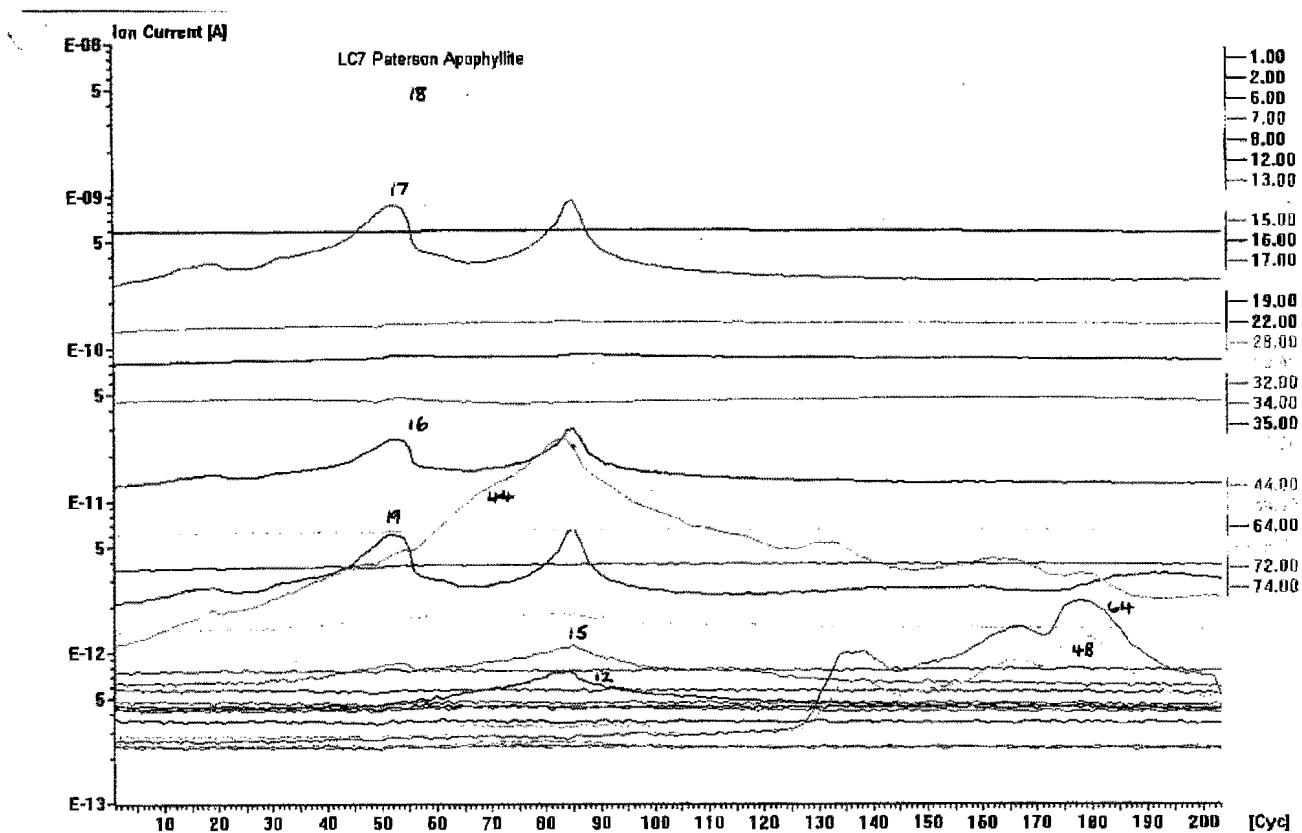
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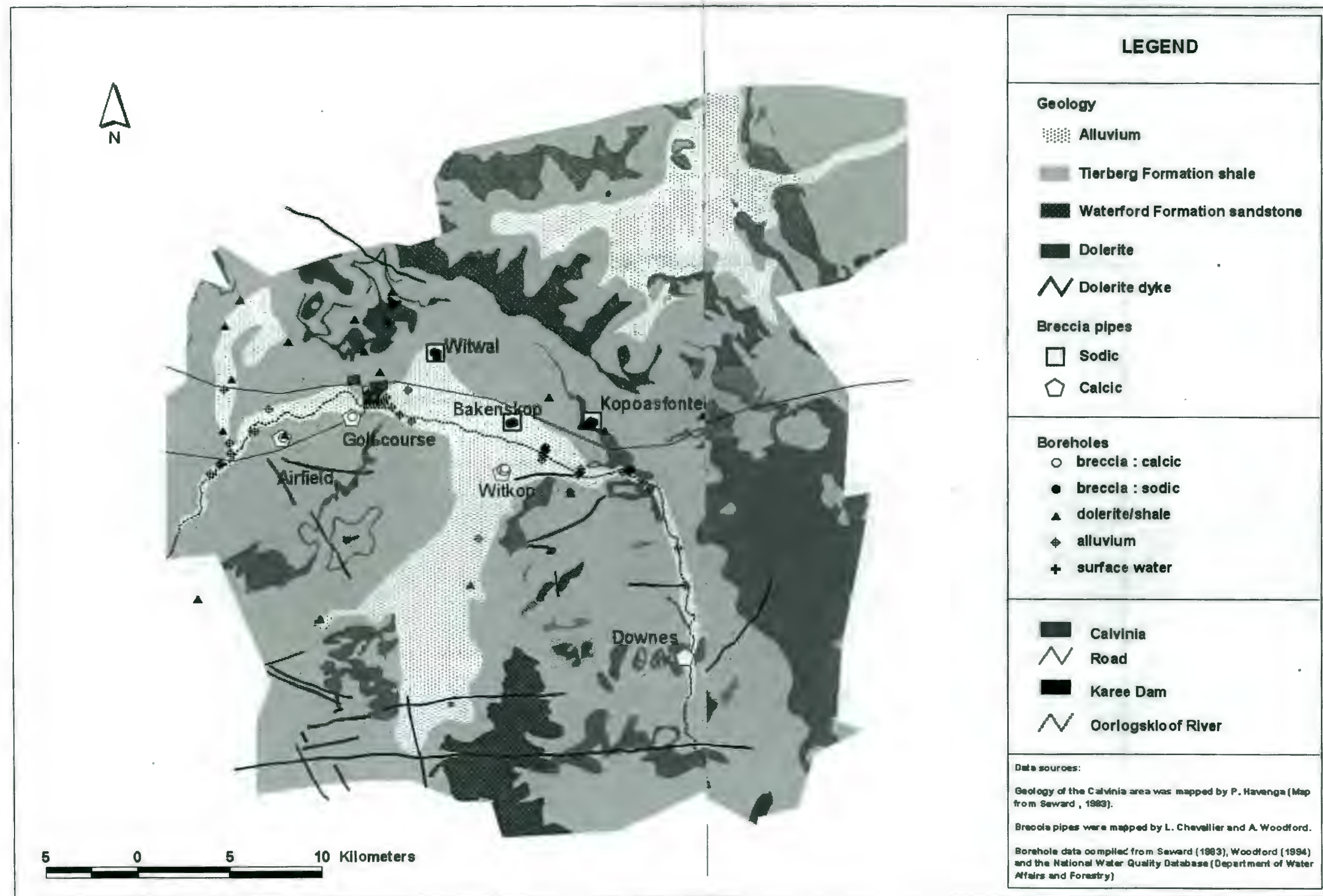
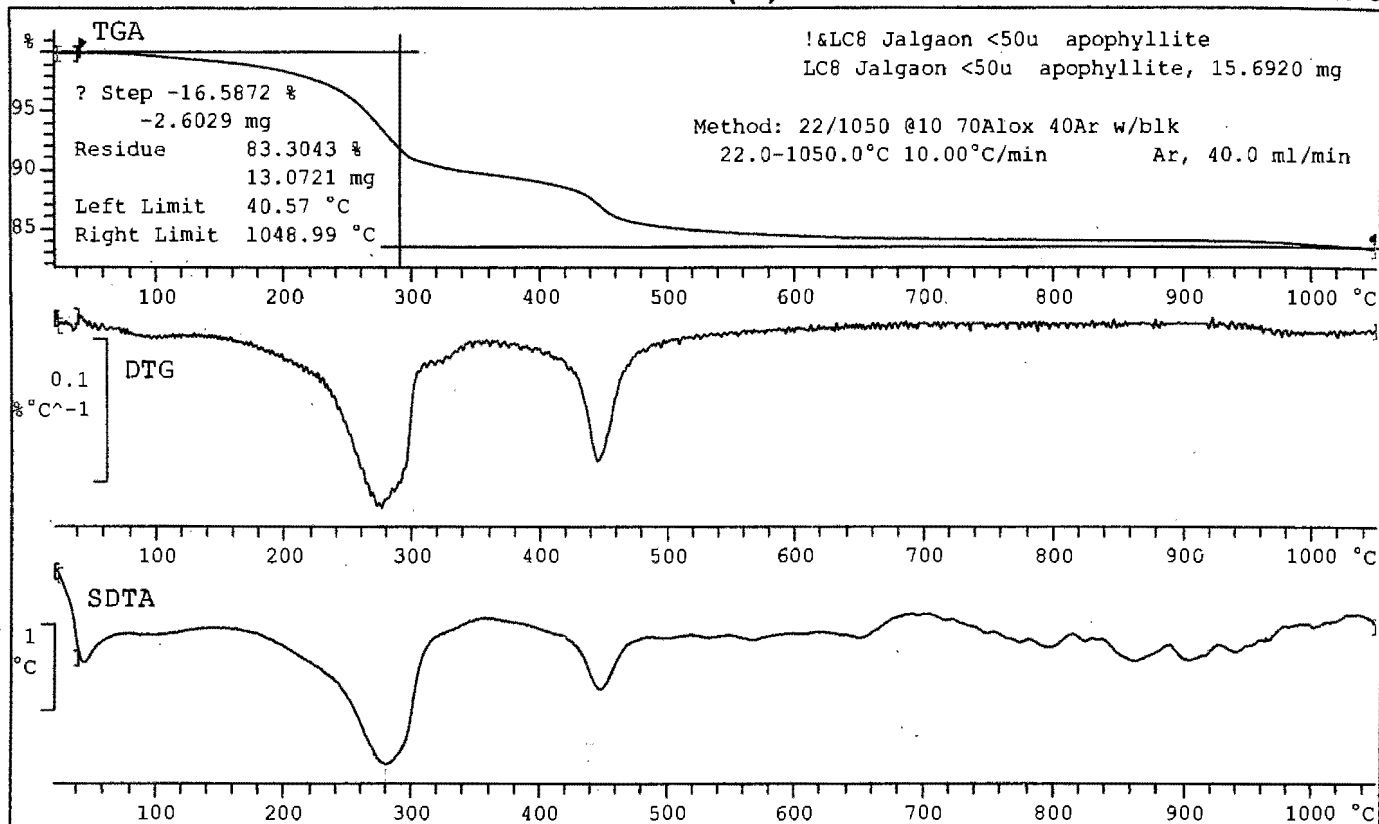


Figure 3.1. Detailed geological map of the Calvinia area showing location of breccia pipes and the position of boreholes used in geochemical characterisation of groundwater.

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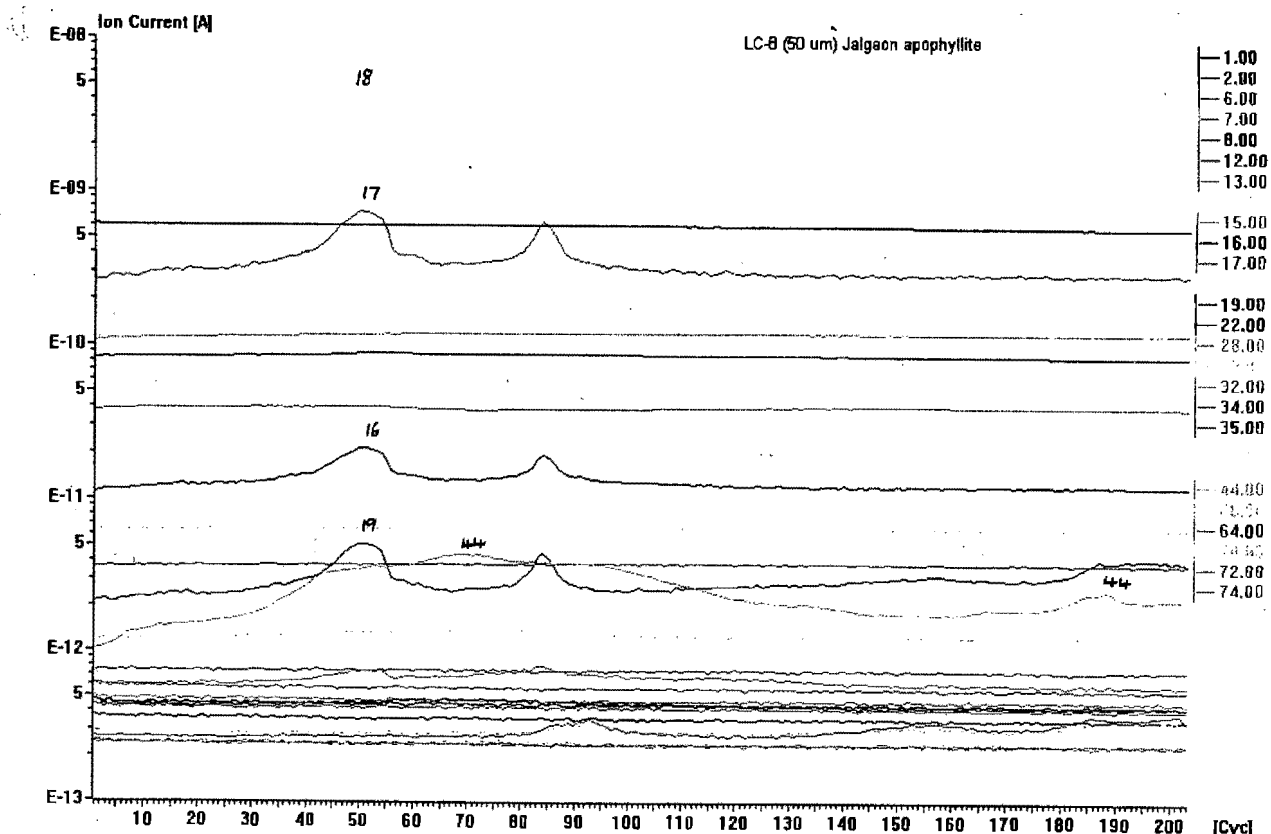
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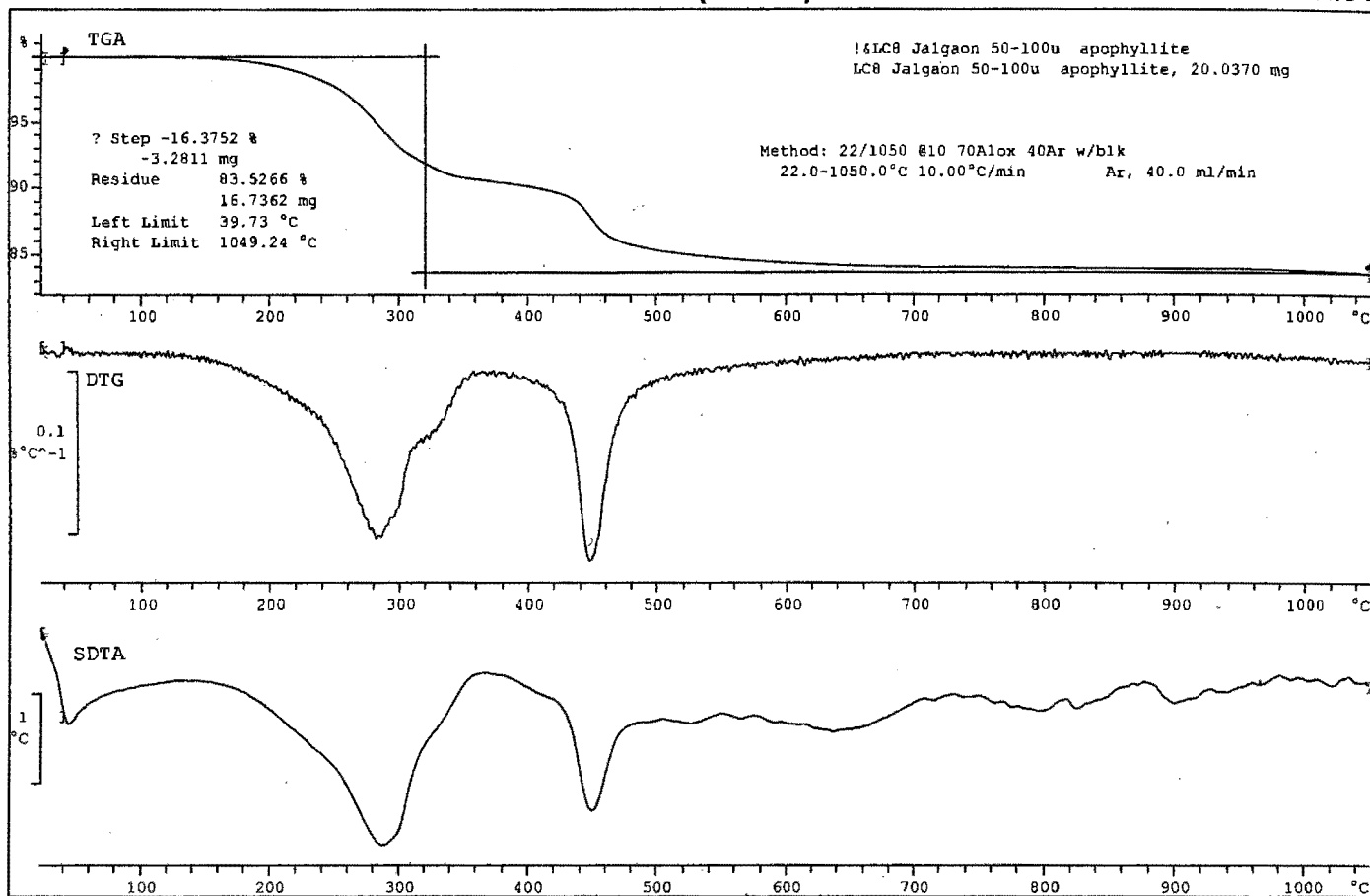
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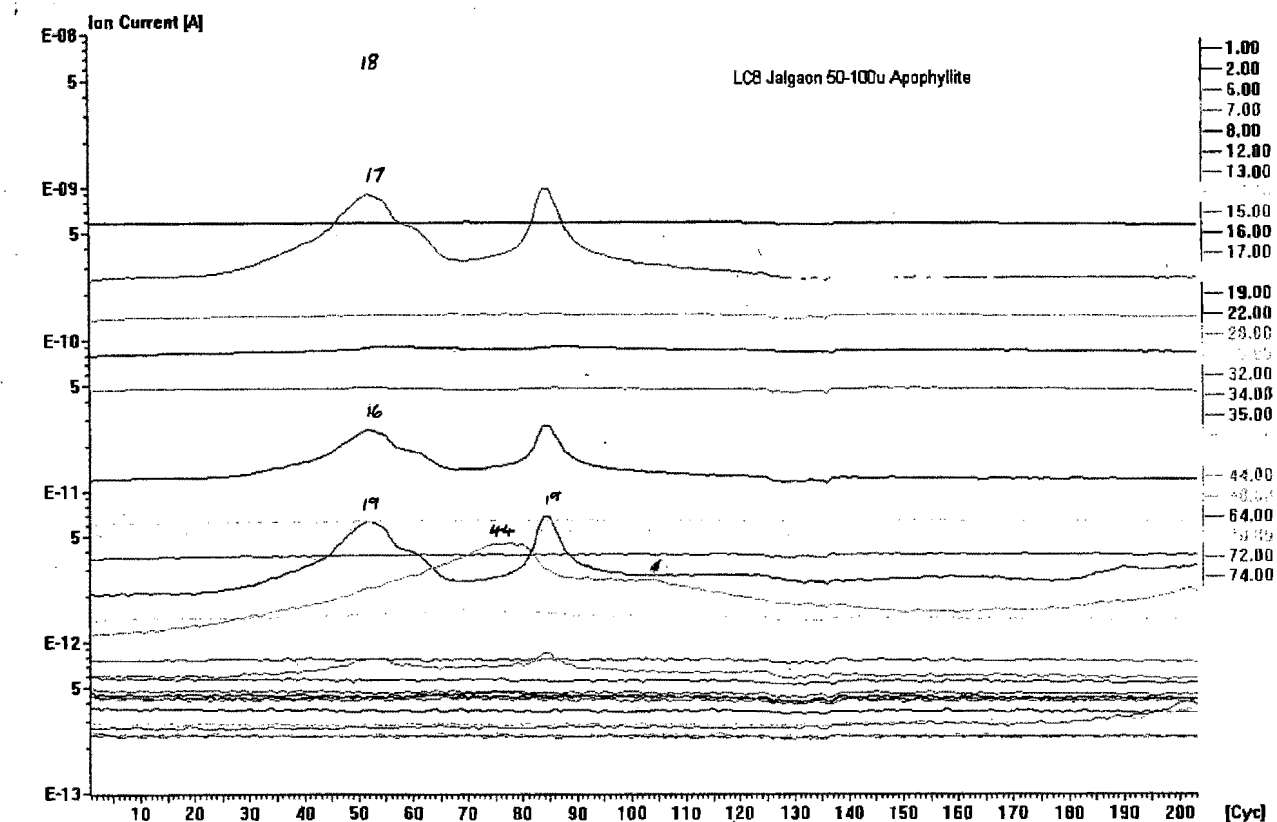
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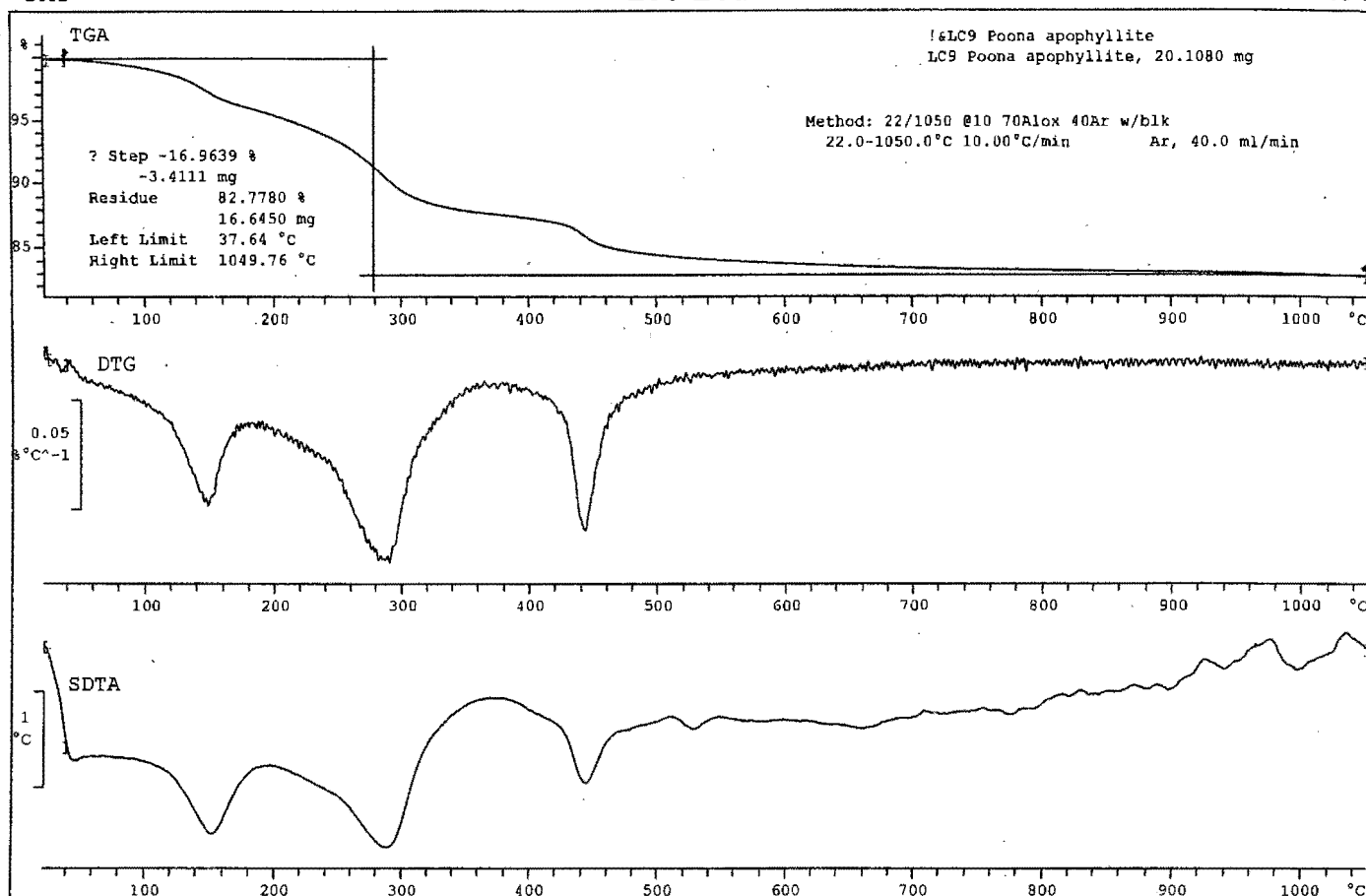
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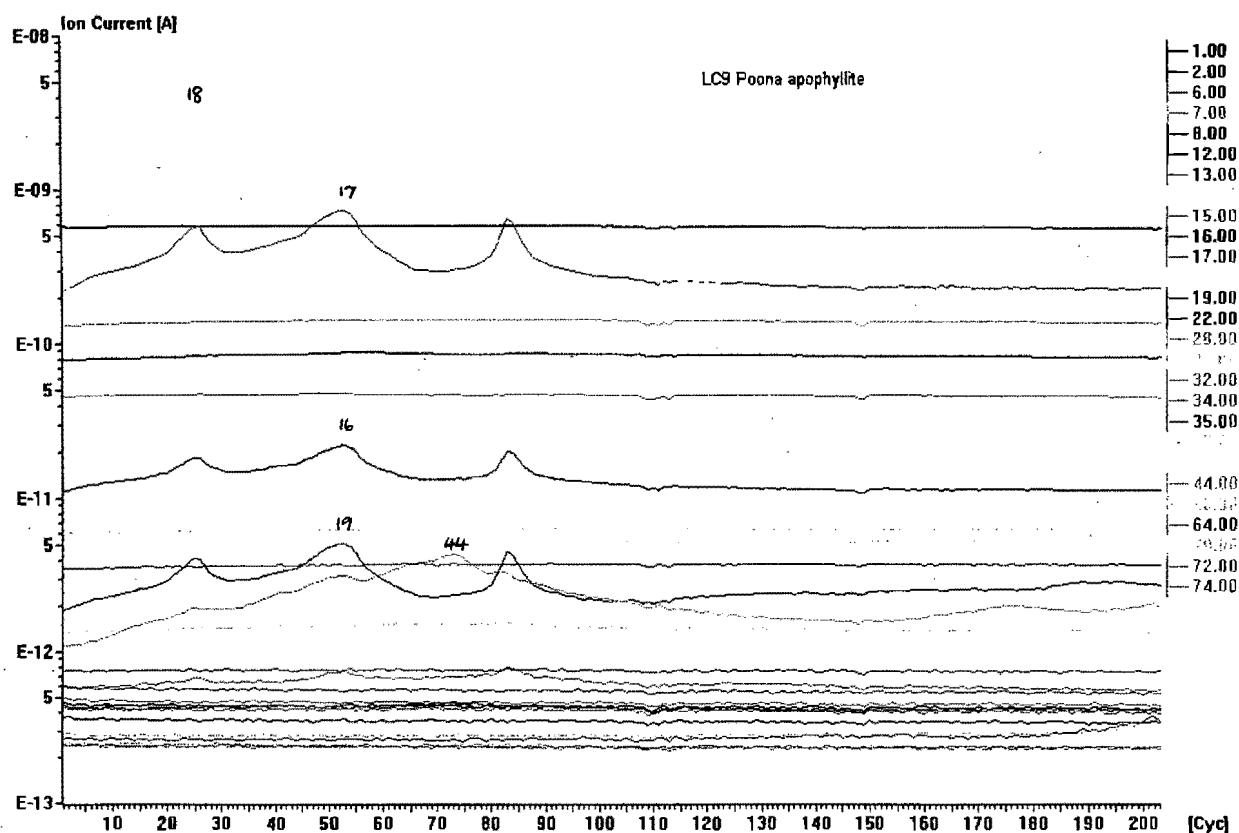
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METTLER TOLEDO STAR^e System

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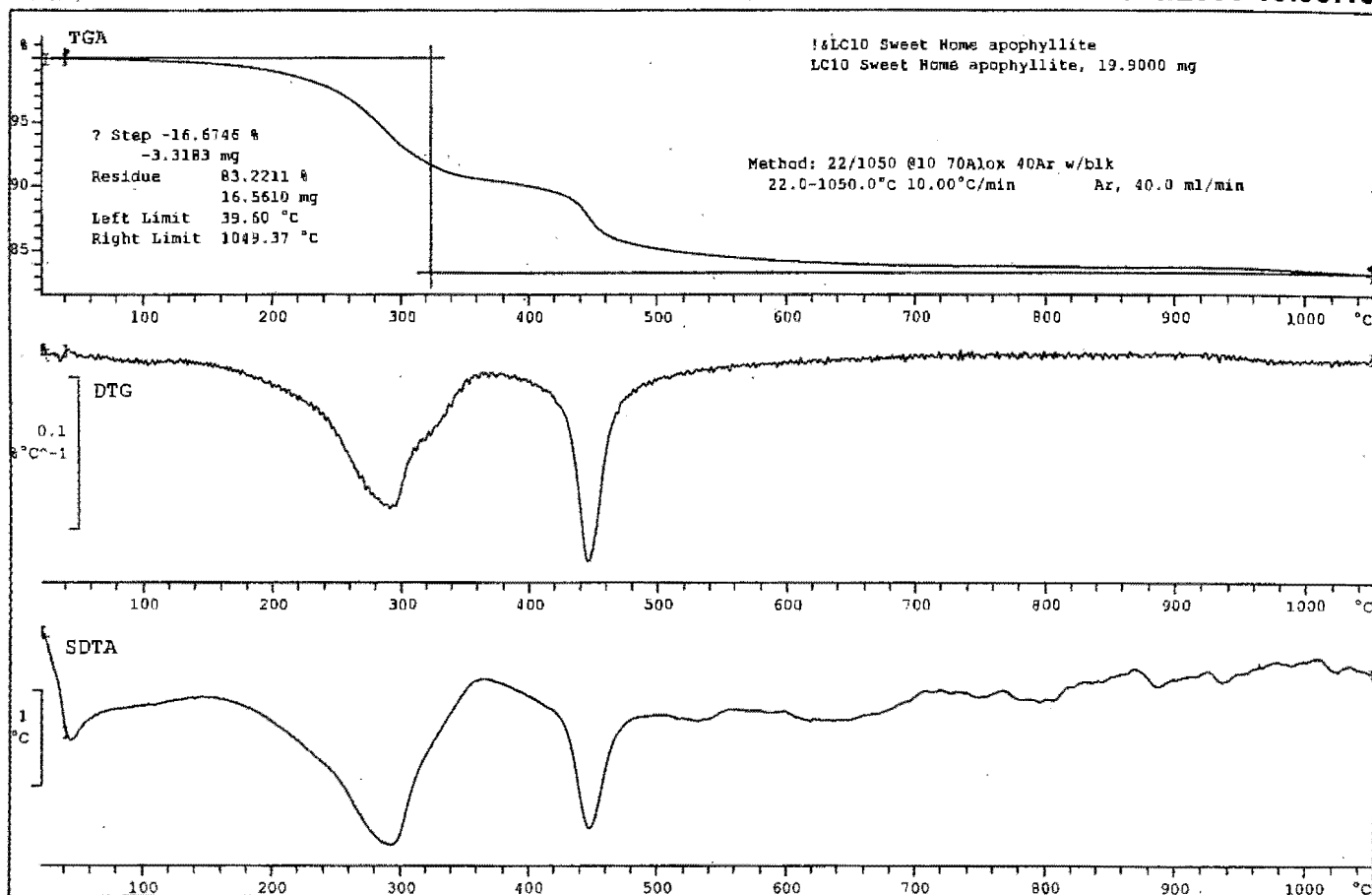
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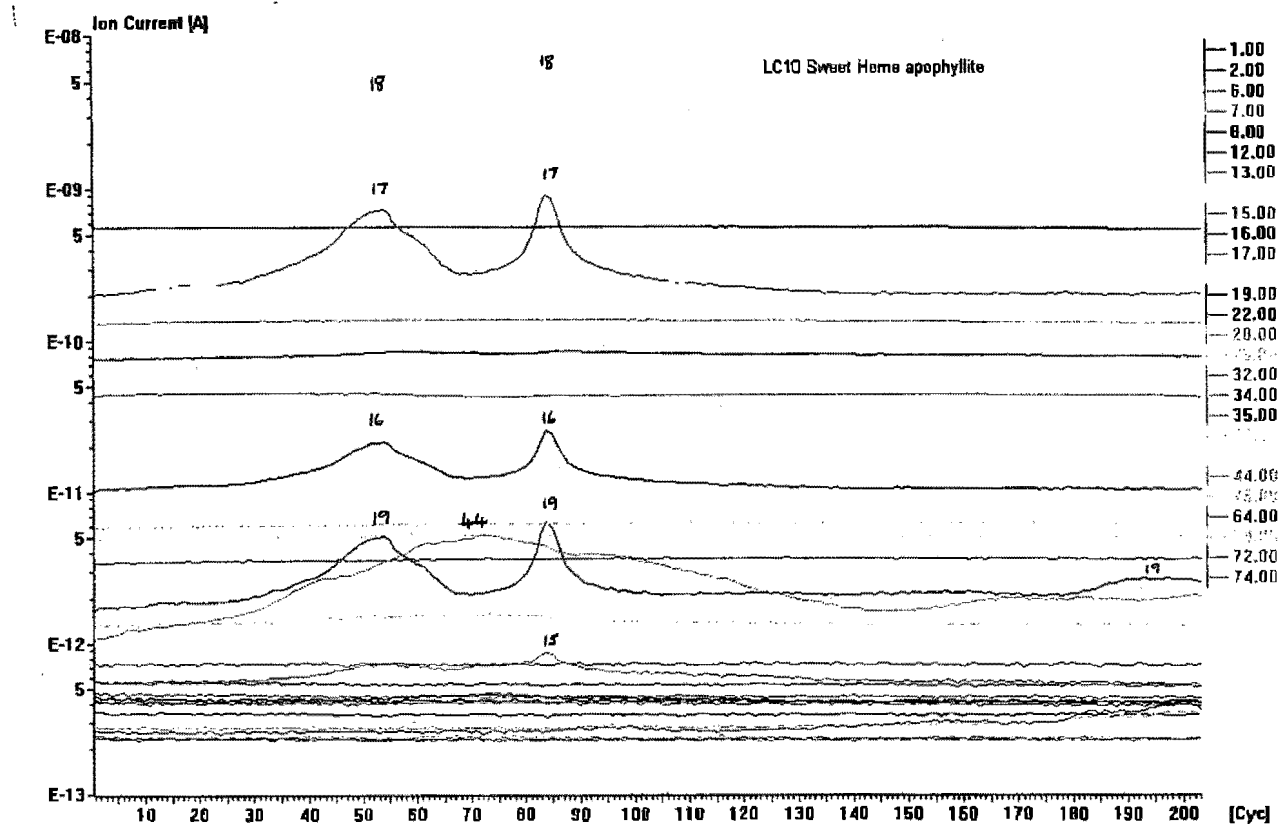
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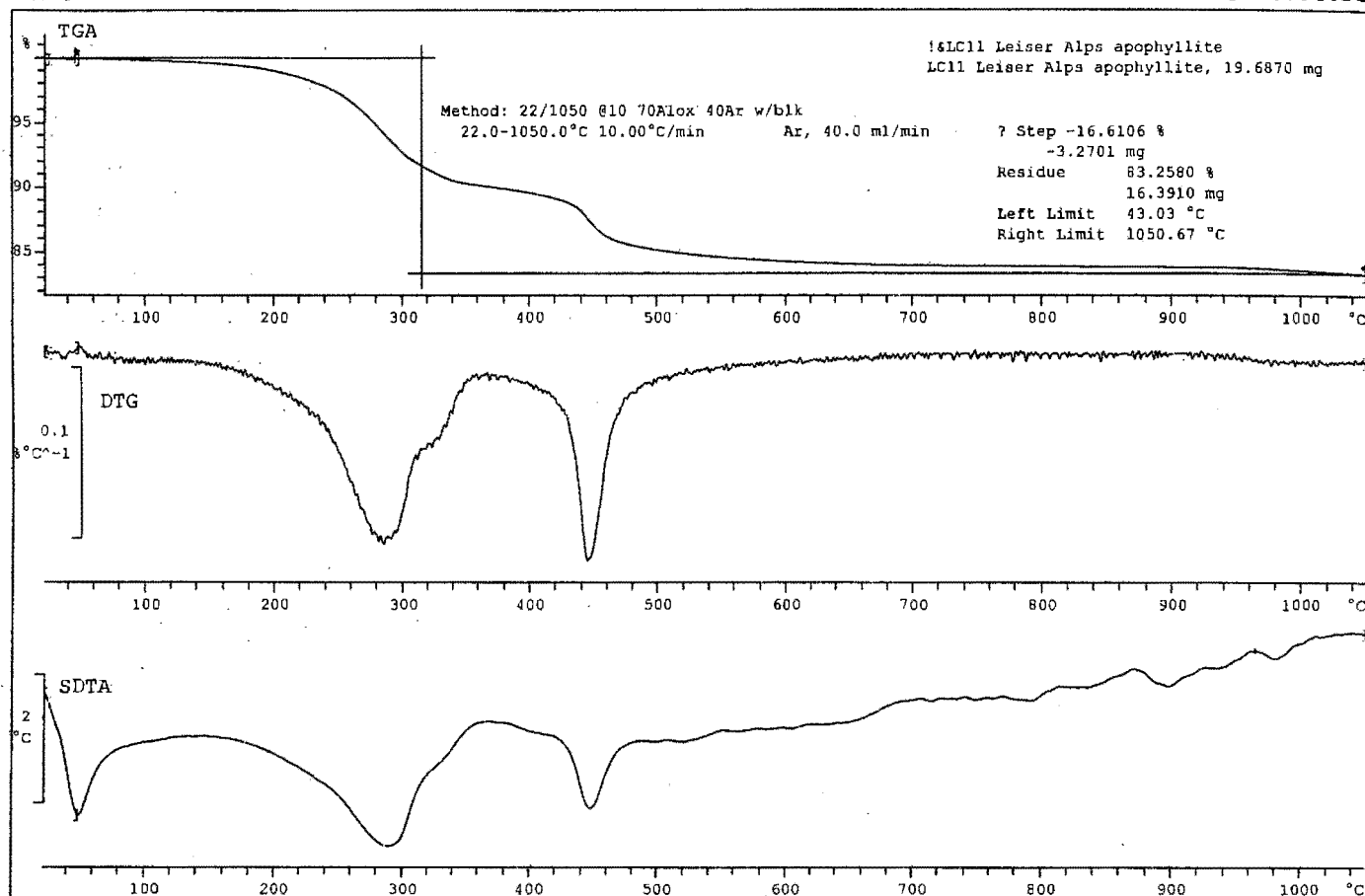
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METTLER TOLEDO STAR^e System

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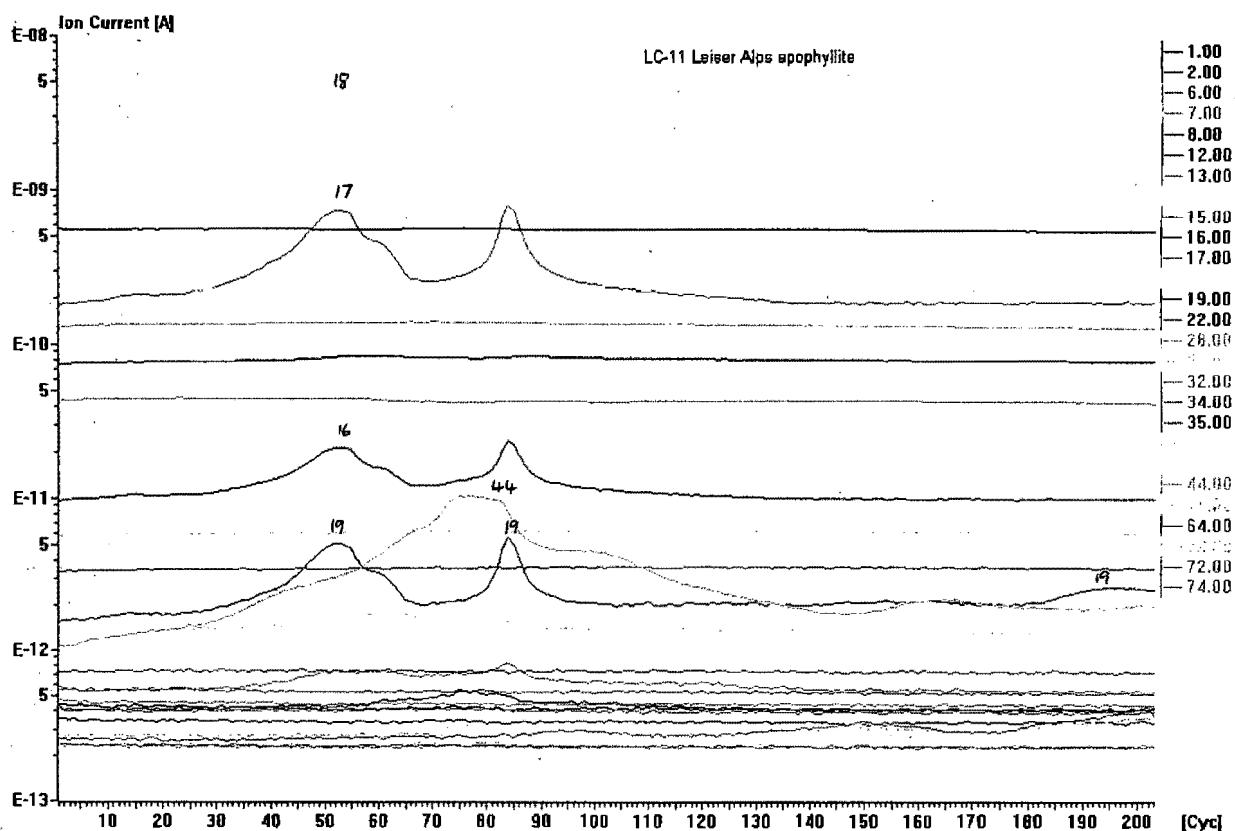
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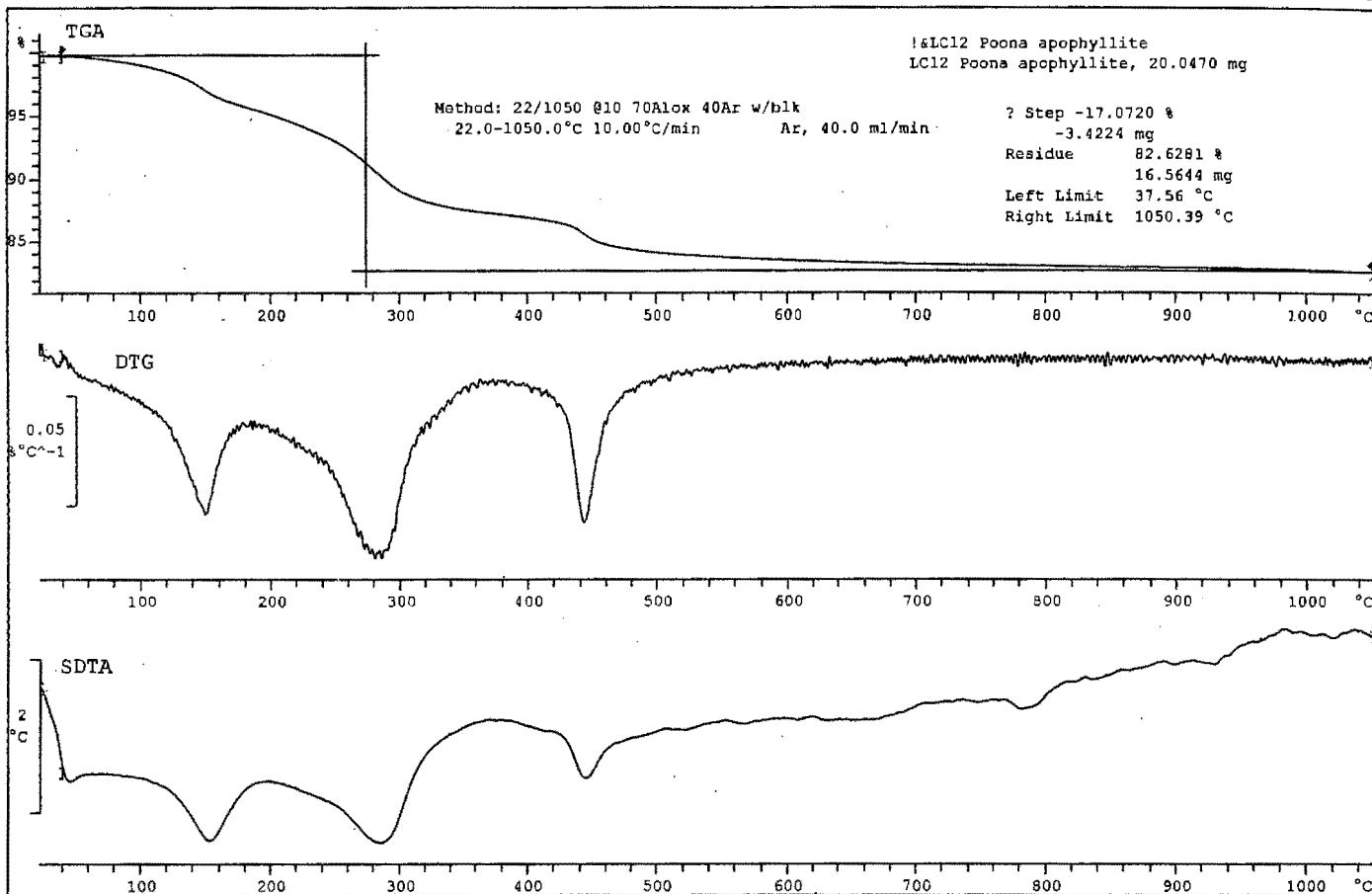
METTLER TOLEDO STAR® System



^exo

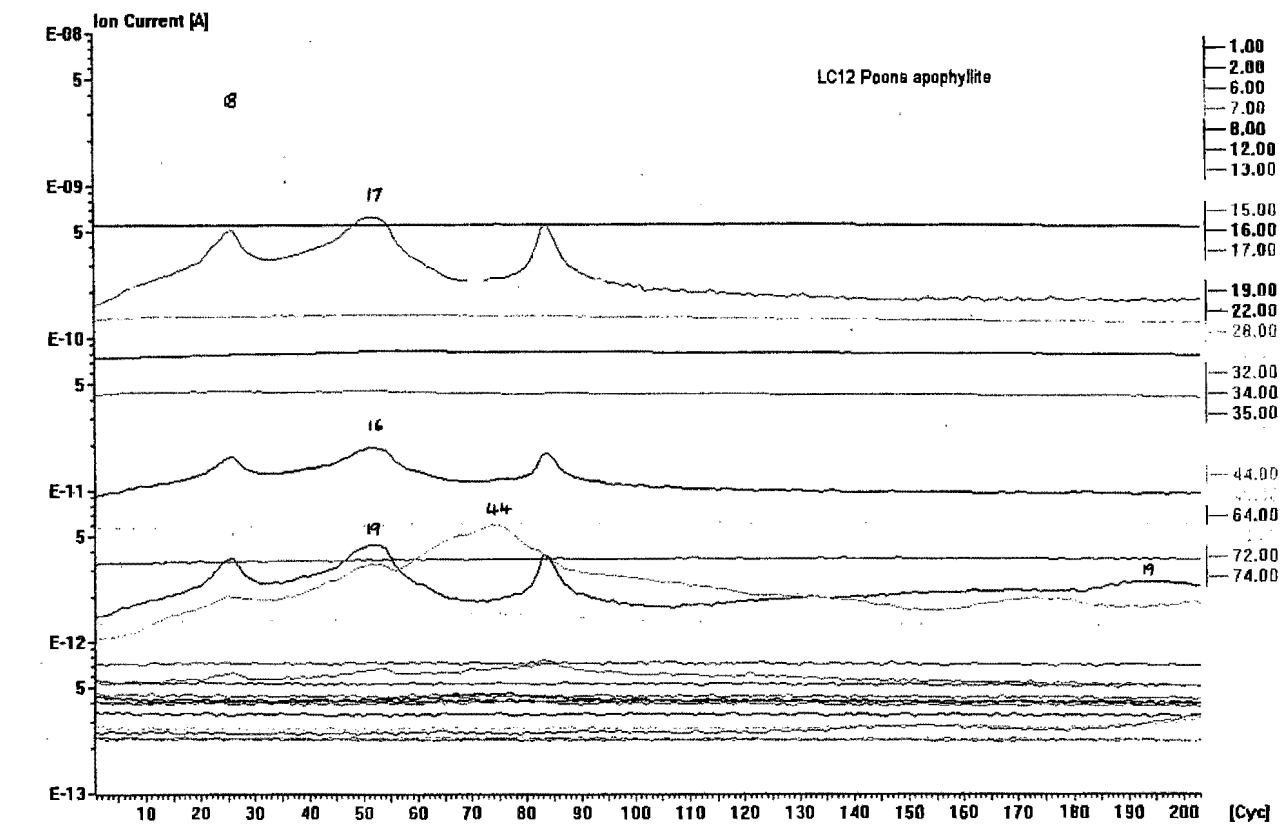
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USGS: METTLER

METTLER TOLEDO STAR® System



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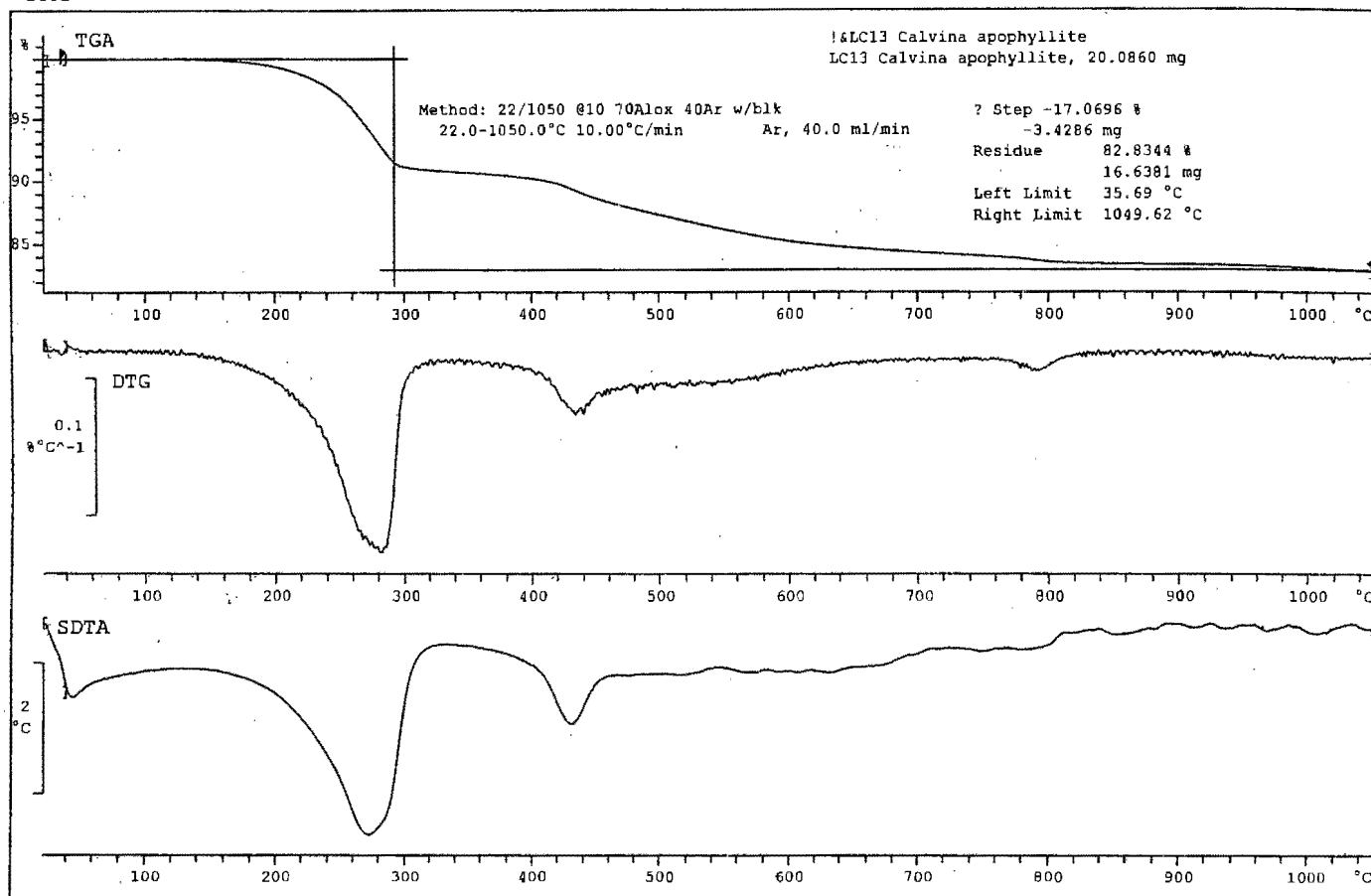
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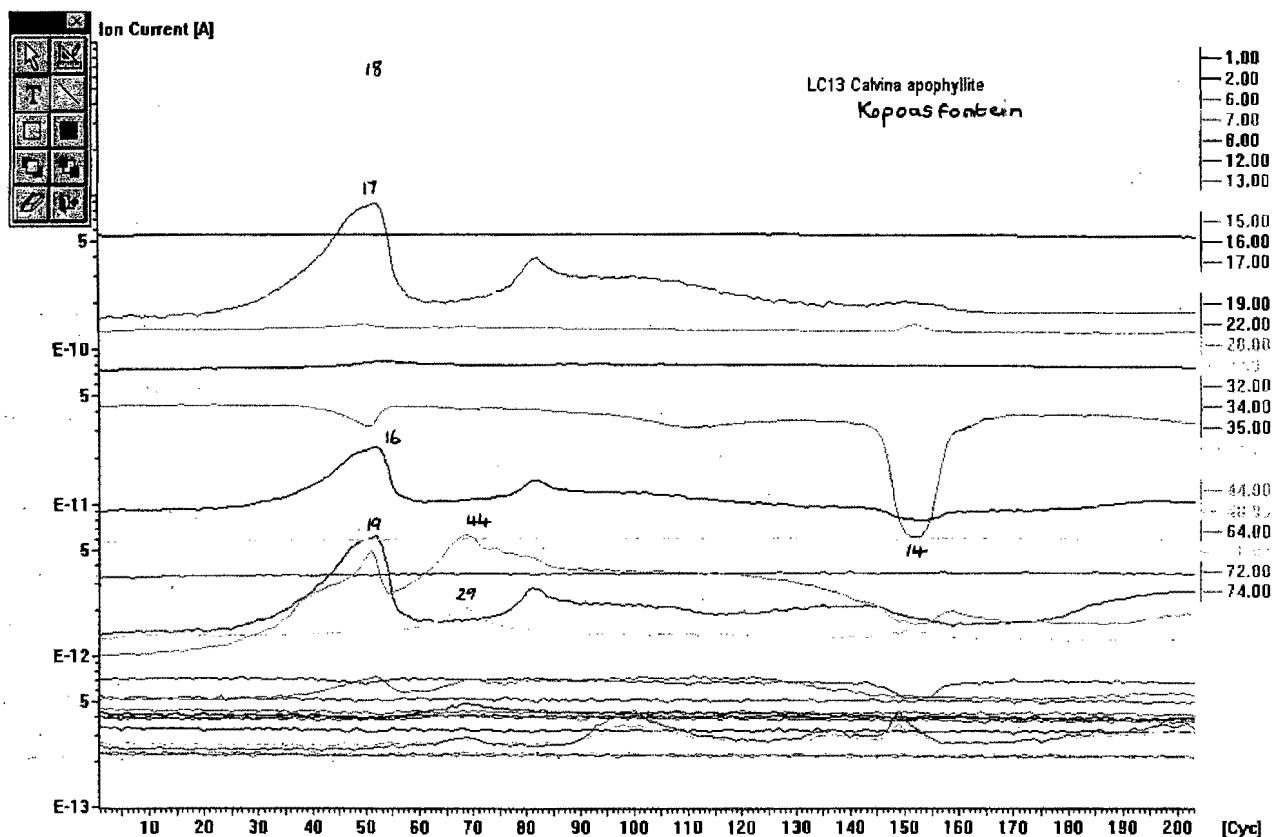
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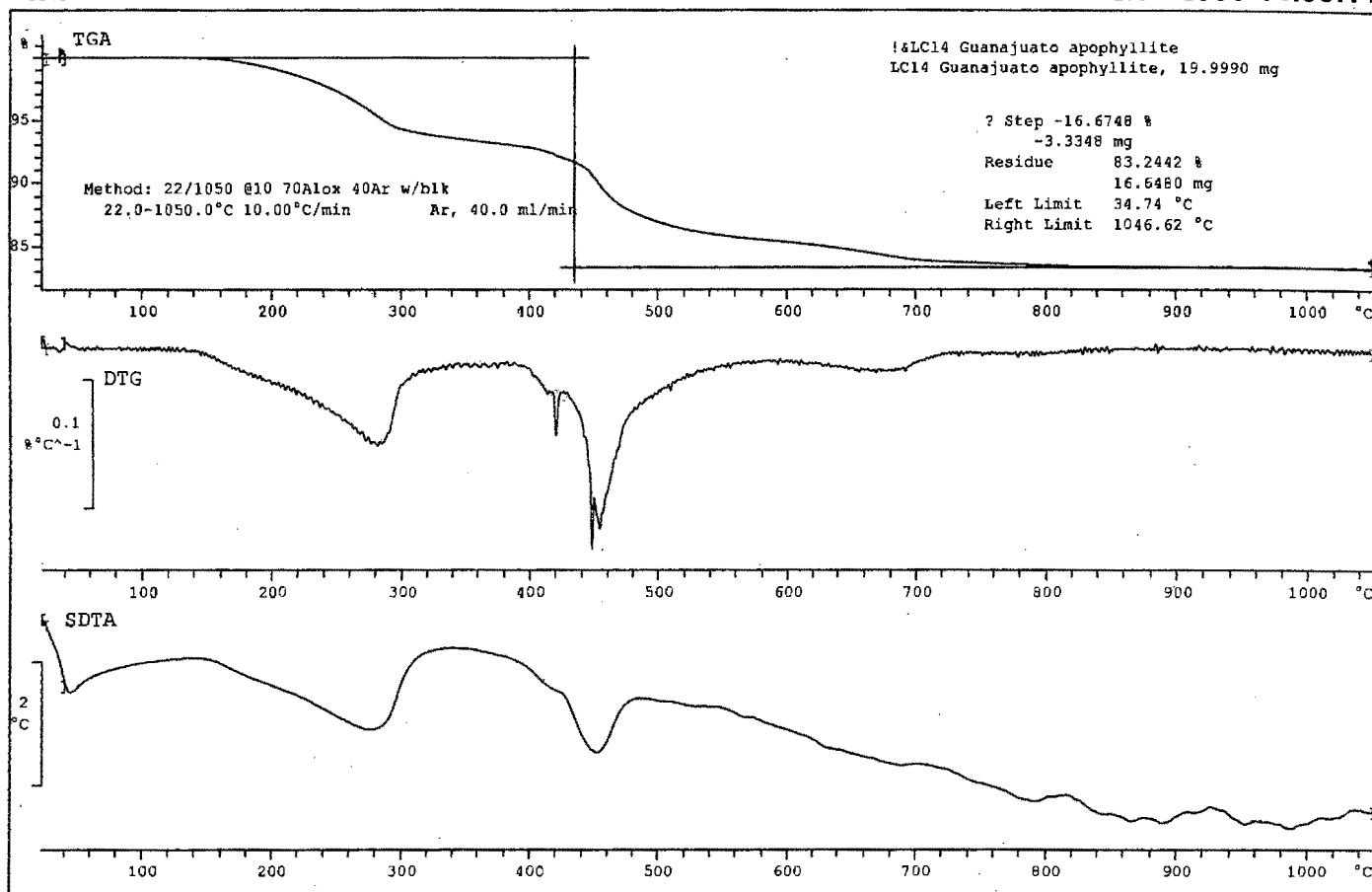
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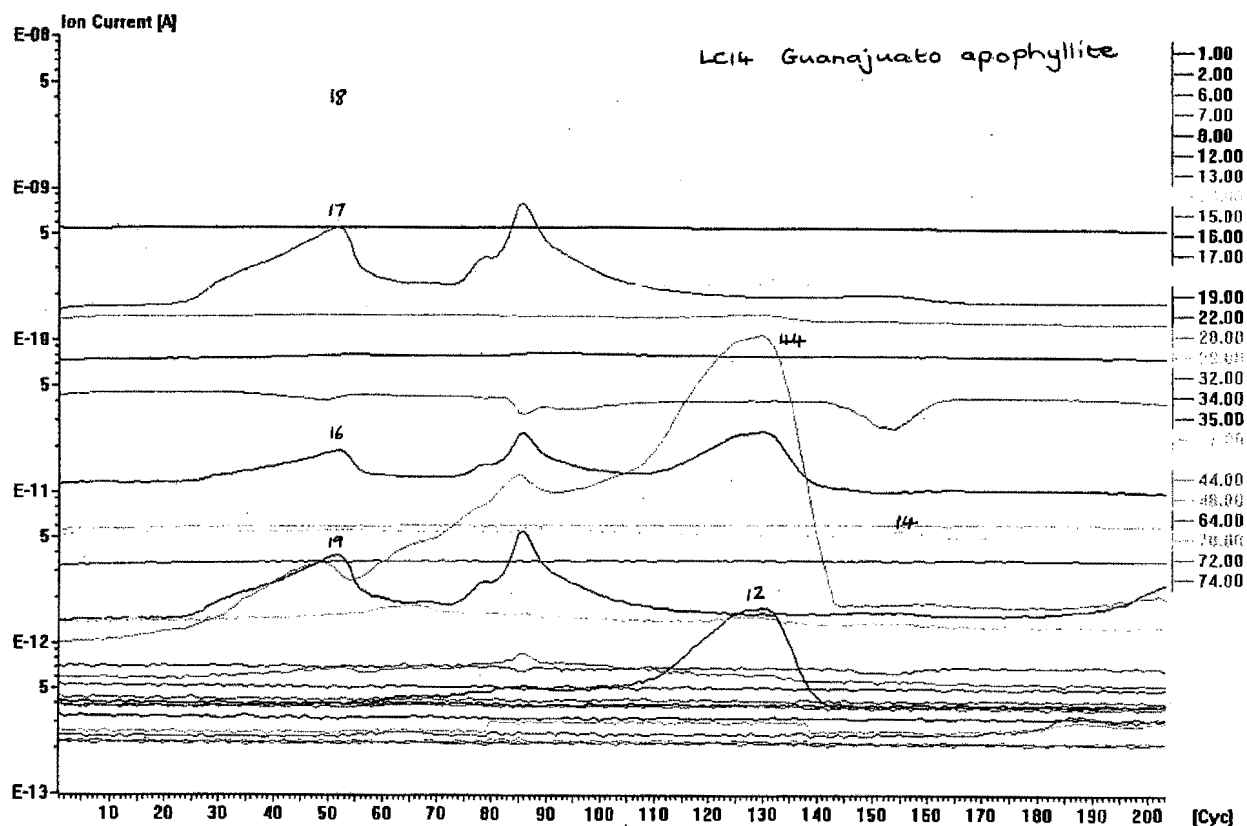
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USGS: METTLER

METTLER TOLEDO STAR® System



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Start

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TGA/SDTA851e/SP1100/

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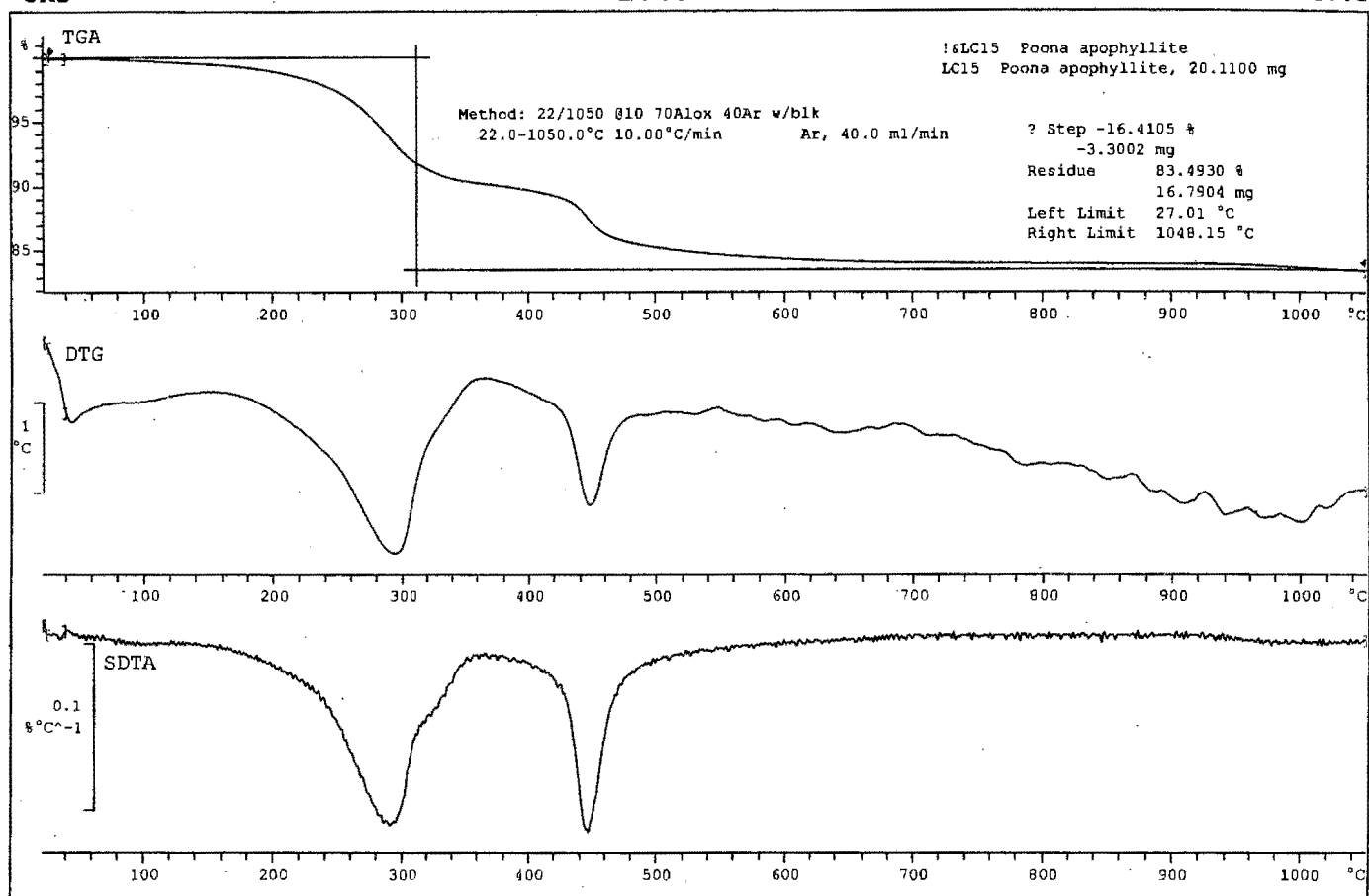
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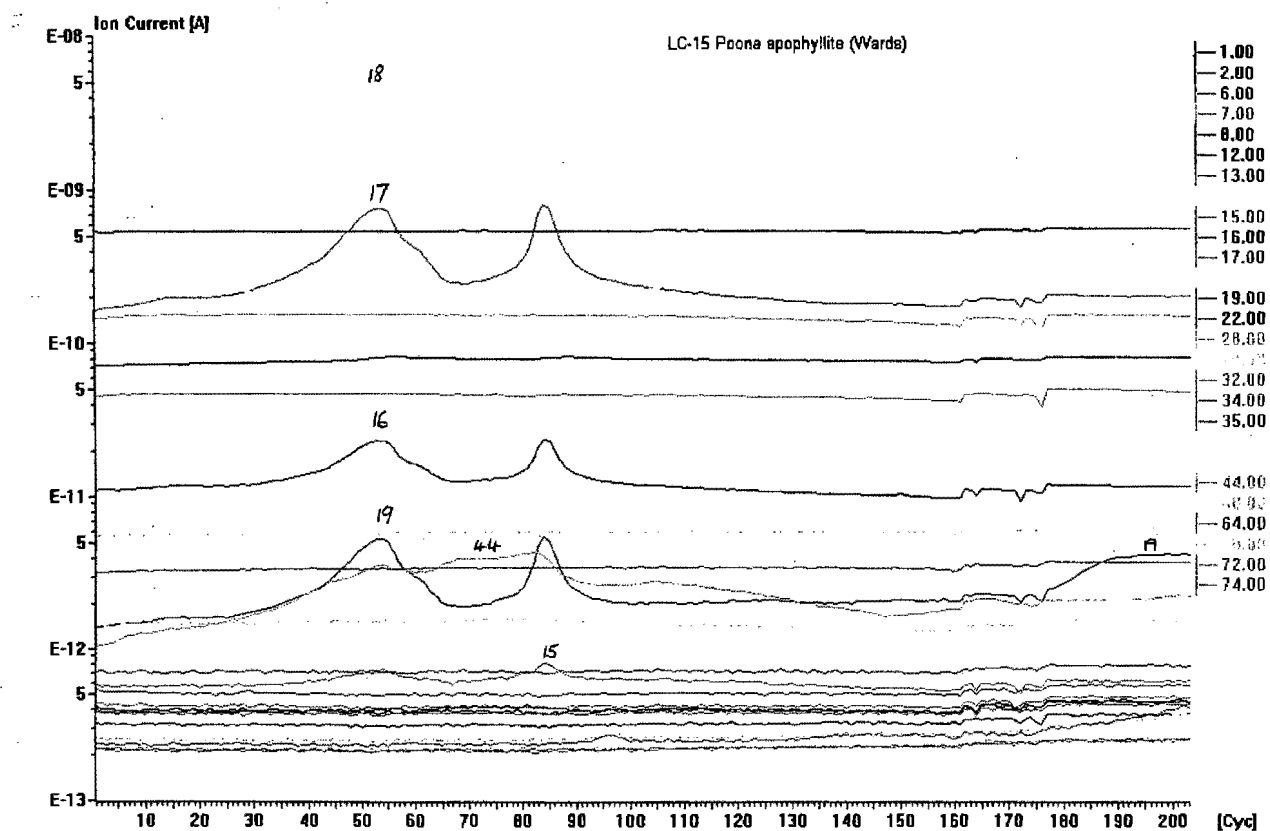
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USGS: METTLER

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APPENDIX H

ANALYTICAL DATA FROM APOPHYLLITE DISSOLUTION BATCH TESTS

H.1 Batch test 1: Long-term dissolution

Table H.1. Analytical results for long-term batch dissolution of Kopoasfontein apophyllite in 0.01M LiCl.

Time (h)	Start mass (g)	Mass loss (%) ³	pH	Si		Ca		K		F	
				mg/L	$\times 10^{-5}$ mol/m ²	mg/L	$\times 10^{-5}$ mol/m ²	mg/L	$\times 10^{-5}$ mol/m ²	mg/L	$\times 10^{-5}$ mol/m ²
3	0.1994	0.25	9.09	6.3	5.0	4.6	2.6	3.8	2.2	0.23	0.28
9	0.1979	0.33	9.41	9.3	7.5	4.9	2.8	3.0	1.7	0.58	0.69
12	0.1990	0.44	9.39	9.9	7.9	8.6	4.8	1.3	0.74	0.56	0.66
26	0.1985	0.37	9.30	10.4	8.3	5.9	3.3	1.1	0.63	0.58	0.68
48	0.1994	0.39	9.37	10.3	8.2	6.5	3.6	1.2	0.69	0.63	0.74
96	0.1999	0.42	9.32	10.9	8.7	7.4	4.1	0.7	0.40	0.78	0.91
192	0.2002	0.47	9.08	11.1	8.8	8.8	4.9	1.3	0.74	0.76	0.88
288	0.2000	0.54	8.84	n.d. ¹	9.0	9.7	5.4	1	0.57	0.44	0.52
579	0.1999	0.55	7.25	11.5	9.1	11.3	6.3	2.1	1.2	0.96	1.1
985	0.1989	0.48	7.16	11.1	8.9	9.3	5.7 ²	2.2	1.3	0.19	0.52 ²
985*	0.2004	0.62	7.16	n.d.		11.1		360		0.67	

¹ n.d. = not determined because of insufficient sample volume.

* data in *italic text* is for the control sample, used to monitor pH during the batch test.

² average concentration of test sample and control sample.

³ Mass loss percentage was calculated using dissolved Si and Ca to calculate the number of grams of apophyllite removed by dissolution.

H.2 Batch test 2: sequential rinse dissolution

Table H.2a. Composition of batch test solutions and quantity of solutes released during sequential rinse experiment with Kopoasfontein apophyllite.

Kopoasfontein : KF (LC13)

Sample area (m ² /L)	Time (hours)	pH	Silica		Fluoride		Calcium		Potassium		Ammonium	
			mg/L as SiO ₂	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²
0.919	0	2.00										
	208	5.78	150	2.72×10^{-3}	13.9	7.97×10^{-4}	200	5.43×10^{-3}	19	5.29×10^{-4}	12.9	7.79×10^{-4}
	376	5.37	130	4.73×10^{-3}	16.2	1.63×10^{-3}	150	8.82×10^{-3}	14	8.52×10^{-4}	9.58	1.26×10^{-3}
	568	3.24	140	7.01×10^{-3}	15.9	2.43×10^{-3}	190	1.36×10^{-2}	19	1.34×10^{-3}	12.2	1.93×10^{-3}
	736	2.21	140	9.26×10^{-3}	15.8	3.24×10^{-3}	75	1.50×10^{-2}	9	1.53×10^{-3}	4.07	2.09×10^{-3}
0.920	0	4.00										
	208	8.20	13	2.35×10^{-4}	0.45	2.55×10^{-5}	4.5	1.22×10^{-4}	1	2.78×10^{-5}	0.05	2.72×10^{-6}
	376	7.14	9.0	3.68×10^{-4}	0.40	4.53×10^{-5}	3.1	1.91×10^{-4}	9	2.74×10^{-4}	0.09	7.67×10^{-6}
	568	7.08	9.1	5.16×10^{-4}	0.32	6.11×10^{-5}	3.0	2.63×10^{-4}	13	6.05×10^{-4}	0.09	1.27×10^{-5}
	736	7.05	8.3	6.48×10^{-4}	0.33	7.78×10^{-5}	2.9	3.33×10^{-4}	6	7.30×10^{-4}	0.11	1.88×10^{-5}
0.915	0	7.00										
	208	9.35	9.1	1.65×10^{-4}	0.32	1.84×10^{-5}	2.9	7.91×10^{-5}	5	1.40×10^{-4}	0.05	2.88×10^{-6}
	376	8.32	5.0	2.36×10^{-4}	0.24	2.99×10^{-5}	1.7	1.16×10^{-4}	2	1.78×10^{-4}	0.01	3.05×10^{-6}
	568	8.30	4.4	3.07×10^{-4}	0.13	3.56×10^{-5}	1.4	1.49×10^{-4}	12	5.09×10^{-4}	<0.01	b.d.l.
	736	7.92	3.0	3.53×10^{-4}	<0.125	b.d.l.*	1.0	1.72×10^{-4}	5	6.07×10^{-4}	<0.01	b.d.l.
0.930	0	10.00										
	208	9.54	9.2	1.65×10^{-4}	0.34	1.92×10^{-5}	2.8	7.51×10^{-5}	3	8.25×10^{-5}	0.03	1.59×10^{-6}
	376	10.02	3.8	2.12×10^{-4}	0.18	2.72×10^{-5}	1.1	9.52×10^{-5}	2	1.27×10^{-4}	0.04	3.76×10^{-6}
	568	9.56	2.8	2.56×10^{-4}	0.17	3.60×10^{-5}	0.83	1.15×10^{-4}	4	2.32×10^{-4}	<0.01	b.d.l.
	736	9.68	2.0	2.86×10^{-4}	<0.125	b.d.l.	0.41	1.23×10^{-4}	5	3.56×10^{-4}	<0.01	b.d.l.

Table H.2b. Composition of batch test solutions and quantity of solutes released during sequential rinse experiment with Guanajuato apophyllite.

Guanajuato : GJ (LC6)												
Sample area (m ² /L)	Time (hours)	pH	Silica		Fluoride		Calcium		Potassium		Ammonium	
			mg/L as SiO ₂	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²
0.989	0	2.00										
	208	6.62	130	2.19×10^{-3}	8.6	4.56×10^{-4}	190	4.80×10^{-3}	28	7.24×10^{-4}	5.6	3.16×10^{-4}
	376	5.95	120	3.94×10^{-3}	10.5	9.57×10^{-4}	150	7.98×10^{-3}	21	1.18×10^{-3}	4.5	5.26×10^{-4}
	568	4.16	130	5.91×10^{-3}	9.7	1.41×10^{-3}	200	1.26×10^{-2}	32	1.95×10^{-3}	6.1	8.39×10^{-4}
	736	2.49	130	7.85×10^{-3}	12.4	2.02×10^{-3}	120	1.51×10^{-2}	20	2.37×10^{-3}	3.5	9.97×10^{-4}
0.998	0	4.00										
	208	9.99	44	7.34×10^{-4}	0.95	5.04×10^{-5}	14	3.50×10^{-4}	3	7.69×10^{-5}	0.17	9.68×10^{-6}
	376	9.27	21	9.92×10^{-4}	0.49	6.99×10^{-5}	6.6	4.71×10^{-4}	10	3.23×10^{-4}	0.10	1.41×10^{-5}
	568	8.76	11	1.14×10^{-3}	0.29	8.25×10^{-5}	3.7	5.48×10^{-4}	14	6.51×10^{-4}	0.01	1.42×10^{-5}
	736	8.28	9.6	1.28×10^{-3}	0.26	9.44×10^{-5}	3.1	6.16×10^{-4}	7	7.90×10^{-4}	0.04	1.66×10^{-5}
0.976	0	7.00										
	208	10.20	45	7.67×10^{-4}	0.93	5.00×10^{-5}	14	3.58×10^{-4}	7	1.83×10^{-4}	0.14	7.90×10^{-6}
	376	9.60	25	1.10×10^{-3}	0.42	6.62×10^{-5}	7.2	4.97×10^{-4}	3	2.39×10^{-4}	0.08	1.14×10^{-5}
	568	9.31	7.2	1.18×10^{-3}	0.22	7.59×10^{-5}	2.3	5.38×10^{-4}	12	5.46×10^{-4}	<0.01	b.d.l.
	736	9.32	4.5	1.25×10^{-3}	<0.125	b.d.l.*	1.5	5.72×10^{-4}	5	6.39×10^{-4}	<0.01	b.d.l.
0.995	0	10.00										
	208	10.28	46	7.69×10^{-4}	1.05	5.57×10^{-5}	14	3.51×10^{-4}	5	1.28×10^{-4}	0.18	9.88×10^{-6}
	376	10.09	23	1.06×10^{-3}	0.41	7.03×10^{-5}	6.0	4.58×10^{-4}	3	1.90×10^{-4}	0.08	1.30×10^{-5}
	568	9.78	7.8	1.15×10^{-3}	0.23	8.05×10^{-5}	2.4	5.04×10^{-4}	4	2.85×10^{-4}	<0.01	b.d.l.
	736	9.90	4.3	1.21×10^{-3}	<0.125	b.d.l.	1.3	5.31×10^{-4}	6	4.27×10^{-4}	<0.01	b.d.l.

Table H.2c. Composition of batch test solutions and quantity of solutes released during sequential rinse experiment with Paterson apophyllite.

Paterson : PT (LC7)												
Sample area (m ² /L)	Time (hours)	pH	Silica		Fluoride		Calcium		Potassium		Ammonium	
			mg/L as SiO ₂	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²
0.985	0	2.00										
	208	6.64	140	2.36×10^{-3}	9.2	4.89×10^{-4}	190	4.81×10^{-3}	35	9.08×10^{-4}	1.88	6.82×10^{-5}
	376	6.16	130	4.26×10^{-3}	9.8	9.50×10^{-4}	140	7.75×10^{-3}	26	1.47×10^{-3}	1.04	9.71×10^{-5}
	568	4.31	130	6.22×10^{-3}	8.6	1.35×10^{-3}	200	1.24×10^{-2}	39	2.41×10^{-3}	1.36	1.43×10^{-4}
	736	2.44	120	8.00×10^{-3}	9.6	1.82×10^{-3}	120	1.49×10^{-2}	25	2.94×10^{-3}	0.92	1.70×10^{-4}
1.00	0	4.00										
	208	10.02	36	5.99×10^{-4}	0.64	3.37×10^{-5}	12	2.99×10^{-4}	3	7.67×10^{-5}	0.12	4.25×10^{-6}
	376	9.10	23	9.07×10^{-4}	0.40	5.05×10^{-5}	7.8	4.57×10^{-4}	10	3.23×10^{-4}	0.14	8.74×10^{-6}
	568	8.37	10	1.04×10^{-3}	0.25	6.15×10^{-5}	3.3	5.19×10^{-4}	14	6.50×10^{-4}	<0.01	b.d.l.
	736	8.4	9.4	1.18×10^{-3}	0.24	7.26×10^{-5}	3.0	5.86×10^{-4}	6	7.63×10^{-4}	<0.01	b.d.l.
0.978	0	7.00										
	208	10.14	36	6.12×10^{-4}	0.67	3.58×10^{-5}	11	2.80×10^{-4}	7	1.83×10^{-4}	0.08	2.93×10^{-6}
	376	9.64	18	8.42×10^{-4}	0.36	5.07×10^{-5}	5.9	3.96×10^{-4}	3	2.39×10^{-4}	0.04	3.91×10^{-6}
	568	9.38	7.4	9.39×10^{-4}	0.25	6.21×10^{-5}	2.3	4.40×10^{-4}	12	5.45×10^{-4}	<0.01	b.d.l.
	736	9.30	4.4	1.00×10^{-3}	<0.125	b.d.l.*	1.3	4.68×10^{-4}	5	6.38×10^{-4}	<0.01	b.d.l.
0.994	0	10.00										
	208	10.22	38	6.36×10^{-4}	0.63	3.32×10^{-5}	11	2.76×10^{-4}	5	1.29×10^{-4}	0.13	2.93×10^{-6}
	376	10.10	15	8.08×10^{-4}	0.32	4.62×10^{-5}	3.2	3.22×10^{-4}	3	1.90×10^{-4}	0.03	3.91×10^{-6}
	568	9.88	6.7	8.98×10^{-4}	0.23	5.68×10^{-5}	1.6	3.56×10^{-4}	4	2.85×10^{-4}	<0.01	b.d.l.
	736	9.85	4.2	9.57×10^{-4}	<0.125	b.d.l.	0.98	3.77×10^{-4}	6	4.27×10^{-4}	<0.01	b.d.l.

Table H.2d. Composition of batch test solutions and quantity of solutes released during sequential rinse experiment with Jalgaon apophyllite.

Jalgaon : JL (LC8)												
Sample area (m ² /L)	Time (hours)	pH	Silicon		Fluoride		Calcium		Potassium		Ammonium	
			mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²
1.124	0	2.00										
	208	5.71	110	1.63×10^{-3}	10.2	4.80×10^{-4}	190	4.22×10^{-3}	38	8.65×10^{-4}	0.11	5.62×10^{-6}
	376	5.71	120	3.20×10^{-3}	10.9	9.29×10^{-4}	140	6.80×10^{-3}	29	1.42×10^{-3}	0.04	6.82×10^{-6}
	568	4.40	150	5.23×10^{-3}	12.5	1.46×10^{-3}	200	1.09×10^{-2}	43	2.33×10^{-3}	<0.01	b.d.l.
	736	2.31	160	7.34×10^{-3}	19.2	2.29×10^{-3}	110	1.28×10^{-2}	22	2.71×10^{-3}	<0.01	b.d.l.
1.135	0	4.00										
	208	9.64	25	3.67×10^{-4}	0.71	3.31×10^{-5}	7.7	1.69×10^{-4}	3	6.76×10^{-5}	0.06	3.08×10^{-6}
	376	7.50	12	4.97×10^{-4}	0.38	4.64×10^{-5}	3.8	2.32×10^{-4}	9	2.62×10^{-4}	0.02	3.57×10^{-6}
	568	7.19	9.4	6.18×10^{-4}	0.36	6.13×10^{-5}	3.2	2.94×10^{-4}	14	5.53×10^{-4}	<0.01	b.d.l.
	736	7.19	8.4	7.26×10^{-4}	0.34	7.54×10^{-5}	2.9	3.50×10^{-4}	6	6.52×10^{-4}	<0.01	b.d.l.
1.127	0	7.00										
	208	9.91	22	3.25×10^{-4}	0.69	3.23×10^{-5}	7.0	1.55×10^{-4}	6	1.36×10^{-4}	0.21	1.03×10^{-5}
	376	9.21	8.2	4.05×10^{-4}	0.29	4.16×10^{-5}	2.6	1.93×10^{-4}	2	1.64×10^{-4}	0.02	9.98×10^{-6}
	568	9.05	4.5	4.62×10^{-4}	0.22	5.05×10^{-5}	1.4	2.19×10^{-4}	12	4.33×10^{-4}	<0.01	b.d.l.
	736	8.77	2.5	4.91×10^{-4}	<0.125	b.d.l.*	0.72	2.32×10^{-4}	5	5.13×10^{-4}	<0.01	b.d.l.
1.137	0	10.00										
	208	10.05	21	3.07×10^{-4}	0.70	3.26×10^{-5}	6.2	1.36×10^{-4}	3	9.00×10^{-5}	0.07	3.24×10^{-6}
	376	10.04	8.4	3.92×10^{-4}	0.25	4.02×10^{-5}	1.8	1.59×10^{-4}	2	1.46×10^{-4}	0.02	3.68×10^{-6}
	568	9.75	3.5	4.32×10^{-4}	<0.125	b.d.l.	0.69	1.71×10^{-4}	4	2.29×10^{-4}	<0.01	b.d.l.
	736	9.80	2.1	4.58×10^{-4}	<0.125	b.d.l.	0.48	1.80×10^{-4}	5	3.54×10^{-4}	<0.01	b.d.l.

* b.d.l. = could not be calculated because concentration is below analytical detection level.

H.3 Batch test 3: Kopoasfontein apophyllite sequential rinse dissolution

Table H.3. Composition of batch test solutions and calculated quantities of solutes released during sequential rinse experiment with Kopoasfontein apophyllite.

Time (hours)	Mass at start (g) & mass loss (%)	pH	Si		F ⁻		Ca ²⁺		K ⁺		NH ₄ ⁺ mg/L	Alkalinity mg /L as HCO ₃ ⁻
			mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²		
0	0.10053	2.00										
182		6.15	57.3	1.35 × 10 ⁻³	22	7.68 × 10 ⁻⁴	230	3.81 × 10 ⁻³	25	4.24 × 10 ⁻⁴	11.4	46
304		5.67	61.4	2.58 × 10 ⁻³	25	1.51 × 10 ⁻³	125	5.25 × 10 ⁻³	24	7.68 × 10 ⁻⁴	11.8	8
465		5.17	70.2	4.03 × 10 ⁻³	23	2.19 × 10 ⁻³	195	8.24 × 10 ⁻³	31	1.23 × 10 ⁻³	11.1	7
650	50	2.18	34.2	4.59 × 10 ⁻³	4.0	2.22 × 10 ⁻³	20	8.07 × 10 ⁻³	3.1	1.21 × 10 ⁻³	0.93	0
0	0.10014	3.00										
182		6.97	28.9	6.86 × 10 ⁻⁴	2.5	8.76 × 10 ⁻⁵	27	4.48 × 10 ⁻⁴	6.5	1.11 × 10 ⁻⁴	n.d.*	7
304		6.73	28.1	1.24 × 10 ⁻³	2.9	1.75 × 10 ⁻⁴	23	7.57 × 10 ⁻⁴	6.3	1.99 × 10 ⁻⁴		5
465		6.25	36.0	2.00 × 10 ⁻³	3.0	2.65 × 10 ⁻⁴	29	1.18 × 10 ⁻³	17	4.68 × 10 ⁻⁴		5
650	17	6.43	31.4	2.62 × 10 ⁻³	3.0	3.55 × 10 ⁻⁴	15	1.36 × 10 ⁻³	3.9	4.90 × 10 ⁻⁴		n.d.
0	0.10044	4.00										
182		8.19	6.9	1.64 × 10 ⁻⁴	0.57	1.99 × 10 ⁻⁵	7.8	1.29 × 10 ⁻⁴	4.8	8.15 × 10 ⁻⁵		11
304		7.33	7.8	3.20 × 10 ⁻⁴	0.59	3.72 × 10 ⁻⁵	6.7	2.18 × 10 ⁻⁴	5.7	1.64 × 10 ⁻⁴		6
465		6.76	8.6	4.97 × 10 ⁻⁴	0.67	5.77 × 10 ⁻⁵	7.1	3.21 × 10 ⁻⁴	6.7	2.63 × 10 ⁻⁴		9
650	7	6.88	7.1	6.35 × 10 ⁻⁴	0.59	7.49 × 10 ⁻⁵	4.4	3.77 × 10 ⁻⁴	2.0	2.81 × 10 ⁻⁴		8
0	0.09948	5.00										
182		8.82	5.8	1.38 × 10 ⁻⁴	0.52	1.83 × 10 ⁻⁵	6.8	1.14 × 10 ⁻⁴	1.9	3.26 × 10 ⁻⁵		15
304		7.35	5.7	2.51 × 10 ⁻⁴	0.43	3.05 × 10 ⁻⁵	5.3	1.83 × 10 ⁻⁴	5.0	1.12 × 10 ⁻⁴		11
465		6.99	5.3	3.58 × 10 ⁻⁴	0.46	4.47 × 10 ⁻⁵	5.0	2.55 × 10 ⁻⁴	16	3.71 × 10 ⁻⁴		n.d.
650	4	6.92	3.9	4.32 × 10 ⁻⁴	0.37	5.53 × 10 ⁻⁵	1.9	2.75 × 10 ⁻⁴	2.7	3.73 × 10 ⁻⁴		9

Table H.3 (continued). Composition of batch test solutions and calculated quantities of solutes released during sequential rinse experiment with Kopoasfontein apophyllite.

Time (hours)	Mass at start (g) & mass loss (%)	pH	Si		F ⁻		Ca ²⁺		K ⁺		NH ₄ ⁺	Alkalinity
			mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	mg /L as HCO ₃ ⁻
0	0.09978	6.00										
182		7.66	6.9	1.63×10^{-4}	0.57	2.00×10^{-5}	8.5	1.42×10^{-4}	5.7	9.74×10^{-5}		17
304		7.47	4.8	2.51×10^{-4}	0.44	3.22×10^{-5}	5.2	2.04×10^{-4}	5.2	1.70×10^{-4}		11
465		7.09	4.8	3.51×10^{-4}	0.44	4.56×10^{-5}	4.7	2.72×10^{-4}	6.5	2.70×10^{-4}		11
650	3	6.82	3.0	4.06×10^{-4}	0.30	5.39×10^{-5}	2.2	2.97×10^{-4}	1.7	2.82×10^{-4}		9
0	0.09986	7.00										
182		9.25	5.5	1.31×10^{-4}	0.44	1.55×10^{-5}	6.6	1.10×10^{-4}	4.3	7.34×10^{-5}		17
304		7.47	3.8	2.00×10^{-4}	0.35	2.52×10^{-5}	4.2	1.62×10^{-4}	8.1	1.99×10^{-4}		13
465		7.20	3.2	2.63×10^{-4}	0.35	3.59×10^{-5}	3.7	2.14×10^{-4}	17	4.65×10^{-4}		10
650	7	7.10	1.9	2.97×10^{-4}	0.26	4.32×10^{-5}	1.8	2.35×10^{-4}	2.7	4.67×10^{-4}		8
0	0.10018	8.00										
182		9.14	4.8	1.13×10^{-4}	0.51	1.79×10^{-5}	6.2	1.03×10^{-4}	4.1	6.98×10^{-5}		18
304		7.74	3.4	1.75×10^{-4}	0.33	2.64×10^{-5}	4.8	1.65×10^{-4}	10	2.36×10^{-4}		13
465		7.31	3.7	2.52×10^{-4}	0.37	3.80×10^{-5}	3.9	2.20×10^{-4}	17	4.89×10^{-4}		12
650	6	7.20	1.9	2.85×10^{-4}	0.24	4.45×10^{-5}	1.4	2.35×10^{-4}	2.9	4.96×10^{-4}		n.d.
0	0.10019	9.00										
182		9.32	5.7	1.35×10^{-4}	0.43	1.51×10^{-5}	6.4	1.06×10^{-4}	2.7	4.59×10^{-5}		21
304		8.16	2.2	1.65×10^{-4}	0.30	2.31×10^{-5}	8.5	2.29×10^{-4}	24	4.44×10^{-4}		10
465		7.53	2.4	2.16×10^{-4}	0.30	3.22×10^{-5}	4.5	2.83×10^{-4}	17	6.70×10^{-4}		10
650	7	7.31	1.2	2.36×10^{-4}	0.19	3.74×10^{-5}	2.1	3.09×10^{-4}	2.8	6.80×10^{-4}		n.d.

Table H.3 (continued). Composition of batch test solutions and calculated quantities of solutes released during sequential rinse experiment with Kopoasfontein apophyllite.

Time (hours)	Mass at start (g) & mass loss (%)	pH	Si		F ⁻		Ca ²⁺		K ⁺		NH ₄ ⁺	Alkalinity
			mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	cumulative mol/m ²	mg/L	mg /L-as HCO ₃ ⁻ #
0	0.10028	10.00										
182		9.54	4.7	1.12 × 10 ⁻⁴	0.44	1.54 × 10 ⁻⁵	6.5	1.08 × 10 ⁻⁴	3.2	5.44 × 10 ⁻⁵		28
304		9.61	1.7	1.34 × 10 ⁻⁴	0.34	2.47 × 10 ⁻⁵	4.3	1.62 × 10 ⁻⁴	6.1	1.50 × 10 ⁻⁴		20
465		9.53	1.0	1.54 × 10 ⁻⁴	0.30	3.37 × 10 ⁻⁵	3.0	2.02 × 10 ⁻⁴	15	3.81 × 10 ⁻⁴		18
650	5	9.66	0.5	1.62 × 10 ⁻⁴	0.15	3.74 × 10 ⁻⁵	1.1	2.13 × 10 ⁻⁴	4.0	4.11 × 10 ⁻⁴		18
0	0.09996	11.00										
182		10.80	5.4	1.28 × 10 ⁻⁴	0.40	1.40 × 10 ⁻⁵	6.8	1.13 × 10 ⁻⁴	2.0	3.41 × 10 ⁻⁵		77
304		10.82	5.2	2.29 × 10 ⁻⁴	0.27	2.12 × 10 ⁻⁵	5.9	1.92 × 10 ⁻⁴	5.2	1.16 × 10 ⁻⁴		97
465		10.95	2.2	2.65 × 10 ⁻⁴	0.20	2.70 × 10 ⁻⁵	2.2	2.15 × 10 ⁻⁴	8.5	2.47 × 10 ⁻⁴		90
650	<9	10.95	1.4	2.94 × 10 ⁻⁴	0.14	3.10 × 10 ⁻⁵	0.67	2.23 × 10 ⁻⁴	2.3	2.64 × 10 ⁻⁴		n.d.
0	0.09992	12.00										
182		12.09	10.6	2.52 × 10 ⁻⁴	0.54	1.90 × 10 ⁻⁵	7.1	1.18 × 10 ⁻⁴	1.8	3.07 × 10 ⁻⁵		n.d
304		12.05	8.8	4.20 × 10 ⁻⁴	0.26	2.49 × 10 ⁻⁵	8.3	2.37 × 10 ⁻⁴	2.1	6.10 × 10 ⁻⁵		612
465		12.01	8.6	5.96 × 10 ⁻⁴	0.30	3.45 × 10 ⁻⁵	3.5	2.75 × 10 ⁻⁴	7.1	1.77 × 10 ⁻⁴		600
650	3	12.07	8.1	7.60 × 10 ⁻⁴	0.25	4.17 × 10 ⁻⁵	1.5	2.94 × 10 ⁻⁴	1.1	1.76 × 10 ⁻⁴		610

* n.d. = not determined due to insufficient sample volume for analysis.

Alkalinity at high pH is not strictly present as HCO₃⁻, since CO₃²⁻ and OH⁻ ions are also neutralised by HCl titration.

APPENDIX I

INPUT DATA FILES AND SELECTED THERMODYNAMIC CONSTANTS FOR PHREEQC MODELLING

I.1 Forward modelling of apophyllite dissolution

I.1.1 Simulation 1 - Artificial recharge under open system conditions

```

TITLE Simulated dissolution of apophyllite
TITLE Artificial recharge - open system
PHASES 1
FApoph
    KCa4Si8O20F:8H2O + 8H+ + 4H2O = K+ + 4Ca+2 + F- + 8H4SiO4
    log_k      20
END
SELECTED_OUTPUT
    -file c:\phrqcdat\PhD\apopdis2.txt
    -activities      H+ Ca+2 F- HCO3- H4SiO4
    -molalities      K+ Ca+2 F- HCO3- H4SiO4
    -saturation_indices  calcite fluorite SiO2(a) FApoph CO2(g)
    -equilibrium      calcite fluorite SiO2(a)
END
SOLUTION 1      PURE WATER
                pH      7.0      charge
                temp 25
EQUILIBRIUM_PHASES 1      soil water
                CO2(g)      -2.0
                calcite      0.0      10
SAVE solution 1
END
TITLE Add fluorapophyllite to pure water - closed system
REACTION 1
    KCa4Si8O20F:8H2O 1.0
    1 mmol in 40 steps
END
USE solution 1
USE reaction 1
EQUILIBRIUM_PHASES 2
    calcite      0.0      0.0
    SiO2(a)      0.0      0.0
    fluorite      0.0      0.0
END

```

I.1.2 Simulation 2 - Artificial recharge under closed system conditions

```

TITLE Simulated dissolution of apophyllite
TITLE Artificial recharge - closed system
PHASES 1
FApoph
    KCa4Si8O20F:8H2O + 8H+ + 4H2O = K+ + 4Ca+2 + F- + 8H4SiO4
    log_k      20
END

```

```

SELECTED_OUTPUT
    -file c:\phrqcdat\PhD\apophdis.txt
    -activities      H+ Ca+2 F- HCO3- H4SiO4
    -molalities      K+ Ca+2 F- HCO3- H4SiO4
    -saturation_indices  calcite fluorite SiO2(a) FApoph CO2(g)
    -equilibrium      calcite fluorite SiO2(a)
END
SOLUTION 1      PURE WATER
                pH      7.0    charge
                temp 25
EQUILIBRIUM_PHASES 1    rain water
                CO2(g)      -3.5
SAVE solution 1
END
TITLE Add fluorapophyllite to pure water - closed system
REACTION 1
    KCa4Si8O20F:8H2O 1.0
    1 mmol in 40 steps
END
USE solution 1
USE reaction 1
EQUILIBRIUM_PHASES 2
    calcite      0.0    0.0
    SiO2(a)      0.0    0.0
    fluorite     0.0    0.0
END

```

1.1.3 Simulation 3 - Natural recharge under open system conditions

```

TITLE Simulated dissolution of apophyllite
TITLE Natural recharge - open system
PHASES 1
FApoph
    KCa4Si8O20F:8H2O + 8H+ + 4H2O = K+ + 4Ca+2 + F- + 8H4SiO4
    log_k      20
END
SELECTED_OUTPUT
    -file c:\phrqcdat\PhD\apopdis4.txt
    -activities      H+ Ca+2 F- HCO3- H4SiO4
    -molalities      K+ Ca+2 F- HCO3- H4SiO4
    -saturation_indices  calcite fluorite SiO2(a) FApoph CO2(g)
    -equilibrium      calcite fluorite SiO2(a)
END
SOLUTION 1      PURE WATER
                pH      7.0    charge
                temp 25
EQUILIBRIUM_PHASES 1    soil water
                CO2(g)      -2.0
                calcite     0.0          10
SAVE solution 1
END
TITLE Add fluorapophyllite to pure water - closed system
REACTION 1
    KCa4Si8O20F:8H2O 1.0
    1 mmol in 40 steps
END
USE solution 1
USE reaction 1
EQUILIBRIUM_PHASES 2
    calcite      0.0    0.0

```

SiO2(a)	0.0	0.0
fluorite	0.0	0.0
CO2(g)	-2.0	10

END

I.1.4 Simulation 4 - Natural recharge under closed system conditions

TITLE Simulated dissolution of apophyllite

TITLE Natural recharge - closed system

PHASES 1

FApoph

KCa4Si8O20F:8H2O + 8H+ + 4H2O = K+ + 4Ca+2 + F- + 8H4SiO4

log_k 20

END

SELECTED_OUTPUT

-file c:\phrqcdat\PhD\apopdis3.txt

-activities H+ Ca+2 F- HCO3- H4SiO4

-molalities K+ Ca+2 F- HCO3- H4SiO4

-saturation_indices calcite fluorite SiO2(a) FApoph CO2(g)

-equilibrium calcite fluorite SiO2(a)

END

SOLUTION 1 PURE WATER

pH 7.0 charge

temp 25

EQUILIBRIUM_PHASES 1 rain water

CO2(g) -3.5

SAVE solution 1

END

TITLE Add fluorapophyllite to pure water - open system

REACTION 1

KCa4Si8O20F:8H2O 1.0

1 mmol in 40 steps

END

USE solution 1

USE reaction 1

EQUILIBRIUM_PHASES 2

calcite 0.0 0.0

SiO2(a) 0.0 0.0

fluorite 0.0 0.0

CO2(g) -3.5 10

END

I.2 Inverse modelling (mass balance) of Kopoasfontein groundwater

I.2.1 Run 1 - observed mineral phases

TITLE Inverse modeling of G39973 - observed minerals, no redox, ion exchange

SOLUTION 1 Simulated recharge

Temp 25

pH 7 charge

pe 4

EQUILIBRIUM_PHASES

CO2(g) -2 10

Calcite 0.0 10

SAVE SOLUTION 1

END

SOLUTION 2 G39973 07/07/1999

-units mg/L
pH 9.83
Si 29.6 as SiO2
Ca 3.5
Mg 1.2
Na 157
K 0.7
Alkalinity 181 as HCO3
F 10.6
Cl 99

SOLUTION 3 PS27 08/01/1980

-units mg/L
pH 7.5
Si 23.5 as SiO2
Ca 42
Mg 22
Na 46
K 4.1
Alkalinity 235 as HCO3
F 1.03
Cl 50

PHASES 1

Fluorapophyllite

$\text{KCa}_4\text{Si}_8\text{O}_{20}\text{F} \cdot 8\text{H}_2\text{O} + 8\text{H}^+ + 4\text{H}_2\text{O} = \text{K}^+ + \text{F}^- + 4\text{Ca}^{2+} + 8\text{H}_4\text{SiO}_4$

log_k 0.0

Halite

$\text{NaCl} = \text{Na}^+ + \text{Cl}^-$

log_k 1.582

H2O

$\text{H}_2\text{O} = \text{H}_2\text{O}$

Log_k 0.00

END

INVERSE_MODELING 1 Simulated recharge to G39973

-solutions 1 2

-uncertainty 0.1

-phases

SiO2(a)

Calcite

Chlorite(14A) # or Dolomite

Fluorapophyllite dis

Halite

Illite

Kaolinite.

KX

CaX2

NaX

-minimum

END

INVERSE_MODELING 2 PS27 to G39973

-solutions 3 2

-uncertainty 0.1

-phases

```

        SiO2(a)
        Calcite
        Chlorite(14A)      # or Dolomite
        Fluorapophyllite  dis
        Halite
        Illite
        Kaolinite
        KX
        CaX2
        NaX
    -minimum
END

```

1.2.2 Run 2 - feldspar dissolution, no ion exchange

TITLE Inverse modeling of G39973 - No exchange, feldspar dissolution

SOLUTION 1 Simulated recharge

Temp 25

pH 7 charge

pe 4

EQUILIBRIUM PHASES

CO2(g) -2 10

Calcite 0.0 10

SAVE SOLUTION 1

END

SOLUTION 2 G39973 07/07/1999

-units mg/L

pH 9.83

Si 29.6 as SiO2

Ca 3.5

Mg 1.2

Na 157

K 0.7

Alkalinity 181 as HCO3

F 10.6

Cl 99

Al 0.068

SOLUTION 3 PS27 08/01/1980

-units mg/L

pH 7.5

Si 23.5 as SiO2

Ca 42

Mg 22

Na 46

K 4.1

Alkalinity 235 as HCO3

F 1.03

Cl 50

PHASES 1

Fluorapophyllite

$\text{KCa}_4\text{Si}_8\text{O}_{20}\text{F} \cdot 8\text{H}_2\text{O} + 8\text{H}^+ + 4\text{H}_2\text{O} = \text{K}^+ + \text{F}^- + 4\text{Ca}^{2+} + 8\text{H}_4\text{SiO}_4$

log_k 0.0

Halite

$\text{NaCl} = \text{Na}^+ + \text{Cl}^-$

log_k 1.582

H2O


```

H2O = H2O
Log_k 0.00

Plagioclase
Na0.62Ca0.38Al1.38Si2.62O8 + 5.52H+ + 2.48H2O = 0.62Na+ + 0.38Ca+2 + \
1.38Al+3 + 2.62H4SiO4
Log_k 0.00
END

INVERSE_MODELING 1 Simulated recharge to 73
  -solutions 1 2
  -uncertainty 0.1
  -phases
    SiO2(a)
    Calcite
    Dolomite
    Albite      # or Plagioclase
    Kaolinite   pre
    Illite
    Fluorapophyllite dis
    Halite
    CO2(g)
  -minimum
END
INVERSE_MODELING 2 PS27 to 73
  -solutions 3 2
  -uncertainty 0.1
  -phases
    SiO2(a)
    Calcite
    Dolomite
    Albite      # or Plagioclase
    Kaolinite   pre
    Illite
    Fluorapophyllite dis
    Halite
    CO2(g)
  -minimum
END

```

1.2.3 Run 3 - alternate fluoride sources

```

TITLE Inverse modeling of G39973 - fluorite and illite-F included
SOLUTION 1 Simulated recharge
  Temp 25
  pH 7 charge
  pe 4
EQUILIBRIUM_PHASES
  CO2(g) -2 10
  Calcite 0.0 10
SAVE SOLUTION 1
END
SOLUTION 2 G39973 07/07/1999
  -units mg/L
  pH 9.83
  Si 29.6 as SiO2
  Ca 3.5
  Mg 1.2
  Na 157
  K 0.7

```

```

    Alkalinity    181 as HCO3
    F             10.6
    Cl            99
    Al            0.068
SOLUTION 3 PS27 08/01/1980
    -units mg/L
    pH            7.5
    Si            23.5 as SiO2
    Ca            42
    Mg            22
    Na            46
    K             4.1
    Alkalinity    235 as HCO3
    F             1.03
    Cl            50

```

PHASES 1

Fluorapophyllite

```

    KCa4Si8O20F:8H2O + 8H+ + 4H2O = K+ + F- + 4Ca+2 + 8H4SiO4
    log_k 0.0

```

Halite

```

    NaCl = Na+ + Cl-
    log_k 1.582

```

H2O

```

    H2O = H2O
    Log_k 0.00

```

Illite-F

```

    K0.6Mg0.25Al2.3Si3.5O10(OH)F + 10H2O = 0.6K+ + 0.25Mg+2 + 2.3Al+3 + \
    3.5H4SiO4 + F- + 7OH-
    log_k -40.267

```

END

INVERSE_MODELING 1 Simulated recharge to 73

```

    -solutions 1 2
    -uncertainty 0.1
    -phases
        SiO2(a)
        Calcite
        Dolomite
        Fluorapophyllite dis
        Fluorite
        Halite
        Illite
        Illite-F
        Kaolinite pre
        NaX KX CaX2
    -minimum

```

END

INVERSE_MODELING 2 PS27 to 73

```

    -solutions 3 2
    -uncertainty 0.1
    -phases
        SiO2(a)
        Calcite
        Dolomite
        Fluorapophyllite dis
        Fluorite
        Halite
        Kaolinite pre

```

```

        Illite-F
        Illite
        NaX    KX    CaX2
    -minimum
END

```

1.2.4 Run 4 - ammonian fluorapophyllite

TITLE Inverse modeling of G39973 - Ammonian fluorapophyllite mass balances

SOLUTION 1 Simulated recharge

Temp 25

pH 7 charge

pe 4

EQUILIBRIUM PHASES

CO2(g) -2 10

Calcite 0.0 10

SAVE SOLUTION 1

END

SOLUTION 2 G39973 07/07/1999

-units mg/L

pH 9.83

Si 29.6 as SiO2

Ca 3.5

Mg 1.2

Na 157

K 0.7

Alkalinity 181 as HCO3

F 10.6

Cl 99

Al 0.068

Amn 1.7 as AmnH

SOLUTION 3 PS27 08/01/1980

-units mg/L

pH 7.5

Si 23.5 as SiO2

Ca 42

Mg 22

Na 46

K 4.1

Alkalinity 235 as HCO3

F 1.03

Cl 50

Amn 0.04 as AmnH

PHASES 1

Halite

NaCl = Na+ + Cl-

log_k 1.582

H2O

H2O = H2O

Log_k 0.00

F-illite

$K_0.6Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)F + 10H_2O = 0.6K^+ + 0.25Mg^{+2} + 2.3Al^{+3} + 3.5H_4SiO_4 + F^- + 7OH^-$

log_k -40.267

Amn-apophyllite

$K0.3(AmmH)0.7Ca_4Si_8O_{20}F:8H_2O + 8H^+ + 4H_2O = 0.3K^+ + 0.7AmmH^+ + F^- +$
 $4Ca^{+2} + 8H_4SiO_4$
 log_k 20.0
 END

INVERSE_MODELING 1 Simulated recharge to 73

-solutions 1 2
 -uncertainty 0.1
 -phases
 SiO2(a)
 Calcite
 Dolomite
 Amm-apophyllite dis
 Halite
 Illite
 F-illite
 KX
 CaX2
 NaX
 AmmHX
 -minimum

END

INVERSE_MODELING 2 PS27 to 73

-solutions 3 2
 -uncertainty 0.1
 -phases
 SiO2(a)
 Calcite
 Dolomite
 Amm-apophyllite dis
 Halite
 KX
 CaX2
 NaX
 AmmHX
 -minimum

END

1.2.5 Run 5 - sulphide oxidation

TITLE Inverse modeling of G39973 - Mass balance with pyrite oxidations

SOLUTION 1 Simulated recharge

Temp 25
 pH 7 charge
 pe 4

EQUILIBRIUM_PHASES

CO2(g) -2 10
 Calcite 0.0 10

SAVE SOLUTION 1

END

SOLUTION 2 G39973 07/07/1999

-units mg/L
 pH 9.83
 Si 29.6 as SiO2
 Ca 3.5
 Mg 1.2
 Na 157
 K 0.7
 Alkalinity 181 as HCO3

```

F      10.6
Cl     99
Al     0.068
Amm 1.7 as AmmH
Fe     0.08
S(6)   64 as SO4
SOLUTION 3 PS27 08/01/1980
-units mg/L
pH     7.5
Si     23.5 as SiO2
Ca     42
Mg     22
Na     46
K      4.1
Alkalinity 235 as HCO3
F      1.03
Cl     50
Amm    0.04 as AmmH
S(6)   28 as SO4

```

PHASES 1

Halite

```

NaCl = Na+ + Cl-
log_k 1.582

```

H2O

```

H2O = H2O
Log_k 0.00

```

F-illite

```

K0.6Mg0.25Al2.3Si3.5O10(OH)F + 10H2O = 0.6K+ + 0.25Mg+2 + 2.3Al+3 + \
3.5H4SiO4 + F- + 7OH-
log_k -40.267

```

Amm-apophyllite

```

K0.3(AmmH)0.7Ca4Si8O20F:8H2O + 8H+ + 4H2O = 0.3K+ + 0.7AmmH+ + F- + \
4Ca+2 + 8H4SiO4
log_k 20.0

```

END

INVERSE_MODELING 1 Simulated recharge to 73

```

-solutions 1 2
-uncertainty 0.05
-phases
  SiO2(a)
  Calcite
  Dolomite
  Amm-apophyllite dis
  Halite
  Illite
  F-illite
  KX
  CaX2
  NaX
  AmmHX
  Pyrite dis
  Fe(OH)3(a) pre
  O2(g)

```

-minimum

END

```

INVERSE_MODELING 2 PS27 to 73
  -solutions 3 2
  -uncertainty 0.05
  -phases
    SiO2(a)
    Calcite
    Dolomite
    Amm-apophyllite dis
    Halite
    KX
    CaX2
    NaX
    AmmHX
    O2(g)
    Pyrite dis
    Fe(OH)3(a) pre
  -minimum
END

```

I.2.6 Run 6 - perched water at Kopoasfontein

TITLE Inverse modelling of KF1

PHASES 1

Halite

NaCl = Na+ + Cl-
log_k 1.582

Sylvite

KCl = K+ +Cl-
log_k 0.0

F-illite

$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)F + 10H_2O = 0.6K^+ + 0.25Mg^{+2} + 2.3Al^{+3} + /$
 $3.5H_4SiO_4 + F^- + 7OH^-$
log_k -40.267

SOLUTION 1 Simulated recharge

Temp 25
pH 7 charge
pe 4

EQUILIBRIUM PHASES

CO2(g) -2 10
Calcite 0.0 10

SAVE SOLUTION 1

SOLUTION 3 PS27 08/01/1980 (Seward, 1983)

-units mg/L
pH 7.5
Si 23.5 as SiO2
Ca 42
Mg 22
Na 46
K 4.1
Alkalinity 235 as HCO3
F 1.03
Cl 50
S(6) 28 as SO4

SOLUTION 4 KF1 08/07/1999

-units mg/l
pH 7.26

Si	27.17	as SiO2
Ca	90	
Mg	47	
Na	94	
K	1.2	
Alkalinity	319	as HCO3
S(6)	78	as SO4
F	1.4	
Cl	175	
Fe	0.41	
Al	0.013	

END

INVERSE_MODELING 1 Simulated recharge to KF1

-solutions 1 4
 -uncertainty 0.05
 -phases
 SiO2(a)
 Calcite
 Dolomite
 Halite
 Sylvite
 Gypsum
 Kaolinite
 Illite
 Fluorite # or F-illite
 Pyrite dis
 Fe(OH)3(a) pre
 O2(g)
 -minimum

END

INVERSE_MODELING 2 PS27 to KF1

-solutions 3 4
 -uncertainty 0.05
 -phases
 SiO2(a)
 Calcite
 Dolomite
 Halite
 Sylvite
 Gypsum
 # Fluorite # or F-illite
 Kaolinite
 Illite
 Pyrite dis
 Fe(OH)3(a) pre
 O2(g)
 -minimum

END

I.3 Selected thermodynamic constants used for PHREEQC modelling

Table I.1 Selected equilibrium constants at 25°C from PHREEQC database (Parkhurst and Appelo, 1999), used for saturation index calculations and forward modelling of Calvinia groundwaters.

Reaction	log K at 25°C
$\text{H}_2\text{O} = \text{OH}^- + \text{H}^+$	-14.0
$2 \text{H}_2\text{O} = \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$	-86.08
$2 \text{H}^+ + 2 \text{e}^- = \text{H}_2$	-3.15
$\text{CO}_3^{2-} + \text{H}^+ = \text{HCO}_3^-$	10.329
$\text{CO}_3^{2-} + 2 \text{H}^+ = \text{CO}_2 + \text{H}_2\text{O}$	16.681
$\text{CO}_3^{2-} + 10 \text{H}^+ + 8 \text{e}^- = \text{CH}_4 + 3 \text{H}_2\text{O}$	41.071
$\text{SO}_4^{2-} + \text{H}^+ = \text{HSO}_4^-$	1.988
$\text{HS}^- = \text{S}^{2-} + \text{H}^+$	-12.918
$\text{SO}_4^{2-} + 9 \text{H}^+ + 8 \text{e}^- = \text{HS}^- + 4 \text{H}_2\text{O}$	33.65
$\text{HS}^- + \text{H}^+ = \text{H}_2\text{S}$	6.994
$\text{NO}_3^- + 2 \text{H}^+ + 2 \text{e}^- = \text{NO}_2^- + \text{H}_2\text{O}$	28.570
$2 \text{NO}_3^- + 12 \text{H}^+ + 10 \text{e}^- = \text{N}_2 + 6 \text{H}_2\text{O}$	207.08
$\text{NH}_4^+ = \text{NH}_3 + \text{H}^+$	-9.252
$\text{NO}_3^- + 10 \text{H}^+ + 8 \text{e}^- = \text{NH}_4^+ + 3 \text{H}_2\text{O}$	119.077
$\text{NH}_4^+ + \text{SO}_4^{2-} = \text{NH}_4\text{SO}_4^-$	1.11
$\text{H}^+ + \text{F}^- = \text{HF}$	3.18
$\text{H}^+ + 2 \text{F}^- = \text{HF}_2^-$	3.76
$\text{Ca}^{2+} + \text{H}_2\text{O} = \text{CaOH}^+ + \text{H}^+$	-12.78
$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3$	3.224
$\text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}^+ = \text{CaHCO}_3^+$	11.435
$\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4$	2.3
$\text{Ca}^{2+} + \text{F}^- = \text{CaF}^+$	0.94
$\text{Mg}^{2+} + \text{H}_2\text{O} = \text{MgOH}^+ + \text{H}^+$	-11.44
$\text{Mg}^{2+} + \text{CO}_3^{2-} = \text{MgCO}_3$	2.98
$\text{Mg}^{2+} + \text{H}^+ + \text{CO}_3^{2-} = \text{MgHCO}_3^+$	11.399
$\text{Mg}^{2+} + \text{SO}_4^{2-} = \text{MgSO}_4$	2.37
$\text{Mg}^{2+} + \text{F}^- = \text{MgF}^+$	1.82
$\text{Na}^+ + \text{H}_2\text{O} = \text{NaOH} + \text{H}^+$	-14.18
$\text{Na}^+ + \text{CO}_3^{2-} = \text{NaCO}_3^-$	1.27
$\text{Na}^+ + \text{HCO}_3^- = \text{NaHCO}_3$	-0.25
$\text{Na}^+ + \text{SO}_4^{2-} = \text{NaSO}_4^-$	0.7
$\text{Na}^+ + \text{F}^- = \text{NaF}$	-0.24
$\text{K}^+ + \text{H}_2\text{O} = \text{KOH} + \text{H}^+$	-14.46
$\text{K}^+ + \text{SO}_4^{2-} = \text{KSO}_4^-$	0.85
$\text{H}_4\text{SiO}_4 = \text{H}_3\text{SiO}_4^- + \text{H}^+$	-9.83
$\text{H}_4\text{SiO}_4 = \text{H}_2\text{SiO}_4^{2-} + 2 \text{H}^+$	-23.0
$\text{H}_4\text{SiO}_4 + 4 \text{H}^+ + 6 \text{F}^- = \text{SiF}_6^{2-} + 4 \text{H}_2\text{O}$	30.18

Table I.2 Selected solubility constants at 25°C from PHREEQC database (Parkhurst and Appelo, 1999), used for saturation index calculations and forward modelling of Calvinia groundwaters.

Mineral	Chemical formula	log k_p at 25°C
calcite	CaCO_3	-8.48
fluorite	CaF_2	-10.6
quartz	SiO_2	-3.98
amorphous silica	SiO_2	-2.71
gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-8.48
gibbsite	$\text{Al}(\text{OH})_3$	8.11
amorphous alumina	$\text{Al}(\text{OH})_3$	10.8
kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	7.435
albite	$\text{NaAlSi}_3\text{O}_8$	-18.002
anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	-19.714
K-feldspar	KAlSi_3O_8	-20.573
K-mica	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	12.703
chlorite(14A)	$\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$	68.38
Ca-montmorillonite	$\text{Ca}_{0.165}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2$	-45.027
talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	21.399
illite	$\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$	-40.267
chrysotile	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	32.2
hematite	Fe_2O_3	-4.008
goethite	FeOOH	-1.0
amorphous iron hydroxide	$\text{Fe}(\text{OH})_3$	4.891
pyrite	FeS_2	-18.479
iron sulphide	FeS	-3.915
Gases		
carbon dioxide	CO_2	-1.468
oxygen	O_2	-2.8983
hydrogen	H_2	43.0016
nitrogen	N_2	-3.1864
hydrogen sulphide	H_2S	-7.9759
ammonia	NH_3	-2.8502
methane	CH_4	1.7966

Table I.3. Solubility constants at 25°C from WATEQ4F database (Ball and Nordström, 1991), used for saturation index calculations in batch test 3.

Mineral	Chemical formula	log K_p at 25°C
calcite	CaCO_3	-8.48
fluorite	CaF_2	-10.6
quartz	SiO_2	-3.98
amorphous silica	SiO_2	-3.018
portlandite	Ca(OH)_2	22.8
wollastonite ^a	CaSiO_3	19.996

^a K_{sp} for wollastonite taken from MINTEQA2 database (Allison et al., 1991).

References

- Allison, J.D., Brown, D.S. and Novo-Gradac, K.J. (1991). *MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems*. Version 3.11 User's Manual. US Environmental Protection Agency.
- Ball, J.W. and Nordström, D.K. (1991). *User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, minor, trace and redox elements in natural waters*. Open-File Report No. 91-183. U.S. Geological Survey, Menlo Park, California, 189 p.
- Parkhurst, D.L. and Appelo, C.A.J. (1999). *User's guide to PHREEQC (version 2) - a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*. Water-resources investigations report 99-4259. U.S. Geological Survey, Denver, Colorado, 312 p.

between boreholes 73 and 54 inside the pipe, and 52 on the edge of the pipe, which intercepts brecciated material from a depth of 60 m downwards (Murray and Tredoux, 1998b).

3.4.2 Vertical profiles

The difference in physical and chemical properties of groundwater inside and outside of the breccia is also evident from vertical logging of field parameters down the boreholes. Figure 3.4 illustrates how pH, EC, dissolved oxygen, pe and temperature vary with depth in uncased boreholes 53, 54B and 55. The measurements were taken during dewatering of the Kopoasfontein breccia pipe in August 1999. Borehole 54B is located in the breccia pipe, while the other two are outside, 55 in the Tierberg shales and 53 through a dolerite sheet, approximately 100 m and 300 m away from the pumping borehole, 73, respectively (See Figure 3.3).

Temperature

Typical heat flow in continental crust is in the order of 40 to 70 mW/m², which produces temperature gradients that increase with depth at a rate of 20 to 35°C/km, assuming a typical thermal conductivity of 2 W/(m.K). Stable cratons will produce geothermal gradients towards the lower edge of this range, while higher heat flow is found in tectonically active areas (Ingebritsen and Sanford, 1998; p. 178-180). The temperature gradients for boreholes 53 (26°C/km) and 55 (32°C/km) fall within the typical range.

Perturbations of the natural thermal gradient are usually related to groundwater flow (Ingebritsen and Sanford, 1998; p.180) and areas of high recharge may be characterised by isothermal or even negative temperature gradient profiles to substantial depths. The near-vertical temperature profile for borehole 54B is related to the high permeability of the brecciated rock material and suggests that mixing by advection, rather than thermal conduction is controlling the temperature of groundwater inside the pipe. This could be strongly influenced by the pumping at nearby 73. The higher temperature in the breccia pipe groundwater, compared with the near surface temperatures in the other boreholes, is in agreement with the values measured at the wellhead (Table 3.2).