ASPECTS OF THE GEOCHEMISTRY OF SOME SELECTED SOUTH AFRICAN FINE GRAINED SEDIMENTS

by

R.V. DANCHIN

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A. SUMMARY

Major and trace element abundance data are reported for a total of 323 Southern African argillaceous rocks, ranging in age from the unique three billion year old Fig Tree shales to those of the Triassic Beaufort Series of the Karroo System. In addition, less than two micron clay fractions have been separated from thirty-three of these sediments, and analysed for their major components, as well as the alkali and alkaline earth trace metals. Estimates of the average chemical and mineralogical compositions of these sediments are presented, and compared with similar compilations recorded for argillites from other parts of the world.

Studies pertaining to the origin of the clay minerals are reviewed, and it is concluded that the bulk of these minerals, present in shales and siltstones, do not originate in their depositional environments. It is shown that the clay minerals can rarely be employed to provide direct evidence relating to the chemistries of their depositional environments, and that in many instances they are more useful in providing information as to the chemical natures of their source rocks, and the climatic conditions prevailing in the provenance areas.

The major element abundances and inter-element ratios have been used, where possible, to define the degree of chemical uniformity within the various sequences studied, and to provide information pertaining to the physical and chemical conditions prevailing during the deposition of many

of these sediments. Particularly interesting in this respect are the shales of the Fig Tree Series, which are believed to have been derived from basic or ultrabasic provenance areas, and deposited in relatively deep water. Shales sampled from the Bokkeveld Series of the Cape System show a remarkable degree of chemical uniformity, both with respect to the absolute abundances of the major and trace elements, and also a number of inter-element ratios. Sediments from the Northern Ecca Facies of the Karroo System display a number of distinct chemical differences compared to those sampled from the Central, Western and Southern Ecca Facies. Submarine shales of uncertain stratigraphic location dredged from the Agulhas Bank have major element compositions very similar to onshore Bokkeveld Series shales.

Pyrite and siderite bearing carbonaceous shales from the Northern Ecca Facies of the Karroo System have been studied in some detail. It is shown that in most instances, increased production of pyrite occurs during periods of reduced deposition, and that there is a distinct relationship between organic matter content and pyrite growth. It is suggested that in the presence of both anionic species, the sulphides compete more favourably for dissolved iron than does the carbonate ion. It is further shown that in addition to the pyrite and organic matter contents, the Si/Al ratio may often be effectively used as a measure of relative rates of deposition.

Major element variations with geological age have also been studied in some detail. It is shown that no

systematic variation could be detected for calcium, sodium or aluminium. In the case of potassium, however, there is an increase in abundance from the Ancient Fig Tree Shales, reaching a peak in the late Precambrian or early Cambrian sediments, whereafter the average potassium contents of the samples studied decrease. The possible roles played by various life forms, both marine and terrestrial, are critically examined. Magnesium, on the other hand, decreases in abundance from the Precambrian to the younger shales, and this feature is attributed to the chemical compositions of the respective source rocks, and the more alkaline weathering conditions which are presumed to have been operative during Precambrian and Cambrian times.

Abundance data for the trace alkali and alkaline earth elements are presented for the various shales and separated clay fractions studied, and these are compared with values for other sediments recorded in the literature. The factors influencing the distribution of these elements in the external cycle are examined in some detail.

Particularly interesting in this respect is the element cesium. On the basis of published abundance data for Cs in various sediments and natural waters, it is shown to be highly unlikely that detrital clays could act as a sink for oceanic Cs, and in fact, there is a distinct possibility that Cs is desorbed from the clay minerals in the marine environment. It is also shown that for some sediments, the nature of the detritus entering the basin of deposition, and the rate at which it is deposited, play important roles

in determining the ultimate Cs abundances of these rocks. These factors render suspect the use of Cs as an indicator of fresh water as opposed to marine deposition. In the case of Rb, it is shown that the K/Rb ratios of the shales and clays studied show very little variation about a mean value of 170, which is distinctly lower than K/Rb ratios recorded for the majority of igneous rock types.

The abundance of Li in argillaceous rocks is shown, to an extent, to be dependent on mineralogy, and in many instances this element exhibits well developed relationships with both magnesium and iron. Of the alkali elements, Li shows most promise as a potential indicator of fresh water as opposed to marine deposition.

Abundance data for Ba and Sr in the South African shales and clays are also given, and the factors governing the distribution of these elements in argillaceous rocks are discussed.

It is concluded that the alkali and alkaline earth trace metals are largely incorporated in the clay minerals at their sites of formation, and that ion exchange reactions in the marine environment may not be as widespread as previously believed.

CONTENTS. Volume I

CONTENTS. Volume II

B. INTRODUCTION

Sedimentary rocks blanket most of the Republic of South Africa and South West Africa and almost nothing is known about their chemical or mineralogical compositions, particularly the more fine-grained varieties. Knowledge is also meagre concerning the depositional environments of most of these sedimentary formations, particularly the rocks of the vast Ecca Series of the Karroo System, which, unlike its equivalents in Europe and the United States of America, contain virtually no diagnostic fossils.

Accordingly the present study was commenced in 1965, with the considerable assistance of the Anglo American Corporation of South Africa. Its primary objective was to accumulate a body of sound analytical data, both major and trace element, for some of the more important representatives of the South African stratigraphic sequence. A reconnaissance chemical study of this type was considered desirable for three main reasons.

First, in the absence of any previous information, it would define the degree of chemical variation both within the various sedimentary formations and between them. Second, it was hoped that these data could place limitations both on the nature of the depositional environments of the sediments studied, and also on the chemical nature of their provenance areas. Such information would be most useful in indicating the course of future research in this connection. Finally, the need for sound analytical data in clay rich rocks has been repeatedly stressed because of the

general paucity of such analyses, and the dubious quality of much of the data available in the literature. Information of this type is extremely valuable in the compilation of crustal abundance tabulations, and studies relating to the chemical variation of the world's oceans and crustal rocks with geological age.

To this last end, considerable care was taken to assure both optimum precision and accuracy of the various analyses undertaken. For example, in the case of the major elements, for which results are presented here, approximately two years were devoted in collaboration with other members of the Geochemistry Department of U.C.T. to fully investigating the advantages and limitations of several published X-ray fluorescence sample preparation techniques. The details of these studies are presented in Section I of this text. Likewise for cesium, where determinations were made using an optical spectrographic technique, the working curve was calibrated by isotope dilution mass spectrometry, and for lithium which was also determined using an optical spectrographic technique, calibration was improved using atomic absorption spectrophotometry.

The thesis is composed of two volumes, Volume I is the text and Volume II contains the analytical and mineralogical data as well as details concerning the localities of the various samples studied. The letter "A" affixed to any given table of results indicates that the table concerned is located in Volume II of the thesis. Diagrams referred to in the text are located in Volume II.

C. A DISCUSSION RELATING TO THE DISTRIBUTION OF THE MAJOR ELEMENTS IN ARGILLACEOUS ROCKS

(i) Mineralogy:

The complexity of chemical composition of argillaceous rocks as well as their fine grained nature have made determinations of average mineralogical composition extremely difficult. The few estimates thus far made, (Leith and Mead, 1915; Clark, 1924; and more recently Yaalon 1962; and Shaw and Weaver, 1965), indicate that clay minerals constitute about 50% of the average shale, followed by quartz and chert (30%), feldspar (5 - 10%), with iron oxides, carbonates and a variety of other minor minerals making up the remaining 10 - 15%.

The clay minerals have naturally commanded the most interest, and with the advent of X-ray diffraction techniques there has been an immense stream of publications from geologists, geochemists and mineralogists discussing and debating their geological significance. Undoubtedly the most controversial and fundamental problem confronting clay petrologists concerns the origin of clay minerals in sediments; that is, are these minerals predominantly detrital, or have the effects of diagenesis been sufficiently intense as to mask characteristics of the individual clays inherited from their source areas? Because of the particular significance of this controversy to the problems to be discussed here it is necessary to review the available evidence in some detail.

It is generally accepted that clay minerals undergo various structural and chemical changes during transportation deposition and burial, and that progressive diagenesis tends to erase many original clay distribution features. For this reason a large number of studies have been carried out on Recent sediments where diagenetic processes have not been active to the extent presumed for ancient sediments, and the original patterns are still by and large preserved in sedimentary basins of known extent and provenance.

Early work by Correns (1937, 1939) showed that clay size material of Recent sediments is virtually all crystalline, and that kaolinite and halloysite are often the dominant clays in sediments from the equatorial Atlantic Ocean. Likewise Dietz (1941, see Weaver, 1967) concluded "... clay mineral distribution on the sea floor is regionally similar to that on land in having a relative abundance of kaolinite and iron oxide in tropical regions, and of illite and montmorillonite in temperate regions. This suggests that deep-sea clays are terrestrially derived".

Grim, Dietz and Bradley (1949) studied sediments from the Gulf of California and California coast, and found that all samples contained illite, montmorillonite and kaolinite, and some a chloritic mineral. They observed that illite was the most abundant and kaolinite the least abundant clay type, and attributed lateral variation to the gradual formation of chlorite or illite at the expense of kaolinite. Similar results were noted by a number of

workers (Grim and Johns, 1954; Griffin and Ingram, 1955; Powers, 1957; Milne and Earley, 1958; and Johns and Grim, 1958). In each of these studies lateral variations of clay mineralogy are explained by alteration and modification of pre-existing clay minerals, and in each case the authors attributed the seaward increase of illite and chlorite relative to kaolinite or montmorillonite to various forms of marine diagenesis.

In other studies (Taggart and Kaiser, 1960; and Griffin, 1962; for example) lateral variations are attributed to difference in supply from various source sediments and current distribution, and no appreciable alteration as a result of diagenesis was recorded.

A further mechanism which has been proposed to explain these variations in clay composition is differential flocculation. Van Andel and Postma (1954) suggested that in the Gulf of Paria illite and kaolinite were flocculated earlier than montmorillonite, and that consequently montmorillonite tends to be most abundant in the open gulf in contrast to illite and kaolinite which are concentrated in the delta portion. Whitehouse et al. (1960) and Porrenga (1967) have determined the settling velocities of illite, kaolinite and montmorillonite in waters of varying chlorinities, and they found that on entering the sea the settling velocities of kaolinite and illite increase sharply, whereas montmorillonite was only slightly influenced by the increased salinity.

Hurley et al. (1959, 1961, 1963) in potassium - argon age determinations of Recent marine and deltaic muds

have made an important contribution to this debate. Ages ranging from 100 to over 800 million years were recorded, indicating a detrital origin for the vast majority of these clays. They found that silt sized illitic material from the Mississippi River Delta gave an average age of 280 million years, whereas the clay size fractions from the same samples give an average age of only 166 million years. They concluded that this age could not be explained solely in terms of the Palaeozoic shales from the central and eastern portions of the source area, but could possibly be due to mixing of clay detritus from younger sediments in a western source area. These variations could equally be explained by adsorption of potassium during deposition in the marine environment.

Clay mineral studies on Recent non-marine sediments are considerably scarcer than for their marine counterparts. Cuthbert (1944), Rateev (1952), Grim et al. (1960), Moore (1961) and Droste (1961) all examined clay mineral assemblages in various lacustrine environments, and in each case found no evidence of diagenetic changes.

With regard to ancient sediments, numerous works relating to the clay mineral assemblages in a vast variety of different rocks have appeared in the literature in recent years. In most of these studies, attempts have been made to correlate various clay groupings with depositional environments and/or source areas.

Much of the pioneering work appears to have been done by Millot (1949, 1952, 1953 for example), who was the

first person to make a detailed attempt to relate clay minerals to environment of deposition. He has studied large numbers of rocks from various European stratigraphic sequences whose modes of origin are well documented on palaeontological or petrographic evidence. He differentiates between three major depositional environments, thus:-

(a) In lacustrine sediments where the lake is believed to have contained "aggressive", or acid waters, that is to say waters of low pH engaged in active alkali leaching, the dominant clay mineral is kaolinite (80 - 100%) with accessory amounts of illite, chlorite and montmorillonite. K_2O in these sediments is less than 2%, while MgO is less than 1%.

(b) In non-aggressive lacustrine or lagoonal sediments, where stagnant conditions generally prevail, and carbonate accumulation is a common feature, illite is the most abundant clay followed by chlorite and montmorillonite, and occasionally minerals of the sepiolite-attapulgite group. Kaolinite is rare. The pH in these environments is believed to be between 7.4 and 8.8, and according to Millot the K_2O content of the sediments lies between 5 and 8%, and the MgO content is about 4%.

(c) In sediments of marine origin illite is invariably present, and is particularly abundant in calcareous sediments. Chlorite and kaolinite are usually the subordinate clays, except in carbonate rocks where the latter is rare. K_2O lies commonly between 3 and 5.5%, while MgO is generally close to 2.5%.

Numerous studies since Millot's early work have shown that this relationship exists in many instances. For example, Degens et al. (1957) studied a series of Pennsylvanian sediments and found that the illite - kaolinite ratio is statistically higher in marine and brackish-water shales than in fresh-water shales. Pryor and Glass (1961) studied the clay compositions of Cretaceous and Tertiary sediments, and found that clays deposited in the fluviatile environment were dominantly kaolinitic, whereas in the outer neritic environment montmorillonite predominated, and those from the inner neritic environment contained approximately equal amounts of illite, montmorillonite and kaolinite.

A review of a substantial number of other clay mineral studies (Parham 1966) has shown that in basins of sediment accumulation kaolinite is concentrated closer to the shore with respect to illite, and that illite reaches a maximum abundance seaward of kaolinite.

Grim (1951) pointed out that kaolinite is relatively less abundant in ancient marine sediments, and must therefore be altered during burial and diagenesis to some other mineral, but Weaver (1958) says that this relationship probably exists rather because nearshore sediments tend to be preferentially destroyed by erosion.

Weaver (1960) showed that marine black shales rich in carbonaceous material contain clay mineral assemblages of either pure illite or mixed layer illite-montmorillonite or both, whereas fresh-water shales of this type almost invariably have kaolinite as the abundant clay.

Brack-water shales show groupings transitional between the two types.

It would therefore appear from these data that certain broad generalizations linking clay mineralogy to depositional environment are permissable, and Weaver (1958), who for many years has stressed the importance of detrital contribution as opposed to that of diagenesis in controlling ultimate clay mineral assemblages, has reviewed data from many parts of the world, and lists the following conclusions:-

(i) No particular clay mineral is restricted to any particular depositional environment.

(ii) Illite, montmorillonite, and mixed layer illite-montmorillonite can occur in abundance frequently as the only clay minerals present, in any one of the major depositional environments.

(iii) Kaolinite is mainly dominant in fluviatile environments, although it occurs in abundance in all environments.

(iv) Chlorite is seldom, if ever the dominant clay mineral and is generally least abundant in the marine environment.

(v) Continental shales are seldom monomineralic.

(vi) Contrary to previous opinion (Grim, 1951) montmorillonite is quite common in ancient sediments, and is found in abundance in Jurassic, Pennsylvanian and Mississippian sediments, and is present combined with illite and chlorite in the

Middle and Lower Ordovician, and the Upper and Middle Cambrian. Weaver acknowledges that montmorillonite is rarer in Palaeozoic sediments than in those from the Tertiary, but attributes this in part to differences in weathering between the two eras, rather than diagenesis over a long period.

(vii) Glauconite is often considered as an ideal example of a clay which forms by diagenesis under marine conditions, but Weaver notes that even in this case the nature of the source material will determine the type of glauconitic clay produced. Moreover several authors (Parry and Reeves, 1966; Porrenga, 1967; 1968) have cited instances of glauconite formation in the lacustrine environment. Apart from a few exceptions, however, glauconite is recognised as a marine mineral often formed as an alteration product of biotite (Galliher, 1936) or a variety of other minerals (Hendricks and Ross, 1941) with the alteration taking place under reducing conditions and slow deposition. Hurley et al. (1960) investigated the age of glauconites, and found ages consistent with the geological age and with currently held views concerning the marine diagenesis of this clay.

Weaver concludes on the basis of his studies that clay minerals do not as a rule originate in their depositional environments, and that they are not strongly modified by diagenesis during and after deposition. In a

discussion of clay mineral reactions in the marine environment Weaver (1958b) differentiates between ion exchange reactions, the regrading of degraded clay lattices, and what he refers to as diagenesis proper. He regards the formation of a clay mineral from a gel or from colloidal material or by altering the basic lattice of a pre-existing mineral as the only true forms of diagenesis. Moreover Weaver contends that the most common process acting on clays in the marine environment is cation exchange.

There is therefore conflict of opinion as to whether processes such as the regeneration of degraded chlorite or the collapse of montmorillonite after potassium adsorption should be considered diagenetic or not. Weaver cites several examples of how degraded clays, according to the environment in which they find themselves, adsorb locally available cations and in so doing come to equilibrium with their surrounding environment. This is a particularly important conclusion from the geochemist's point of view, for, regardless of whether the basic clay lattice is altered during deposition and burial, or not, if they reach even partial equilibrium with the surrounding media, they should for certain key elements e.g. Ca, K, Na and Mg, be capable of retaining sufficient of their newly acquired characteristics as to provide information relating to the chemical nature of the depositional environment. The degree of equilibrium attained by any particular clay will depend largely on the length of time that it is exposed to the environment and the degree of degradation or capacity to partake in ion exchange reactions of this type.

Important in this respect are the possible effects of post depositional alteration (epigenesis), and it would appear that these effects have been somewhat under-estimated by earlier workers, and that they are in fact comparatively widespread. It is emphasized that these effects are distinct from those acting on the sediment during deposition and the early stages of burial. More data are available for sandstones than for shales. Glass (1958) showed that kaolinite is more abundant in Pennsylvanian sandstones than in intercalated shales, and that ".... kaolinite crystals form in sand bodies prior to exposure, and that exposure in outcrop augments the process".

Kulbicki and Millot (1961) described the post depositional alteration in a series of Cambrian sandstones of the Sahara, and found that those sediments containing petroleum contain kaolinite, whereas in non-petroliferous bearing strata illite has formed at the expense of kaolinite. They believed that the presence of petroleum in the sand had blocked the secondary formation of illite by interstitial saline waters. Permeability is therefore an important factor in clay mineral formation not only in outcrop, but also subsurface.

Smoot (1960) studied sediments from pre-Pennsylvanian strata in Illinois and found that in the permeable sandstones the clay assemblage consisted of degraded illites, chlorites and kaolinite whereas in the shales the clays were well crystallized illite and chlorite, together with some degraded illite and chlorite and rare traces of kaolinite. Since these strata were intimately

associated and presumed to have had identical depositional environments and clay mineral suites, Smoot suggested that the observed differences were produced after compaction by percolating fluids. Clearly the more permeable sandstones would be more susceptible to alteration of this type.

In shales, studies of post depositional alteration have been concentrated on montmorillonite bearing strata (Burst, 1958); (Powers, 1958; Weaver, 1958b). These authors showed that in Gulf Coast Tertiary sediments montmorillonite decreased with depth, and mixed layer illite-montmorillonite increased. It would seem as if the collapse of expanded montmorillonite layers starts at depths of only 5,000 feet, from where there is a gradual increase to 12,000 - 14,000 feet where about 70% of the montmorillonite layers have collapsed. In this respect the work of Szádeczky-Kardoss et al. (1968a,b) is of interest. These workers converted montmorillonite to illite in the laboratory at low porosity and water content, and temperatures below 550°C.

These phenomena are of particular importance to petroleum geologists, many of whom believe (see Weaver, 1960; 1967) that clay minerals may act as catalysts in the formation of petroleum, and also affect the migration of hydrocarbons. Hence Weaver has suggested that shales which contain little expanded clay are frequently oil shales in contrast to shales with more abundant expandable clays which could, given the correct conditions, provide sufficient water to flush out the contained hydrocarbons.

In summary, therefore, several points of considerable interest to the sedimentary geochemist have emerged from this survey of clay mineral studies in rocks and Recent sediments.

(a) Each of the five major types of clay are commonly found in all depositional environments.

(b) In fluviatile environments kaolinite is the dominant clay.

(c) In basins of sediment accumulation kaolinite is concentrated closer to the shore with respect to illite.

(d) Clay minerals are detrital in origin, and most strongly reflect the character of their source material. Consequently it is difficult on the basis of clay studies alone to identify specific depositional environments. Clays have however been shown to be useful in assigning a series of environments sequentially, ranging from those with predominantly marine characteristics to those with predominantly continental characteristics. In addition clay mineral studies have been shown to be particularly useful in single sedimentary basins of limited extent (Weaver, 1958; Gauthier, 1967; Stevaux, 1967; Fontes et al; 1967), but it is clear that only rarely will environmental criteria from one basin be directly applicable to sediments of other basins unless they both had similar source areas and similar types of tectonic development. Furthermore

it has been shown that clays are best used for environmental studies in rocks younger in age than Carboniferous, since clay assemblages become less complex with age; and in areas where major changes of depositional environment are involved, for example continental versus marine shales rather than representatives from inner and outer neritic environments.

Lastly, since most chemical changes during deposition and early burial are believed to result predominantly from ion exchange reactions it is deduced that, provided post depositional changes have not been too severe, and that some measure of equilibrium was attained during deposition, it should theoretically be possible to differentiate chemically between fine grained sedimentary rocks laid down in different environments.

(ii) <u>The Sedimentary Norm</u>

The desirability of a sound knowledge of the mineralogical composition of argillaceous rocks has been repeatedly stressed, as also have the deficiencies of the X-ray diffraction techniques generally used to derive this information. As will be shown in a later section, a knowledge of the abundances of certain key indicator minerals such as pyrite and siderite are essential in environmental studies. In almost all cases these minerals are present in sufficiently small amounts as to escape detection by X-ray diffraction analysis. Quantitative studies are impossible.

For the major minerals, the degree of success attained by quantitative X-ray diffraction studies depends largely on the mineralogy of the rocks under consideration. Wedepohl (1964), for example, has presented meaningful data for the "Kupferschiefer" of North-Western and Central Germany. The samples studied by Wedepohl (op.cit., p.322) contain abundant carbonates, together with lesser amounts of feldspar and quartz; clay minerals do not generally comprise more than 35% of the rock. Further, the clay mineralogy is not complex, illite being by far the most abundant contributor. For shales containing only minor amounts of carbonate and feldspar, and a preponderance of assorted clay minerals, on the other hand, semi-quantitative X-ray diffraction analysis is considerably more hazardous.

In the first instance, many of the mounting techniques used in X-ray diffraction studies produce erroneous results. Gibbs (1965, 1966) has shown that many of these techniques produce size segregated mounts. Included in this category are the pipette-on-glass slide, centrifuge-on-glass slide and centrifuge-through-ceramic tile techniques.

Further, more serious problems arise in the interpretation of the diffraction data, and the methods generally used to calculate the relative amounts of the different minerals present in the sample. Pierce and Siegel (1969) have calculated the percentages of different clay minerals present in a complex assemblage in twenty-five samples by five different methods in common usage, but using the same diffractograms. The results are most alarming. Not only are the actual abundances significantly different for each

of the five methods chosen, but also different methods show different trends between adjacent samples. The authors noted however that although calculation by each of the methods gave different results, each method is internally consistent, and can give results which suggest meaningful geological trends. Difficulty arises however when results from different laboratories are compared.

In addition to these two difficulties the semi-quantitative analysis of fine grained sediments by X-ray diffraction is fraught with numerous other problems - sample preparation, degree of crystallinity and chemical uniformity within and between mineral species, particle size and preferred orientation effects to mention but a few.

Inherent and other difficulties in X-ray diffraction techniques such as those mentioned above have prompted a number of workers (Imbrie and Poldevaart, 1959; Miesch, 1962; and Nicholls, 1962; for example) to devise schemes for recalculating chemical analyses of sediments to produce normative amounts of minerals presumed to be present in the rock. These authors have correctly pointed out that used in conjunction with instrumental techniques such as X-ray diffraction or differential thermal analysis, considerably more meaningful data are made available to sedimentary petrologists and geochemists.

One reason why these methods, and for that matter geochemical methods in general, have only infrequently been employed to assist in problems of sedimentary geology, is that techniques of major element analysis of silicate rocks have been considered too difficult, time consuming, and in

many cases inadequate. However recent advances in analytical techniques, particularly those involving automated or semi-automated instrumental methods have made the determination of nearly all the major components of silicate rocks relatively simple and very rapid.

Of the numerous sedimentary norm schemes which have been proposed, the most flexible is that of Nicholls (1962). In this method, unlike that of Imbrie and Poldevaart (1959), no attempt is made in the initial stages to recalculate in terms of minerals actually known to be present. Before determining the normative "clay" abundances, the following molecules are cast - FeS, excess Fe_2O_3, $Ca_5(PO_4)_3OH$, $CaCO_3$, $MgCO_3$, and $FeCO_3$. These in turn provide the normative abundances of pyrite, excess iron, apatite, calcite, dolomite and siderite in the final grouping, and a knowledge of each is essential in environmental studies, as will be shown in a later section. It is emphasized that each of these minerals is generally present in shales at levels far below the limits of detection, or at any rate levels suitable for even semi-quantitative analysis by X-ray diffraction techniques.

(iii) NORMATIVE SILICATE MINERALS

Whereas the allocation of major elements for the recalculation of the non-silicate minor minerals enumerated above is relatively straightforward, the method runs into severe difficulties in the allocation of alumina, and the recalculation of the normative "clays". The scheme caters for the following molecules:- $Fe_{12}Si_8O_{20}(OH)_{16}$ and $Mg_{12}Si_8O_{20}(OH)_{16}$ which are grouped together as normative

chlorite, $K_2\ Al_4\ (Si_6\ Al_4\ (Si_6\ Al_2)\ O_{20}\ (OH)_4$, $Na_2\ Al_4\ (Si_6\ Al_2)\ O_{20}\ OH_4$, $Al_4\ Si_8\ O_{20}$, which are grouped as normative illite, and $Al_4\ Si_4\ O_{10}\ (OH)_8$ which is returned as normative kaolinite. Excess SiO_2 is taken to represent normative quartz. It will be appreciated that the generalizations involved in such a scheme are broad indeed, since of the clays only Kaolinite has what might be described as a normative formula. The variations encountered in the compositions of all other clays are large, as may be seen in the analyses of illites, chlorites and montmorillonites presented by Grim (1968), or in Table 26A of this work.

A further problem is that neither plagioclase or K-feldspar appear amongst the normative formulae, and Nicholls (1962) points out that if feldspar is in fact present (as is usually the case,) in the rock, the mica-type formulae will be seriously overestimated. In the Imbrie and Poldevaart (1959) scheme, normative albite is calculated, but no allowance is made for the possible presence of K-feldspar. This is the major defect of the scheme, since shales frequently contain as much as ten percent or more total feldspar (Yaalon 1962).

Also of interest is the fact that all the K in the rock is allocated to illite, and all the available Fe and Mg in the silicate fraction to chlorite. Consequently an illite-chlorite trend, for example, could be equally well demonstrated by the use of ratios such as K/Fe+Mg or Al/Mg (Porrenga 1967). Similarly in predominantly illite-kaolinite assemblages the Al/K ratio would be as informative as the calculated normative ratios, since the same assumptions

i.e. the absence of feldspar and the normative nature of kaolinite are implied in each case.

The above mentioned difficulties detract somewhat from the versatility of this technique, but the norm nevertheless provides a means of usefully comparing the analyses of different argillaceous rocks, albeit broad, and, more importantly, it provides information as to the non-clay mineral composition of the rock generally unobtainable from X-ray diffraction studies.

In this work emphasis will be laid on the use of interelement ratios for studying the chemical variations in the rocks under consideration, and for the preliminary examination of the overall silicate mineral contents, an alternative procedure has been devised, more pertinent to the type of problems confronted in a study of this nature.

In both local and regional sedimentary geochemical studies a knowledge of the quartz, total clay, and feldspar contents of the rocks often provides useful information. Frequent examples, especially of the use of the quartz content of argillites appear in the literature.

In the former category Spears (1964) in a study of the Westphalian Mansfield Marine Band of Yorkshire, relates the quartz content of samples taken at even intervals from a 20 foot section, to the rate of sedimentation, and in turn to the grain size of the sediments. Bloxam and Thomas (1969) in three studies of the Gastrioceras Subcrenatum marine band of the South Wales Coal field successfully equate quartz content to sedimentation rate, and ultimately, distance of

deposition from the shoreline. In this work 63 samples were collected from three vertical sections ranging in total thickness from 5 to 14 feet.

On the other hand, on a more regional basis, Shaw and Weaver (1965) have demonstrated the existence of a significant relationship between gross mineralogy and environment of deposition. These authors have prepared a series of mineral variation diagrams for environments ranging from fluviatile to deep-sea, reproduced here as Fig. 1.

Surveillance of these plots shows large scale variations in the relative amounts of quartz, clay, feldspar and carbonate, as one traverses from the riverine environment to the deep-sea. It is seen that quartz and most of the feldspar are preferentially deposited near the shore, while the clay minerals predictably, are carried further to the shelf, slope and deep-sea environments.

The variations observed by Shaw and Weaver are of considerable magnitude. Quartz varies from greater than 50% in the fluviatile-bay environment to less than 20% in the slope and deep-sea sediments, while the total clays vary from about 30% to greater than 70% in the same sequence. These data are summarized in Table 1.

Table 1.

Depositional Environment	% Quartz	% Clay	% Carbonate	% Feldspar
Fluviatile	52	29	4	15
Lagunal	52	44	2	2
Deltaic	29	65	2	4
Slope	18	72	8	2
Deep-sea	16	62	15	4

Clearly many exceptions to this general trend will be found, but in reconnaissance studies of the type under consideration here where knowledge of depositional environment is extremely scant in most instances, and fossil evidence lacking, a broad (even if somewhat arbitrary) classification of this type appears attractive. Fruitful interpretation seems likely therefore if the approximate quartz, total clay, feldspar and carbonate contents are known, due to the ranges of variation involved.

Several alternative methods for estimating the total free quartz contents of sediments have been proposed. The most widely used method is that of Trostell and Wynne (1940), a chemical technique involving pyrosulphate fusion, and alkali dissolution of the fusion product which leaves free silica for gravimetric determination. The method is precise but time consuming, requiring about eight hours for each batch of analyses, and Till and Spears (1969) have pointed out that limited platinum ware and laboratory

facilities added to the fact that determinations must be done in duplicate, render the technique ideal for small or localised studies but prohibitive when a large number of samples is involved.

Till and Spears (1969) have noted that while X-ray diffraction techniques for the determination of quartz are generally more rapid than chemical ones, the results are usually considerably less precise. These authors have described an attractive diffraction technique involving the use of an added internal standard (boehemite) to the ashed sediment prior to diffraction. Coefficient of variation is claimed to be of the order of 2%. For studies of the type attempted by Bloxam and Thomas (1969) and Spears (1964) where constructive use is made of small variations of quartz content in single rock sections of moderate extent, the latter method seems highly suitable.

In this study, less than 2/u fractions were separated from 33 representative rocks ranging in age from the 3.2 billion year Precambrian Fig Tree shales to those from the Triassic Beaufort Series of the Karroo System. The primary objective was to obtain an accurate picture of their major and trace element contents, but these analyses may also be put to use in the present context along the lines suggested by Miesch (1962).

In this approach a knowledge of the overall clay composition is used to compute, by means of a series of simultaneous equations, the abundance of the total clay in the rock as well as those of quartz and the feldspars. Two major assumptions are involved. First, it is assumed that

the clays collected in the $< 2\mu$ fraction are quantitatively representative of the clays in the total rock. In this case the $< 2\mu$ fractions were collected by gravity settling in a column of distilled water after a 7 hour dissaggregation treatment in an ultrasonic tank. Further details of this technique are given in Chapter I. In addition to the $< 2\mu$ fraction, samples from the 2-10μ and $> 10\mu$ fractions were also retained.

X-ray diffraction analyses of the three fractions produced no detectable differences in the relative clay type abundances between each group. Similar tests using an electron microscope (R.C. McKenzie, pers. comm.) produced equivalent results in fractions from shales which had been previously exposed to ultrasonic treatment.

The second, and more serious assumption is that the $< 2\mu$ fraction contains only clay minerals. This is almost invariably not the case. Various estimates have been made regarding the quartz content of $< 2\mu$ separates from shales, and these range from zero to about 10% (Bradley 1965). It would appear that "clay" fractions collected from recent, unindurated sediments tend to contain more fine quartz than do ancient, lithified sediments.

X-ray diffraction traces of the 33 separated "clays" showed that for some samples (e.g. Ec 14, Table 26 A) the diffraction lines of quartz were completely absent, whereas for others small amounts of quartz were detected. Attempts at semi-quantitative analyses of these separates indicated that for the majority of samples the quartz content was less

than about 7%. Porrenga (1967) in his study of Recent sediments from tropical areas found the quartz content of $< 2\mu$ separates to average between 3 and 5%. Nevertheless in the calculation scheme to follow allowance will be made for probable quartz contamination.

Similarly the clay fractions may contain small amounts of $< 2\mu$ feldspar, but in this case attempts at semi-quantitative determination were unsuccessful below about 5% feldspar. In the vast majority of cases however feldspar diffraction lines were not detected in the separates and the maximum feldspar level in these fractions is believed to be considerably less than 5%. Similar observations were made by Porrenga (1967). Moreover clays where traces of feldspar were detected were invariably separated from shales containing relatively large amounts of feldspar, and the presence of further minute amounts in the clay fraction would not significantly alter the results.

Consider, therefore, a hypothetical shale containing only quartz and clay minerals, and where the composition of the clay fraction is accurately known. For this mixture

$$a_1 \frac{X}{100} + a_2 \frac{Y}{100} = a_3 \qquad \text{——} \quad 1$$

$$b_1 \frac{X}{100} + b_2 \frac{Y}{100} = b_3 \qquad \text{——} \quad 2$$

where a_1, a_2 and a_3 are the amounts of Al_2O_3 in the clay, quartz and total rock respectively. X and Y are the percentage abundances of clay and quartz in the mixture. In equation 2, b_1, b_2 and b_3 refer to the SiO_2 contents of the three components. As an illustrated example, these re-

lationships are expressed graphically in Figs. 2a and 2b. using the overall average values of the 33 separated clay fractions. On a volatile free basis, this average clay (Table 29A) contains 51% SiO_2 and 28% Al_2O_3. In Figs. 2a and 2b. line AB represents the variation of SiO_2 and Al_2O_3 respectively for all possible quartz-clay mixtures. For any given concentration of these elements in the total rock, the percentage clay (quartz) contribution to the mixture may be read off in each case.

Clearly, if the so called pure clay contained a proportion of less than 2 micron quartz, then the measured SiO_2 content of the clay would be too high, and its Al_2O_3 content correspondingly low.

In Figs. 2a and 2b the errors caused by the 5%, 10% and 15% quartz contamination of the clay fraction at any given dilution are given by lines 1, 2 and 3 respectively. A more quantitative estimate of the errors produced by progressive quartz contamination of the "clay" fraction is given by taking as an example concentration values of the average South African shale which contains 66% SiO_2 and 19% Al_2O_3. These errors are given in Table 2.

Table 2.

% Quartz in clay fraction	Estimated % clay	Resultant Absolute error for % clay	Percentage error a) clay	b) quartz
0	68.0	0	0	0
1	67.4	0.6	0.9	1.9
2	67.0	1.0	1.5	3.0
3	66.2	1.8	2.8	5.3
5	64.8	3.2	4.7	9.1
10	61.0	7.0	10.8	18.0
15	57.6	10.4	15.3	24.6

Recalling the variations of these two components recorded by Shaw and Weaver (1965) (Table 1) for the various depositional environments, it is seen that errors produced by up to 10% quartz contamination of the clay fraction are not excessive.

It has already been shown, however, that shales are seldom completely free of feldspar, and therefore three further equations catering for the presence of K-feldspar, sodic and calcic plagioclase may be introduced. Consequently for any particular shale from which a clay fraction has been separated we may write five simultaneous equations of the form:

$$\frac{a_1 X}{100} + \frac{a_2 Y}{100} + \frac{a_3 Z}{100} + \frac{a_4 U}{100} + \frac{a_5 V}{100} = a_6$$

These equations may be solved; with the aid of a computer, for the required 5 unknowns, i.e. the amounts of quartz, clay, K-feldspar, Na-plagioclase and Ca-plagioclase present in the shale. This treatment may be applied to shales where no other Si, Al, K, Na or Ca phase is known to be present. Where necessary, however, a suitable carbonate correction can be made for the Ca content of the whole rock. In this study, the abundances of these elements in orthoclase, albite and anorthite used, were taken from the average values reported by Deer et al. (1965) (Table 3).

Table 3.

Mineral	% SiO_2	% Al_2O_3	% K_2O	% Na_2O	% CaO
K-Feldspar	65	19	16	0	0
Albite	67	20	0	11	0
Anorthite	44	35	0	0	18

The results for various individual shale samples treated in this manner will be discussed later in this volume, but one significant factor to emerge from these calculations is that this treatment has afforded an independent means of calculating the average mineralogic composition of 27 of the shales from which clay fractions were extracted, and these results are presented in Table 4 together with a selection of previous estimates taken from the literature.

Table 4.

Average Mineralogical Composition of Shales

Component (%)	Leith and Mead (1915)	Clarke (1924)	Yaalon (1962)	Shaw and Weaver (1965)	This study (a)	This study (b)
Clay minerals	34	25.0	59	60.9	55	58
Quartz	32	22.3	20	30.8	30	32
Na-Plagioclase	-	-	-	-	4	4
K-Feldspar	-	-	-	-	2	2
Ca-Plagioclase	-	-	-	-	0.5	0.5
Total Feldspar	18	30.0	8	4.5	6	6
Carbonates	8	5.7	7	3.6	2	2
Fe-Oxides	5	5.6	3	0.5	1	1
Others *	2	11.4	3	3	6	1

* Includes organic fraction

The two sets of data, (a) and (b) have both been arbitrarily corrected for 5% quartz contamination in the separated "clay" fractions. For the former, the overall organic matter average for the entire sample population (333) has been used. This figure is not representative since the collection of samples was biased towards carbonaceous shales from the Permian Ecca Series of the Karroo System. In the latter case a weighted average more truly representative of the average South African shale has been used. Carbonates were calculated according to the scheme of Nicholls (1962). The iron oxide situation is difficult to assess since some of the Fe_2O_3 in the $< 2\mu$ fraction (Av. 8.74%, all Fe

expressed as Fe_2O_3) may be present as colloidal Fe_2O_3. Shaw and Weaver (1965) carried out a series of X-ray diffraction experiments using artificial mixtures containing varying amounts of Fe_2O_3 and concluded that the average free iron oxide content of shales does not exceed 0.5%. For the purpose of these calculations all Fe_2O_3 in the $< 2\mu$ fractions was assigned to the clays. If one half of this amount is present as free iron oxide then the average value rises from $< 1\%$ to 3%.

The mineralogical estimates given in Table 4 most closely correspond with those of Shaw and Weaver (1965). These authors used an X-ray diffraction-absorption technique, and their samples, which totalled 300, were North American shales ranging in age from Palaeozoic to Tertiary. If the quartz content of the clay fractions has been overestimated at 5%, then clearly the average clay content increases by a few percent, and correspondence is even more exact.

A further significant feature is that estimates of the three different feldspar types have been made possible by this scheme, and it is seen that the most abundant feldspar in the shales is sodic plagioclase followed by K-feldspar. Calcic plagioclase on the other hand is rare, the average abundance being significantly less than 0.5%. The close agreement of the total feldspar content with the estimate of Yaalon (1962) and Shaw and Weaver (1965) would seem to vindicate the assumption that the feldspar content in the separated "clays" is negligible compared to the abundance in the total rock.

It should be borne in mind however, that for studies of this type, (and this applies equally to the data of Shaw and Weaver (1965) and Yaalon (1962)), fine grained argillites are usually sampled in preference to those of higher silt content. Thus on a regional or world-wide basis the average argillaceous sediment would almost certainly tend to be more quartz and feldspar rich, with a corresponding decrease in the amount of total clay, than is indicated by the estimates in Table 4.

(iv) Normative Non Silicate Minerals

It is most desirable to know the Eh-pH conditions under which a sediment accumulated and the studies of Garrels and his colleagues (Castano and Garrels, 1950, Krumbein and Garrels, 1952; Huber and Garrels, 1953; Huber, 1958; and Garrels and Christ, 1965) have demonstrated that limitations on the possible ranges of the prevailing physico-chemical conditions may be deduced from the nature of various authigenic and diagenetic minerals within the rock, particularly the iron minerals.

In natural environments iron commonly occurs in the form of oxides, hydrated oxides, sulphides and carbonate. A distinction is often drawn (see Nicholls, 1963, for example) between the iron minerals originally precipitated and those now present in the rocks. Nicholls believes that original iron sulphide was precipated as the monosulphide ($FeS.n\ H_2O$) and that this was diagenetically converted to pyrite (FeS_2) the most common sedimentary sulphide form. $Fe\ (OH)_3$ is likewise converted to Fe_2O_3. For this reason Nicholls re-calculates his analyses, where possible, to the FeS form as

he believes this to be a closer approximation to prevailing depositional conditions.

Curtis (1967) on the other hand, recasts entirely in terms of FeS_2, since he believes that it is not possible to distinguish between early and late diagenetic conversion in cases where FeS was in fact the early form. Curtis quotes the work of Berner (1964c) who showed that in recent tidal sediments metastable FeS is transforming to pyrite, and in so doing thermodynamic equilibrium is being established, in that Eh and pH measurements have shown that pyrite is in fact the stable phase. In this work the latter procedure has been adopted, and all sulphur has been cast as FeS_2.

Garrels and Christ (1965) have shown in studies of sedimentary iron mineral assemblages that there is sufficient approach to equilibrium within the depositional environment to permit the use of relations based on thermochemical calculations. They demonstrate that any depositional environment can be represented on a two dimensional Eh-pH diagram, provided total carbonate and sulphur in the system are fixed. An example is given in Fig. 3, where the stability relations of the oxides, sulphides, and carbonate in water at $25^{o}C$ and one atmosphere total pressure have been reproduced. In this example, the activity of the total dissolved sulphur is 10^{-6}, and that of total carbonate is 10^{o}.

The authors point out however, that these diagrams provide no information relating to the attainment of equilibrium. Further, this example makes no allowance for the possible presence of iron silicates. The reason for this is that thermochemical data are only available for iron

metasilicate - $FeSiO_3$, whereas in natural systems minerals such as iron chlorite are most abundant.

Also it does not necessarily follow that the minerals now found in the rock are truly authigenic in the sense that they precipitated during the accumulation of the sediment at the sediment-water interface. Zobell (1946) has shown that interstitial solutions in the upper part of the sediment frequently have lower Eh values than those found at the interface. For this reason, discussions such as those to follow in this work refer to the upper dozen centimetres or so of the accummulating sediment and not specifically to the sediment-water interface. pH on the other hand is not usually as strongly affected (Krumbein and Garrels, 1952).

Interesting in this respect is the work of Berner (1963), 1964 a, b, c, d) who has studied the distribution of various sulphur species in the upper zones of recent sediments. He has shown that the sulphate and sulphide species vary inversely with depth below the sediment-water interface due to the action of sulphate reducing bacteria. The sulphide species thus produced is pH dependent in that where pH is greater than 7, HS^-_{aq} is the stable species whereas below 7 it is H_2S_{aq}. Sulphide production is greater where abundant and suitable organic matter is present, and the rate of deposition sufficiently slow to allow the downward diffusion of the sulphate ion.

Conditions controlling the production of siderite in sediments are not as fully understood. Nicholls (1960) and Nicholls and Loring (1962) in studies of sediments in a British Coal Measure cyclothem concluded that siderite

was produced where reducing conditions were somewhat milder than those required for sulphide generation. Curtis (1967) on the other hand has presented evidence to show that the optimum natural environment for sulphide production is strongly reducing and that in sediments from the British Westphalian Coal Measures siderite and pyrite were both formed in conditions where Eh varied from - 0.2 to - 0.3 Volts. In the sequence studied by Curtis these conditions are believed to have prevailed during the deposition of fresh-water, brackwater and marine sediments.

Curtis believes that the growth of pyrite and siderite is controlled by the generation of anionic species, and demonstrates that pyrite forms whenever bacterial reduction of sulphate took place, whereas siderite formed at high partial pressure of CO_2, and usually in the absence of sulphide.

This conclusion confirms the predictions of Garrels and Christ (1965) whose calculations indicated that if siderite is to have an important field of stability, dissolved carbonate must be very high, and reduced sulphur low. However, they point out (Fig. 3) that even under these conditions a considerable field of pyrite remains, and that siderite can be equally indicative of moderate reducing conditions or of very strong reducing conditions.

The presence or absence of calcite and phosphate in argillaceous sediments may provide further information. Both the calcium and the phosphate ions are pH but not Eh dependent (Krumbein and Garrels, 1952). These authors quote a figure of pH 7.0 above which phosphate is stable,

and pH 7.8 above which calcite is stable. Thus a sediment relatively low in calcite but high in phosphate can only form in environments where the activity product of the carbonate is not exceeded, that is to say below pH 7.8 and probably in the range pH 7.0 - 7.5.

Attempts have also been made by Nelson (1967) to estimate paleosalinities using the "sedimentary phosphate method." He proposed that the Al-phosphate variscite, is predominant in fresh water sediments, and that apatite is the predominant phosphate in marine muds. Müller (1969) has however shown that many factors influence the distribution of phosphates other than salinity, not least of which is the pH of the overlying solutions, and that the method has only very limited use.

TRACE ELEMENTS

Various trace elements (notably boron) are often used in environmental studies, particularly those concentrating on paleosalinity measurements, and this aspect will be discussed in full in the sections dealing with the alkali and alkaline earth trace metals. (Chapters G and H).

D. THE MAJOR ELEMENT GEOCHEMISTRY OF SOME SELECTED SOUTH AFRICAN SHALES.

In this section major element variations in the shales, (and in some instances siltstones), sampled from various South African stratigraphic sequences will be discussed. Details of the analytical procedures followed are presented in Chapter I, but it is pertinent to point out at this stage, that the X-ray fluorescence technique used for the majority of these determinations (Norrish and Hutton, 1969) has been found to be both extremely accurate and precise. Statistical information regarding the precision of the method at abundance levels common to shales, and estimates of the accuracy made by analysing a series of international rock standards of well established composition are also given in Chapter I. A further example of the quality of the data thus produced may be found by referring to the work of Von Michaelis et al (1969). These authors used the above mentioned technique to determine the major elements in a series of chondritic meteorites, and were able to detect subtle variations in the abundances of these elements relative to one another, which had been hitherto undetected, mainly as a consequence of analytical error.

It is emphasized at the outset that due to the exploratory nature of this study individual sequences were not always sampled for detailed sequential environmental studies, although for several Ecca Series borehole sequences, samples are sufficiently closely spaced for certain such conclusions to be drawn. Rather, it was considered more important to compromise somewhat between detailed study of a single sedi-

mentary basin, or part thereof, and complete countrywide random sampling.

It will be shown that this approach has been successful in that information regarding the physical and chemical conditions prevailing during the deposition of many of the sediments has been forthcoming. At the same time a number of regional uniformities of a chemical nature have been detected particularly in sediments from the Karroo System. These inter-element regularities have proved to be well developed in a vertical sense, and frequently statistically distinguishable from similar parameters recorded for horizontally separated stratigraphic equivalents. An attempt has been made to relate these features to the nature of the source material, and the distance travelled by it to the site of deposition. The significance and application of these regularities to future studies are discussed.

For reasons outlined below samples from the Middle Group of the Northern Ecca Facies of the Karroo System are discussed first. Thereafter the sample groups are examined in order of decreasing geological age. The section is concluded by a summary of the more important observations, and a discussion of major element variation in the sample population with specific reference to geological age. Finally a series of histograms are presented depicting frequency distributions for each of the major elements in the sample group as a whole.

1. THE NORTHERN ECCA FACIES OF THE KARROO SYSTEM

The rocks of the Karroo System cover about half of the Republic of South Africa. They also blanket the whole of Lesotho and occur extensively in South West Africa, Botswana, Rhodesia, Malawi, Zambia, Swaziland and Mozambique. The system has been divided, mainly on lithological grounds, into the Dwyka, Ecca, Beaufort and Stormberg Series. With the exception of the predominantly volcanic Stormberg Series, argillaceous rocks from each of the remaining three series have been examined and are discussed in the present study.

Attention is however focussed on the Permian Ecca Series, representatives of which occur around the whole of the Karroo Basin. In the Northern Orange Free State, Southern Transvaal and Swaziland, rocks of the Ecca Series are referred to as the Coal Measures. These sediments have been the source of most of South Africa's coal, and in addition, attention has recently been focussed on rocks of the Ecca Series as possible sources of petroleum and natural gas.

Shales from the Ecca Series constitute about one half of those to be discussed in this work, and the reasons for this are twofold. First, in view of the economic implications and the complete lack of knowledge of the chemical nature of these sediments, a preliminary study of a few selected sections was considered necessary. Second, drilling operations in the coal and potential oil fields have produced borehole cores containing fresh samples ideally suited for chemical analysis. In less favourable circumstances such material is very difficult to obtain as outcrop

samples are generally deeply weathered.

The rocks of the Ecca Series have been the subject of an extensive petrological, structural and petrographic study by Ryan (1967) who divided the series into four facies, which he has named the Northern, Central, Western and Southern Facies. For the reasons outlined above the Northern Facies will be considered first in some detail, and since the results of Ryan's work are not as yet easily obtainable, his principal observations and conclusions will first be briefly summarized.

Rocks of the Northern Ecca Facies form an outcrop belt ten to one hundred miles wide from Bloemfontein in the west through Witbank in the North, and then Southwards through Natal into Pondoland. The total outcrop length is about 600 miles, and the sediments have been divided by Ryan on lithological grounds into the Lower, Middle and Upper Groups. Within the coal fields, the Coal Measures rest either upon Dwyka Tillite or upon one of the pre-Karroo systems.

The contact between the Lower and Middle Groups was found to be gradational, and the former reaches peak thickness in the vicinity of Durban (1,500 feet). In Dannhauser from whence one of the series of samples to be discussed in this work is derived, The Lower Ecca Group is only 80-250 feet thick. Ryan observed a general thinning out of the Group in a Northerly direction, so that at Witbank and Middelburg (two further areas represented in this study), the lowermost coal seams from the Middle Group lie only a few feet above the Dwyka Tillite.

The Middle Ecca Group, or Coal Measures proper,

is characterized in the coal fields by thick bands of sandstone and grit alternating with more shaly layers, and the presence of a number of fairly continuous coal seams. False bedding in the sandstones is almost universal. In the Transvaal coal fields, the total thickness of the Middle Group is not known, since the Upper Stage is not present, but at Dannhauser it has an average thickness of 1100 feet. The Group reaches a maximum thickness of 1920 feet in Swaziland (Davies 1961).

With a few minor exceptions invertebrate and fish remains are almost totally lacking (Haughton 1969). This is generally attributed to the deposition of the Ecca Series in an inland cratonic sea containing water of low salinity. In the lowermost Beaufort beds, however, sporadic fresh water lamellibranchs have been recorded. Hart (1964) recorded the presence of phytoplankton near the top of the Middle Group. The evidence is however conflicting and according to Smith (1968, pers. comm.) marine acritarchs and fresh water algae have been identified by different workers from the same samples of Ecca shale from the Bothaville District.

Rocks of the Upper Group are predominantly fine grained with occasional thin limestone bands. In Swaziland the group is comprised of carbonaceous shales, sandstones and coal seams. The group maintains a fairly constant thickness of about 800 feet. According to Ryan it is frequently impossible to determine the top of the Upper Group, and the base of the Beaufort Series.

On the basis of his observations, Ryan concluded that the sediments of the Lower Group of the Northern Facies

were deposited "under relatively deep water conditions" in a continental sea which originally occupied the central portions of the Karroo Basin, and gradually transgressed northwards at this time. During Middle Ecca times he visualises rapid uplift and erosion of a land mass to the east and north-east of the present Natal coast. During this time " .... the shoreline was displaced southwards, and fluvial deltaic conditions are thought to have prevailed over most of the area covered by the Northern Ecca Facies". On the basis of heavy mineral studies he suggests that the source rocks were essentially granitic in composition.

Upper Ecca times saw a second major transgression of the sea due to continued subsidence of the northern portions of the basin coupled with reduced relief of the Eastern Highlands.

(a) Boreholes A/78, A/76, A/62 and Bh 134.
Hendrina - Middelburg - Witbank Districts.

(i) Borehole A/78.

Thirteen samples were taken at regular intervals from this borehole over a vertical distance of 140 feet. Sample details are to be found in Appendix 1.

The major element analyses are recorded in Table 14A. The samples are all highly carbonaceous black shales in which kaolinite is the major clay mineral with minor amounts of illite and traces of montmorillonite. In some samples weak diffraction lines of K-feldspar were observed.

The content of organic material in these samples

is the highest of any group included in the present study; and in two samples (A78/9 and A78/11) where carbon has been determined the values were found to be 13.1% and 29.9%C. These values correspond to losses on ignition at 950°C of 24% and 46% respectively. The average loss on ignition for the thirteen samples is 27%. For black shales such as these the loss on ignition may safely be taken as a semi-quantitative measure of organic matter content, and the variation of loss of ignition for the individual samples is plotted in Fig. 4.

Although the samples from borehole A/78 are probably sufficiently close together (approximately 10 feet) to allow interpretations to be made concerning continuous variation of chemistry with depth in the section, for most of the other borehole sequences to be examined this is not the case. Consequently Fig. 4, and all subsequent borehole variation diagrams are not plotted to a vertical scale, since the object of these diagrams is to convey as effectively as possible the variation of a number of components relative to each other in the individual samples. Therefore unless it is specifically stated to the contrary, vertical continuation is not implied, since in fine grained sediments such as these drastic chemical changes are common over a matter of feet, and often less.

As a consequence of the presence of large quantities of organic matter in the A series shales, the silica contents are low and average 46.5%, the standard deviation being 5.5%. (Table 28A) On a volatile free basis the average SiO_2 content rises to 63.5%, and σ drops to 3.0%. In other words the effect of mutual dilution in this instance partially

obcures the fact that in the inorganic fraction the SiO_2 content is reasonably constant. For Al_2O_3 on the other hand, in the samples prior to ashing the average abundance is 20.3% (σ = 3.1%) whereas in the ash the average is 27.7% and the standard deviation remains at a value of 3.1%.

The Si/Al ratios for the A/78 samples show only minor fluctuations about an average of 2.06 (σ = 0.18) (Table 30A) and this is taken to infer a fairly steady supply of roughly equivalent amounts of quartz and clay minerals to the basin of deposition, variation in clay being the more changeable. It is significant that the highest Si/Al ratio (2.34) occurs in sample A78/6 which also shows the lowest loss on ignition value (14%). Likewise the lowest Si/Al ratio (1.70) occurs in sample A78/10 which has the highest loss on ignition (46%).

Several authors (Eagar 1951, and Bloxam and Thomas, 1969; for example) have noted a close relationship between the amounts of detrital quartz and organic carbon, and have used these constituents as effective measures of relative rates of deposition, and often distance from the shoreline. Thus although the fluctuations noted above for the Si/Al ratio are not great, it is seen that the samples with the highest organic matter content contain the most clays relative to quartz, and were almost certainly deposited at the slowest rate.

Included in Fig. 4. are the variations of normative pyrite (recast as FeS_2) and siderite. The latter was calculated by the method of Nicholls (1962) which was discussed earlier at some length. Clearly in several samples from the

central portion of the section where siderite is abundant the normative pyrite content is very low, whereas in samples where pyrite is present in some quantity siderite is also present, but in much reduced amount.

In cyclothems from the British Coal Measures (Nicholls, 1960; Nicholls and Loring, 1962; and Curtis 1967) sequences are common where basal, pyrite rich, marine sediments grade upwards into sideritic non-marine strata. These workers have however interpreted the significance of the trends differently.

Nicholls (1960) believes that the variations are the result of a strongly reducing environment at the base of the cyclothem, which became progressively less so as accumulation proceeded. Curtis (1967) on the other hand, believes that there is very little evidence for linking this trend with progressive oxygenation of the depositional environment, and attributes it to the generation of different anionic species within the environment.

In the samples from borehole A78 there is no evidence of marine transgression, and it is noteworthy that the boron content of all 13 samples is very constant and averages only 36 ppm. What is interesting however is that a very close relationship exists between the pyrite and organic matter contents of the samples (Fig. 4).

Similar relationships were noted by Eagar (1951) and Spears (1964). Therefore if the amount of organic matter in the sediment is a reflection of the rate of sedimentation, the growth of pyrite below the sediment water interface is

principally related thereto. It is suggested that for this sequence the growth of diagenetic iron minerals is controlled by the rate of deposition, and that in highly stagnant conditions where the amount of detritus inflow is very low, ample opportunity would exist for the development of equilibrium conditions between the downward diffusion of sulphate and its bacterial decomposition to the sulphide species, providing always that suitable organic material was present in sufficient quantity.

Support for this argument may be found by considering the distribution of K_2O in the samples. It has been mentioned that small quantities of orthoclase were detected in the X-ray diffraction analyses of the samples, and this K-feldspar is not believed to exceed a maximum concentration in the range 5-7%. It has also been mentioned that illite is only present in very minor quantities in these shales, and it is therefore reasonable to expect that most of the potassium present is contributed by the detrital orthoclase. Reference to Fig. 4 shows that K_2O varies inversely with normative pyrite and that the correspondence of the two curves is remarkably close. This may be taken to infer that in times where sediment influx to the basin of deposition was relatively rapid, the supply of detrital orthoclase increased correspondingly, whereas in times of low supply the clay/feldspar ratio of material entering the basin was markedly higher. It is also noteworthy that the Na/K ratio is very low, and reasonably constant at 0.10 (δ = 0.004). Thus illite seems to play a minor role in the distribution of these alkali elements and most of the Na in the shales is also apparently

associated with the K-feldspar.

Where siderite is more extensive, seemingly in times of more rapid deposition, it would appear that sulphate reducing bacteria were not as effective, and that sufficient bacterially generated CO_2 was available to produce the necessary partial pressure to render the environment more favourable to the formation of siderite. In other words, unlike the sulphate reducing bacteria, those producing CO_2 do not depend on a downward diffusion of anionic species from the overlying solution. This postulate would explain why pyrite is rare when siderite forms in abundance, and although some siderite is seen to form contemporaneously with pyrite it is difficult to understand why its growth is stunted at all, unless in the presence of both anionic species the sulphide ion competes more favourably for dissolved iron than does the carbonate ion.

A further point of interest is that the abundance of iron in the samples is closely related to the content of diagenetic siderite and/or pyrite. In samples containing only minor amounts of siderite or pyrite the total Fe_2O_3 content is of the order of 1%. This of course is to be expected since none of the dominant minerals, kaolinite, quartz or K-feldspar contain any appreciable amount of iron. In samples where either pyrite or siderite is abundant, (eg. A78/6, 7 and 8) the Fe_2O_3 content rises accordingly. Curtis (1967) in his study of the Westphalian Coal Measure shales studied this phenomenon in great detail. He showed that for these sediments not only was the total iron content controlled by the formation of diagenetic iron minerals, but

also that the total amount of diagenetic iron was inversely related to the non-diagenetic fraction.

This was explained, in the first instance, by a process involving the growth of the diagenetic minerals partly at the expense of iron present in the sample, but more substantially from another, external source. A similar situation clearly holds for the A/78 sediments, except that in this instance, the majority of the diagenetic iron was externally derived; this being necessary because of the extremely low iron content of the quartz - kaolinite matrix. Spears (1964) has pointed out that in some cases an external source for iron is not necessary, as the sediment contains sufficient iron in these instances to cater for the needs of the diagenetic iron minerals.

The distribution of Mn (Fig. 4) closely parallels that of normative siderite in the section, and once again an external source is required as the "matrix" samples contain less than 100 ppm Mn, compared to a value of over 1000 ppm in A78/8 where siderite development is most marked. It is also noteworthy that the Fe/Mn ratio in the three siderite rich samples is in the range 40-60 compared to an average value of about 200 in the remaining samples. It is concluded that during the diagenetic formation of siderite Mn is preferentially incorporated relative to Fe. Spears (1964) has pointed out that the use of this ratio as an indicator of distance from the shoreline (Keith and Degens, 1959) is hazardous for samples containing diagenetic iron minerals and these observations lend weight to this opinion.

The abundances of Ca and P are both very low in these shales (0.20% and 0.06% respectively), and from what has been said earlier about the distribution of these elements in argillaceous rocks, it is clear that pH was low, probably slightly less than 7, during deposition. Both Mg and Ca tend to be slightly enriched in those samples rich in siderite, which is predictable since natural siderites usually contain Mg and Ca in addition to Fe^{2+}. Phosphate is also slightly enriched in shales containing siderite, and it is interesting (Table 30A) that the Mg/P relationship is closer than that displayed by Ca and P.

(ii) Boreholes A/76 and A/62

The three A series boreholes lie on a north-south trending line, at intervals of approximately two miles. A/76 is the most northerly section while A/78 the most southerly. Six samples were taken from each of these two boreholes over a vertical distance of 100 feet in each case, making up a total of 25 samples in all from this area.

As was the case for borehole A/78, the samples are highly carbonaceous, the average loss on ignition for each sequence being of the order of 27%. Carbon was determined in three samples, A76/3, A76/5, and A62/4 and values of 11.8%, 8.3% and 14.9% respectively were recorded. The chemical analyses of these rocks are to be found in Table 15A. Ferrous iron determinations in these samples proved totally unsatisfactory, due to the high contents of organic carbon even though the method devised by Nicholls (1960) for use on carbonaceous shales was used. This method is

only effective for samples with up to 4% carbon equivalent, above which results obtained are unrealistically high due to reduction of ferric iron by organic matter.

Mineralogically the samples are similar to those from A/78 in that kaolinite is the dominant clay in each case. The A/78 shales however tend to contain more illite than those from A/76 or A/72, where this clay together with montmorillonite is only present in trace amounts. Faint feldspar diffraction lines were detected in most samples. The samples from all three localities show similar chemical characteristics and as these have been discussed at some length for borehole A/78, only the more important features will be noted here.

(i) Although individually slightly more erratic the average Si/Al ratios in A/76 and A/62 are the same as found for A/78, the overall average being 2.03, and the standard deviation 0.26. In other words, variations of the quartz/clay ratio during deposition of these sections were not extreme in the samples studied.

(ii) Although the amounts of normative pyrite in the samples (Fig.5) are relatively low, there is a definite relationship between the amount of organic matter in the samples and their pyrite contents. This is interpreted as being a reflection of the rate of deposition, pyrite being most extensively developed where deposition was slowest, and consequently, organic matter most abundant.

(iii) The K_2O content varies inversely with that of organic matter, and as the K_2O is almost exclusively contained in detrital K-feldspar for these samples, it is inferred that most feldspar was supplied to the site of deposition when sedimentation rate increased. The Na/K ratios are slightly lower than in A/78 and this probably signifies that K-feldspar is more abundant relative to illite in these shales.

(iv) Normative siderite and pyrite vary inversely lending support to the suggestion that rate of deposition played a major role in controlling the growth of these minerals.

(v) Manganese is associated with siderite and is enriched relative to iron compared to those samples where no siderite is present. In addition the iron and manganese contents of samples containing no diagenetic iron minerals are extremely low and therefore the formation of these minerals requires an external supply of Fe and Mn which appears to have been the surrounding aqueous phase.

(vi) Ca and P are present in very small amounts indicating pH levels of 7 or less during deposition. Eh on the other hand was of the order of - 0.1 to - 0.3, and these samples were deposited in a lagunal swamp environment and have mineralogical and chemical characteristics corresponding to Millot's (1952) "aggressive" or "acid" lacustrine group. The nature of the source rocks for shales of the Northern Ecca

Facies will be discussed at a later stage, but it is clear from what has been said that the source material was essentially granitic in composition.

(vii) Reference to the compilation of inter-element ratios presented in Table 30A shows that for ratios involving elements unaffected by diagenetic processes (e.g. Si, Al, Ti, K and Na) the three sets of samples are statistically indistinguishable. In other words minor variations in each section caused by varying rates of sediment inflow inhibit interpretation on this scale regarding distance from the shoreline, location of the provenance area and so on.

The increase in illite relative to K-feldspar in the north-south sequence A/76 - A/62 - A/78, as reflected in the average values of the Al/Na, Al/K and Na/K ratios, which if real, would infer a source to the north of the area is not significant at the 95% confidence level although it is in full agreement with available geological evidence.

It is therefore concluded that if geochemical measurements are to be useful in tracing basinal features on a small scale, specific marker beds whose exact positions in the sequence are known, should be used. The effect of this would be to eliminate much of the abovementioned spread and hopefully allow for fruitful interpretation. Such an approach is feasible in coal fields where stratigraphic variations are usually well known, and samples more readily available.

(b) Springbok Colliery Ltd. Borehole Bh 134.

Witbank is some 20 miles south-west of Middelburg, and the samples under discussion here are the stratigraphic equivalents of those from the A series boreholes. Borehole 134 is represented by seven samples, all black carbonaceous shales (Ave. L.O.I. = 18%) taken from 260 feet of core. The samples all contain kaolinite as the dominant clay mineral with subordinate amounts of illite and traces of montmorrillonite. Faint feldspar diffraction lines were detected in most samples. Chemical data for these shales are given in Table 18A, and it is readily seen that they are identical in most respects to A series shales. The conclusions (i) to (vii) enumerated in the discussion of A/76 and A/62 apply equally to these samples, and will not be repeated. The variations of normative siderite, pyrite, K_2O and L.O.I. are depicted in Fig. 6.

The Si/Al ratio once again provides a good estimate of the relative rates of deposition, and for samples Ec. 5 and Ec. 8 where the value of this ratio reaches a maximum, the lowest losses on ignition are recorded. It is noted however that the inverse relationship between K_2O and L.O.I. is not as well developed in these samples as in the cases previously cited, and this is explained in terms of the increased illite contents of these shales.

Identical provenance and extremely similar depositional environments are envisaged for the two sets of shale.

(c) Boreholes GB45/64, GB47/64 and GB48/65 WAKKERSTROOM, EASTERN TRANSVAAL

A total of 37 samples were taken from three boreholes orientated in a north-south line in the Wakkerstroom District of the Eastern Transvaal.

Borehole GB 48 is located about 3 miles north of GB47 which in turn is placed 5 miles north of GB45. All the holes penetrate the Coal Formation of the Middle Group, and in each case argillaceous representatives were taken over a core length of about 700 feet. Included towards the base of each section are samples from above, below, and between the Alfred, Gus, Dundas and Coking coal seams.

The dominant clay minerals are kaolinite and illite (muscovite) together with minor amounts of montmorillonite. Fairly strong plagioclase and orthoclase diffraction lines were detected in most samples. Full sample details are given in Appendix 1. The silica contents of these samples are considerably higher than those previously discussed, as also are the Si/Al ratios. The overall averages are 58.3%, σ = 7.3%; and 3.03, σ = 0.63 respectively. Data for one of the sections (GB48) is plotted in Fig. 7, and the increased production of pyrite during periods of reduced deposition is well illustrated, as also is the relationship between organic matter and pyrite growth. In addition, carbon has been determined in six samples, two from each borehole, and a consistent relationship between these values, the Si/Al ratios, and the CO_2 corrected loss on ignitions is demonstrated in Table 5 of this text. Complete major element analyses are given in Tables 11A, 12A and 13A.

Table 5.

Sample No.	% Carbon	% L.O.I.	Si/Al
GB 48/65/9	7.60	17.1	2.5
GB 48/65/10	6.52	14.6	2.3
GB 45/64/8	5.37	11.5	2.9
GB 47/64/7	3.16	7.6	2.9
GB 47/64/6	1.96	5.7	3.3
GB 45/64/5	0.36	2.8	3.3

All three factors in this instance are related to the rate of deposition.

Overall these rocks do not show as high a degree of correlation between pyrite and organic C as was noted for the A series shales. Moreover, normative siderite is comparatively rare in the rocks sampled from these cores. It is only present in four basal samples from the GB 48 section, one from GB 45, and it is completely absent in GB 47. In all the remaining rocks where carbonate is present it is as calcite, as verified by the X-ray diffraction data in Table 1A. However it is clear that in some of these carbonate bearing samples small amounts of iron carbonate must be present since iron is found to be slightly enriched in these rocks. The recalculation has probably allocated Ca associated with detrital plagioclase to the carbonate molecule.

In addition several calcite rich samples contain

moderate amounts of phosphorus e.g. 45/1 contains 3.7% P_2O_5, and 45/4, 45/5 and 47/3 contain 1.76%, 0.64% and 0.63% respectively. This is unlikely to be detrital in origin since it occurs in calcite rich strata, and an increase of pH is indicated. It is pertinent to point out at this stage that the boron contents of these rocks are very low (Ave. 20 ppm) (Nel 1967).

Compared to the Middle Group shales from the northern part of the basin, where highly stagnant lacustrine conditions were shown to have been operative, these sediments were laid down erratically and at times very rapidly in more mildly reducing conditions, and in more basic waters where pH may have risen as high as 7.8 - 8.0.

The potassium distribution in these rocks is dominated entirely by detrital orthoclase and muscovite, and the overall Si/K average is 9.74, $\sigma = 0.8$. Fig. 7 shows the similarity between K_2O variation and that of the Si/Al ratio, and it is clear that in times where the sedimentation rate was increased, the amounts of detrital orthoclase and muscovite entering the basin rose accordingly, such that the Quartz/K-feldspar + muscovite ratio remained approximately constant.

In spite of the increased K_2O contents of these samples compared to those from the A sections, the Na/K ratios of the former are significantly higher (Ave. 0.23, $\sigma = 0.05$), and this is due to the presence of detrital albite, a constituent not found in the A series shales; ion exchange reactions are not believed to have played any part in the Na-K relationship. Titanium shows a moderate co-

herence with Al, but the relationship is nowhere near as close as is observed for several other shale units discussed in this study. The sedimentary geochemistry of this element will be discussed in more detail at a later stage. Non-diagenetic iron, too, is enriched relative to the A series shales.

Less than 2μ fractions were separated from four of these rocks, and the analytical results are to be found in Table 26A. Using the scheme developed in an earlier section, the approximate mineralogical composition of each of the four rocks was computed on a volatile free basis. The results are presented pictorially in Fig. 8.

In Shaw and Weaver's (1965) classification two samples plotted as deltaic sediments whilst two were classified as fluviatile. Taking into account the abundance of false bedding in the sandstones with which these shales are intercalated, the results support these authors' contention that a broadly based classification of argillaceous sediments on mineralogical grounds can be feasible. Also when cognizance is taken of the organic nature of many of these sediments, together with the aforementioned comments on prevailing Eh-pH conditions during deposition, a fairly comprehensive environmental picture emerges.

(d) SOMKELE BOREHOLE

The Somkele borehole is located in Northern Zululand, near Mtubatuba, on the extreme eastern flank of the basin, and twenty-six samples were obtained representing over 4000 feet of core. The exact locality of the Ecca-

Beaufort boundary in this area is uncertain, and it is probable that the upper few samples are in fact representatives of the Lower Beaufort shales.

The samples are all black shales with an average carbon dioxide corrected loss on ignition of 8%. Kaolinite and illite (muscovite) dominate the clay mineralogy of these shales and various combinations of the two types are represented. Minor amounts of montmorillonite are usually also present. In all samples except Sec. 2 and 25, diffraction lines of plagioclase were observed, and from the low CaO contents of these rocks ($< 0.5\%$) it is seen that the plagioclase is albitic. The K-feldspar contents of the rocks were found to be low. Full sample locality and mineralogical details are given in Table 1A, and the chemical analyses are to be found in Table 16A.

Considering the large vertical thickness of sediment involved and the consequent unrepresentative nature of the sampling, the chemical compositions of these shales are remarkably similar. The SiO_2 contents are consistently higher (Ave. 68.6%, σ=3.3%, volatile free) than any of the Ecca shales thus far discussed, as also are the Si/Al ratios (Ave. 3.5, $\sigma = 0.5$). This is a consequence of increased quartz as well as decreased kaolinite contents compared to their western and northern stratigraphic equivalents. It will be remembered that for the A series boreholes the average Si/Al, ratio was 2.03, $\sigma = 0.26$, whereas for those from Wakkerstroom the values were found to be 3.03, $\sigma = 0.63$. Even in the fine grained highly carbonaceous Somkele shales Si/Al is greater than 2.5. Assuming

a common granitic source area these factors can be interpreted as reflecting both the degree of weathering of the source rocks, and the relative rates of transport and deposition.

A parallel relationship is once again observed between the pyrite abundances and the contents of organic carbon, Fig. 9. In addition a negative correlation is observed between these parameters and the Na/K ratio the average value for which is 0.30, $\sigma = 0.08$, the highest thus far encountered in this discussion. It is clear that in times of profuse deposition quartz and albite made up the bulk of the detritus entering the basin, whereas K-mica and kaolinite become more predominent in samples which have accumulated at a slower rate.

Support may also be found in Fig. 9 for an earlier contention that in a reducing environment (Eh - 0.1 to -0.3) pyrite growth is strongly influenced by the rate of sedimentation, and that in the absence of sufficient time to establish equilibrium between downward diffusing sulphate ions and their bacterial reduction, pyrite will not develop.

Also it is clear that for siderite the situation is more complex. In this section normative siderite is present in several samples, and with one exception, (Sec.9), it is only present in abundance where pyrite is absent. This is in agreement with the observations of Curtis (1967), but it has been shown that mutual incompatability is by no means universal. Curtis has shown that both pyrite and siderite can form under identical pH-Eh conditions, but that

siderite will not form unless a sufficiently high partial pressure of CO_2 can be generated, and it would seem that fulfilment of these conditions is not dependent on a very slow rate of accumulation. Again one is forced to the conclusion that either sufficient quantities of CO_2 are not generated under these conditions, or else that in the presence of both an ionic species iron sulphide is formed preferentially. The latter seems more acceptable. A further point of note in this connection is that in these shales the total iron contents are not as closely controlled by the contents of the diagenetic minerals present, and it seems likely in this case that where conditions favoured the growth of these species, sufficient iron was available from the solid detritus present, and the necessity of invoking an external source is obviated.

The titanium contents of these shales are consistently lower than for any thus far discussed, consequently the Si/Ti and Al/Ti ratios are higher, and this point will be discussed in more detail at a later stage. Small amounts of normative calcite are present in some samples, notably the four uppermost in the succession. P_2O_5 contents are moderately low (Ave. = 0.13%) and the maximum value recorded was 0.23% in Sec. 14. A low ($\pm$ 7) pH environment is thus indicated.

For four samples, $< 2\mu$ fractions were separated and analysed (Table 26A). The average mineralogical compositions, on a volatile free basis, computed for these shales was: total clay 59%, quartz 33%, Feldspar 7% and carbonate 1%. In Shaw and Weaver's (1965) classification these samples

would be grouped as deltaic. They were clearly deposited in a near shore environment where sedimentation was more profuse than for any of the zones thus far considered. Consequently their major element chemistry is overwhelmingly dominated by that of the source rock, and the rate of erosion and deposition.

(e) DANNHAUSER BOREHOLES

Ten samples were made available from two boreholes in the Dannhauser District of Natal. Eight of these are from a 900 foot section of B.h. G.S.O.9, and are black shales moderately rich in carbonaceous material (Average loss on ignition, corrected for CO_2 = 12%). The remaining two samples are from B.h. G.S.O. 10, and were found to be siltstones poor in organic matter. All ten samples contain kaolinite and illite as the dominant clay minerals, together with trace quantities of montmorillonite. Plagioclase and K-feldspar were found to be present in most samples. Sample locality details are given in Table 1A, and chemical analyses in Table 17A.

Mineralogically and chemically these samples were found to be very similar to their stratigraphic equivalents from the Wakkerstroom District some thirty five miles to the north, and conclusions for those samples apply equally well here and will not be repeated. With regard to the diagenetic minerals in B.h G.S.O. 9 one particularly interesting feature emerged. Two of these samples, Ec. Dan. 4 and Ec. Dan. 5 contain normative pyrite contents in excess of any encountered so far, 6.7% and 8.2% respectively. These rocks contain no

normative siderite. The sample above them in the sequence Ec. Dan. 3, on the other hand, contains 7.1% normative siderite and only 0.8% pyrite. The remaining five samples contain small quantities of normative calcite. The boron contents of the pyrite rich shales are 72 ppm and 66 ppm. respectively, compared with an overall average of 39 ppm. for carbonaceous Coal Group shales and 17 ppm for the non-carbonaceous varieties. (Nel 1967).

It follows from these remarks that Nel found an overall correlation between organic matter and boron content in the Ecca shales, illustrated particularly well by the Northern Facies shales from the Western fringe of the basin to be discussed shortly. These two shales (Ec. Dan. 5 and 4) are, however, not extraordinarily carbonaceous, and their boron contents cannot be explained solely on this basis. Nel offered no reason why these rocks should be so markedly enriched in boron. A more detailed account of trace element - paleosalinity relationships will be presented in Part 2, of this volume, but it is pertinent at this stage to note the results of Williams and Keith (1963).

These authors, in a geochemical study of Pennsylvanian coal beds, found that coals in areas of marine overburden were higher in sulphur than the same coal beds overlain by fresh-water sediments. Sprackman (cited by Williams and Keith) in studies of fresh-water and marine peat bogs in Florida, U.S.A. , reports that fresh-water peats contain on the average about six times less sulphur than the corresponding marine peats. Insufficient data is available for the Dannhauser area, but the possibility of a marine

transgression cannot be dismissed in view of the above-mentioned high pyrite and boron contents. Further more detailed work in this area is clearly desirable.

(f) THE VIERFONTEIN AND BOTHAVILLE DISTRICTS

Six carbonaceous shales (E . 11-16) were collected at Vierfontein Collieries in the Western Transvaal. All six contain kaolinite as their dominant clay mineral. Samples Ec 14, 15 and 16 were taken very close to the bottom coal seam in the area and contain organic matter and well crystallized, extremely pure kaolinite with very small amounts of quartz and traces of montmorillonite. An analysis of the $< 2\mu$ fraction of one of these, Ec 14, is presented in Table 26A. The remaining three samples contain minor quantities of illite and montmorillonite as well as albite and K-feldspar.

As might be expected from these descriptions the chemical compositions (Table 18A) vary rather widely depending on the presence or absence of the various detrital phases noted above. Nevertheless these samples are of considerable interest in view of their extremely high boron contents (Nel 1967). The average for the six samples is 131 ppm, values in excess of 100 ppm being recorded in each case. It will be remembered that the overall B average for the Northern Facies shales is only 39 ppm. (Nel 1967) has attributed these high boron contents to the carbonaceous matter present in the samples, but the situation is clearly more complex. The A series shales from the northernmost sector of the basin contain only 20-30 ppm B,

and yet they are extremely rich in organic matter (Average loss on ignition being 28%). The average loss on ignition of the Vierfontein samples on the other hand is 22% (Range 9% - 37%).

Therefore, if as suggested by Nel, the boron in these shales is inherited from the plant matter incorporated in them, then either the organic matter present in the two sets of shales is drastically different in its original total boron content, or else some factor during or soon after deposition resulted in the adsorption of large quantities of boron by the organic matter in the western portion of the basin.

In addition to these high boron values, the samples contain moderate amounts of normative pyrite, for example Ec 11 and Ec 13 contain 1.26% and 1.74% respectively. The work of Williams and Keith (1963) cited in the discussion of the Dannhauser shales is equally applicable here, and the possibility of marine transgression in this area cannot be dismissed.

Hart (1969) has described glauconite occurrences in this area, and also records the presence of phytoplankton near the top of the Middle Group. He suggests that for most of Middle Ecca time the basin was a "desalinated gulf" which received large amounts of fresh water derived from the melting of the Dwyka ice caps, thus explaining the lack of macro-invertebrate fauna from these strata.

Also of interest are the large quantities of TiO_2 present in the kaolinite rich shales Ec 15 and Ec 16 which

contain 1.89% and 3.06% TiO_2 respectively. This is probably in the form of anatase which is a common constituent of kaolins of high purity and consequent slow formation (Grim 1968).

BOTHAVILLE BOREHOLE VB 79/65

Three siltstones and one shale were sampled from B.h. VB 79/65, in the Bothaville District, some 25 miles from Vierfontein. Kaolinite is once again the dominant clay, but for these samples, the subordinate clays are illite and chlorite. Upper Ecca shales from Bothaville which are discussed in a later section have montmorillonite as their dominant clay. All four samples contain abundant plagioclase and K-feldspar, and the shale, BEC 4292 contains a small quantity of normative siderite.

As a consequence of the very high albite contents, the Na/K ratios are high (Ave. = 0.47), and further aspects of their chemical composition will be discussed when discussing the nature of the Upper Group shales from this area in a later section.

CONCLUDING REMARKS

The rocks of the Middle Group of the Northern Ecca Facies have been shown to represent various combinations of the assorted weathering products of an albite-orthoclase-muscovite parent, laid down in a series of very different depositional environments. These vary from the acidic, anaerobic lagunal or inner neritic environments where carbonaceous material has been preserved in some quantity to the

fluviatile-deltaic type of sediments containing lesser quantities of organic remains, and large amounts of detrital quartz, feldspar and K-mica.

The weathering products of such a source rock would differ quite widely depending on the rate of weathering, conditions of drainage, pH, and most important in this instance, the rate of uplift and erosion of the source region itself. Kaolinite is a hydrolysis product of both K-feldspar and albite (Helgeson et al. 1969)., and further, it is the stable clay in the acidic environments commonly represented in the Ecca shales, and it is clear that both the weathering and depositional environments of these Permian rocks have favoured the formation and preservation of this clay. Detrital K-feldspar has been shown to be present in varying amounts in the different sections studied, and Weaver (1967) has noted that most residual kaolins contain some K-feldspar and K-mica showing their relative resistance to weathering compared to albite.

A combination of these factors has resulted in the large differences in the elemental make-up of representatives from different parts of the basin, as illustrated by the discreteness of many of the interelement ratios which have been discussed, and are presented for mutual comparisons in Table 30A.

The variations in the nature of supply and types of depositional environments render the rocks most suitable for further geochemical study, and detailed investigations in selected areas should provide valuable information re-

garding both chemical variations in vertical sections with particular reference to the Eh, pH and salinity of the overlying and interstitial waters - particularly in the western sector where some evidence of possible marine transgressions has been found, and secondly, geochemical - mineralogical studies of individual lateral units should provide further information regarding the direction of sediment inflow, and relative shoreline movements during deposition.

2. SWAZILAND SYSTEM

Fig Tree Series

The Swaziland System in the south-eastern Transvaal is one of the oldest stratified systems exposed. The folded synclinal belt of this system forming the Barberton Mountain Land (Visser et al. 1956) has a length of about 110 km. aligned in a north-easterly direction, and a width of about 30km. The system is divided into three series, the Onverwacht, the Fig Tree, and the Moodies. The basal Onverwacht Series consists mainly of what were originally basic volcanic rocks with subordinate acid types, and in some parts ultra-basic serpentinites, peridotites and gabbros are found within the basic lavas. The Fig Tree Series comprises several thousand feet of shale, grit and graywacke together with well developed horizons of chert, jasper and ironstone. Rb-Sr age determinations by Allsopp et al. (1968) indicate a minimum age of deposition of 3×10^9 years. The Moodies Series consists of about 12,000 feet of thick formations of quartzitic rocks separated one from the next by minor shale units (Haughton 1969).

A total of twenty-two samples from the Fig Tree Series were examined, and the major element analyses are presented in Table 2A. Sample descriptions and localities are to be found in Table 1A. The samples may be subdivided into three groups, as follows:-

(a) The shales proper, which are in a sense, unique, in that they are all finely laminated and remarkably well preserved considering their very great age. Illite and iron - rich chlorite are present in varying amounts, and in some samples the

chlorite is the dominant clay type. Faint diffraction lines of plagioclase were detected in most instances, and a few samples contain trace quantities of K-feldspar.

(b) The graywackes, which are medium to fine grained (Allsopp et al. 1968), and which contain lesser quantities of the abovementioned clay minerals, and moderate amounts of albitic plagioclase. Minor amounts of K-feldspar were detected in several samples.

(c) The ferruginous shales, which contain varying quantities of iron-rich chlorite, together with significant amounts of hematite, magnetite and goethite. The total Fe_2O_3 contents of these samples are in excess of 15%, and in one sample, Fg 2, as high as 40.1%

The most striking aspect of the major element chemistry of all these samples is their high MgO content (Ave. 5.21%, σ = 0.99%). Consequently, as may be seen from Table 30A, these shales have higher Mg/Ti, Mg/K and lower Al/Mg ratios than any other shales included in this work. This feature is interpreted as being indicative of a high magnesium source area, and is in accord with the author's earlier work concerning the Cr and Ni contents of these sediments (Danchin 1967).

In this study it was shown that the Fig Tree argillites contain, on the average, 860 ppm Cr and 495 ppm Ni, compared to 120 ppm and 49 ppm respectively in 228 other South African shales of younger ages.

It was postulated that these large amounts of Cr and Ni entered the basin of deposition in lattice positions within the degraded clays, and that the source areas contained a high proportion of basic and ultra-basic rock types. The high Mg contents of the shales lend further support to this contention. The total iron contents (expressed as Fe_2O_3) of these sediments are also high, and the average value excluding the ferruginous shales is 10.56%, compared to 6.18% (on a volatile free basis) for all South African shales.

In view of the great age of these sediments, and the uncertainties concerning the compositions of the primeval oceans and atmospheres it would be of value to know the true oxidation state of the iron present in them. Unfortunately for a number of samples insufficient material was available for FeO determinations, and, more important, most of the samples were taken from outcrop exposures and have almost certainly been weathered to varying degrees. The ferruginous shales, Fg 1, 2, 8, 9, 10 and 11 are useless in this respect, and with the exception of Fg. 1 are all badly affected. For the shale samples of fresher appearance where FeO was determined it was found that the Fe^{2+}/Fe^{3+} ratios varied rather widely, but in most cases had a value of greater than one. However until very fresh borehole samples become available these results cannot be viewed as anything but an indication of the minimum amount of iron present in the ferrous state. Sulphur is only present in trace quantities, the maximum value observed being 0.11% in sample SH.7.

In the shales, SiO_2 varies from 52% to 59% whereas in the graywackes the range is from 63% to 69%. The Al_2O_3 contents of the rocks are consistently low, the average value for the shales being 14.9%, while for the graywackes it is 10.5%. Consequently there is a distinct difference between the Si/Al ratio of the two types, the values being 3.4 and 5.6 respectively. The TiO_2 contents of the rocks are lower than for any of the younger sediments studied, (Ave. 0.59%, $\sigma = 0.12\%$), but the Al/Ti ratios (Ave. 20.3, $\sigma = 1.6$) are not greatly higher than for the average South African shale, once again illustrating the close coherence displayed by these two elements in fine-grained sedimentary rocks. This relationship is discussed in more detail in a later section.

The Na_2O contents of the rocks vary widely and are dependent on the amounts of detrital plagioclase present, the maximum value observed being 1.70% for graywacke SH7; K_2O also shows wide variations, and is predictably highest in the illite rich shales and lowest in the graywackes. The average K_2O content of the shales is 2.85%, which is somewhat higher than might have been expected in rocks derived from a source area in which basic and ultra-basic rock types predominated, and this feature is discussed in some detail in the section dealing with major element variation with geological age.

Faint diffraction lines of dolomite were detected in a few samples, particularly in several of the graywackes. Unfortunately, insufficient material was available for CO_2

determinations in some of the samples, but it is shown in Table 2A, that the few samples containing small quantities of CO_2 also have increased CaO contents compared to the remainder of the samples where the CaO contents are very low. (Overall average 0.90%). The P_2O_5 contents are invariably low, the average being 0.09%, and the standard deviation 0.02%.

Less than 2μ fractions were separated from two of the shales, Fg 14 and Fg 17, and one ferruginous shale, Fg 1, and the major element analyses are presented in Table 26A. The Fg 14 and Fg 17 separates are very similar in chemical composition, and quite different from other clay fractions separated from younger shales. The high iron and magnesium contents of the chlorites, and the low Al_2O_3 contents are particularly well illustrated. In the case of the ferruginous shale, Fg 1, it is seen that the total Fe_2O_3 content of the $< 2\mu$ fraction is 36.0%, and the SiO_2 content lower than for any other separate. The computed total clay contents of Fg 14 and Fg 17 are 82% and 63% respectively, and are indicative of slow deposition, probably in fairly deep water.

3. PONGOLA SYSTEM.

Mozaan Series

The early Precambrian Mozaan Series covers large areas of Swaziland, and also occurs in the Vryheid and Piet Retief Districts of the south-eastern Transvaal. The series follows the predominantly basic lavas of the Insuzi Series,

and reaches a maximum thickness of about 16,000 feet (Haughton 1969). It comprises a thick succession of quartzites and shales, many of which have been converted to andalusite phyllites or schists.

Seven Mozaan shales from Swaziland, all in an advanced state of weathering, were analysed, and the results are presented in Table 3A. Five of the samples are highly ferruginous shales, Fe_2O_3 varying from 26.1% to 54.2%.

These samples contain very little clay minerals and their mineralogy is dominated by quartz, and a variety of iron oxides and hydroxides, notably goethite, hematite and magnetite. Two samples, Mz 3 and Mz 5, contain moderate amounts of illite (K_2O contents 2.31% and 2.33% respectively). Sample Mz 3 contains 13.5% total Fe_2O_3, and Mz 5 is a siltstone containing 74% SiO_2. The drastic weathering experienced by these Mozaan shales has modified their original compositions and rendered them unsuitable for environmental or comparative geochemical studies.

4. KHEIS SYSTEM

Rocks designated to the Kheis system cover large areas of the north-western Cape, and southern South West Africa. The age of deposition of the Kheis System is unknown, but in the opinion of Martin (1965) it is probably older than 2,600 million years. Major element data for one Kheis siltstone are presented in Table 3A. Illite is the dominant clay mineral, and the K_2O content of the rock is 3.46%. Further discussion of this sample is included

in the section dealing with variation of major element chemistry with geological age.

5. THE WITWATERSRAND SYSTEM.

Due to the presence of large quantities of gold and uranium in the sediments of the Witwatersrand System, the geology of these rocks has been documented in tremendous detail (see for example Haughton 1969).

The great pile of sediments constituting the system is subdivided as follows:-

Kimberley - Elsburg Series Main - Bird Series	Upper Division
Jeppestown Series Government Reef Series Hospital Hill Series	Lower Division

The Jeppestown and Government Reef Series which are represented in this study reach maximum thicknesses of 8000 and 4000 feet respectively (Brock and Pretorius, 1964), and comprise alternating shale and quartzite sequences deposited in a gradually sinking ovoid basin. Allsopp (1964) has tabulated isotopic ages for Archean granites overlain by the younger Witwatersrand sediments. Since the contacts are unconformable, the age given (2720 $\pm$ 100 million years) can be regarded as a maximum age of the lower Witwatersrand sediments, which are in all probability considerably younger.

Haughton (1969) considers that the sediments were deposited in an intracratonic depression comparable in size

with the present day Lake Victoria. Evidence regarding prevailing climatic conditions is conflicting, and in this respect it is interesting that Nel (1967) found the boron contents of the samples described below to be extremely low (Ave. 11 ppm), and concluded that they were deposited in a fresh-water environment.

Ten shales from borehole JY 8 in the Klerksdorp District have been analysed, and the results are presented in Table 4A. Five of the samples, JP 6-10, are from the Government Reef Series, and five, JP 1-5, from the Jeppestown Series. The samples all contain chlorite and illite as the dominant clay minerals, together with variable amounts of albitic plagioclase.

The average MgO content of the ten shales is 4.44%, which is intermediate between the high values recorded for the Fig Tree shales, and all other representatives of younger formations for which analyses are presented in this work. In this respect it is interesting that the Cr and Ni contents of these samples are also intermediate between the very high values observed for the Fig Tree shales, and those recorded for younger shales (Danchin 1967 a). Once again this is taken to be indicative of a source area containing a significant proportion of basic and/or ultrabasic rock types. The total iron contents are also very similar to those of the Fig Tree shales, and in the case of two samples JP 5 and JP 9, the diffraction lines of magnetite were detected. The average Fe_2O_3 content of the remaining eight samples is 8.2%. With the exception of JP 5 which

has 0.14% MnO, all the samples have very low manganese contents, the values lying in the range 50-150 ppm, and the Fe/Mn ratios of these shales are the highest of any group discussed here (Ave. 673).

The Si/Al ratios are markedly different for the two sets of shales, the average for the five Government Reef Shales being 3.4, while that for the Jeppestown shales is 4.5. It has been demonstrated that a close relationship often exists between the Si/Al ratio and the rate of deposition, and since borehole samples from the Witwatersrand System are more easily obtainable than for other less well documented successions, further work on more closely spaced samples should provide useful information in this connection.

Small amounts of normative calcite are present in several of the samples, and the average CaO content is 1.39%. As was the case for the Fig Tree shales, the P_2O_5 contents are low, (Average 0.08%). Also, the Na_2O contents are a reflection of the amounts of detrital albite present, and Na_2O varies between 0.21% and 2.56%, the average being 1.19%. Consequently the Na/K ratios are high, the average value of this ratio being 0.71.

An analysis of the chlorite-illite less than 2μ fraction of one sample, JP7, is presented in Table 26A. As was the case for the Fig Tree separates, the high iron and magnesium contents of the chlorite are well illustrated. The clay content of this sample was found to be 59%.

6. SINCLAIR FORMATION

Kunyas Series

The Kunyas Series attains a maximum thickness of about 5000 feet, and comprises about 1300 feet of arkoses and grits followed by a series of phyllitic shales (Martin 1965). De Villiers (Pers. Comm) estimates that the age of the series is between 1080 and 1260 million years. Beetz (1922) concluded that the sediments are of marine origin, and this conclusion is supported by Nel (1967) who recorded an average of 109 ppm boron for the samples discussed here.

Major element analyses for five Kunyas phyllites are presented in Table 5A. The samples all contain illite as the dominant clay mineral, together with traces of plagioclase and K-feldspar. The samples are all quartz-rich as evidenced by their high average SiO_2 content (72.2%) and Si/Al ratio (4.52). A further feature of interest is that these samples have the lowest Al/Ti ratios of any of the groups studied, and it is suggested that they contain small quantities of detrital ilmenite although these were not detected in the X-ray diffraction traces.

Similar low Al/Ti ratios were observed for a few isolated quartz rich Ecca sediments, and it is probable that the amount of detrital ilmenite entering the basin reached a maximum during periods of rapid erosion and supply, and that any relationship between Al and Ti in the clays themselves in these sediments is masked by the presence of ilmenite.

The average Na/K ratio is very low (0.07) as a result of the presence of significant quantities of K-mica and the absence of plagioclase; and since these rocks are believed to be the products of fairly rapid erosion and deposition, it is likely that the source rocks did not contain plagioclase as a major component. In addition, the CaO and P_2O_5 contents of the rocks are both low, average values being 0.11% and 0.12% respectively.

7. DAMARA SYSTEM

The Damara System has the widest distribution of the Precambrian systems in South West Africa, and the single sample analysed in this study (Table 3A) is an illite-chlorite shale from the south-eastern section of the Damara Syncline, and is believed by H. Martin (Pers. Comm.) to be of marine origin. It has a K_2O content of 4.88% and is relevant to the discussion of major element variation in shales with geological age, presented in a later section.

8. MALMESBURY FORMATION

Considerable portions of the south-western Cape Province are comprised of the thick, folded geosynclinal sediments of the Malmesbury Formation. In the vicinity of the Cape Peninsula the formation consists of quartzites, feldspathic grits and blue shales which vary in grain size from very fine-grained well bedded varieties to more silty, arenaceous members. Allsopp and Kolbe (1965) carried out Rb-Sr isotopic age determinations on these shales, and came

to the conclusion that the age of deposition cannot greatly exceed 595 $\pm$ 45 million years. Kröner (1968) has concluded that sediments of the Vanrhynsdorp area, previously believed to be part of the Malmesbury Formation are in fact members of the Nama System, and that the formation is not represented in the Vanrhynsdorp area. Nel (1967) found the average boron content of the Malmesbury shales to be 136 ppm, and concluded that they are marine in origin.

Three argillaceous and two arenaceous representatives of the Malmesbury Formation were analysed, and the results are presented in Table 6A. The samples all contain illite as the dominant clay mineral, and small quantities of plagioclase were also detected, especially in the more arenaceous variety.

The three argillaceous Malmesbury shales are very similar in chemical composition, and contain moderately high MgO and total Fe_2O_3 contents (3.58% and 8.23% respectively). The K_2O contents in each case exceed 4% and the Na_2O contents average 1.50%.

The more arenaceous members contain lesser amounts of Fe, Mg, Al and K, and as a result of their higher quartz and plagioclase contents, considerably more SiO_2 and Na_2O (73.74% and 2.43% respectively). As a consequence of these variations in chemical composition with grain-size, many more samples will have to be analysed before meaningful conclusions regarding the nature of the source rocks of these shales can be drawn.

9. CANGO FORMATION

Pre-Cape sediments forming a belt 75 miles long and 10 miles wide from Ladysmith in the west to Uniondale Road in the east, south of the Swartberg mountains have been correlated with the Malmesbury Formation. The sediments of the Cango Formation comprise a sequence of shales, quartzites, limestones and grits, which are generally highly folded and sheared.

Four Cango shales were analysed, and the results are presented in Table 6A. The samples all contain illite as the dominant clay, together with minor amounts of chlorite. Weak diffraction lines of plagioclase were detected in only one sample, Cg 3, and no traces of K-feldspar were observed. Notable features of these shales are the high potassium contents (Ave. 5.17%), and the uniformity of chemical composition in spite of the large distances between the sample localities. Cg 3, which contains albite has an Na_2O content of 1.24%.

The three remaining samples each contain less than 0.5% Na_2O. Samples Cg 1 and Cg 2 have small amounts of normative calcite. Nevertheless the average CaO content is low, and the overall average is 0.80%. The average P_2O_5 content is 0.17%

In terms of their major components, the Cango shales are similar to the more argillaceous representatives of the Malmesbury Formation, and different in a number of respects from the younger Bokkeveld shales. For example, the average Al/K ratios in the Malmesbury, Cango and

Bokkeveld shales are 2.39, 2.33 and 3.25 respectively while the Mg/Ti ratios are 3.85, 3.51 and 1.89. Further more detailed chemical studies might afford an excellent means of quantitatively assessing the Malmesbury-Cango correlation which is difficult by other methods due to the very fine-grained nature of the sediments.

Less than 2μ fractions were separated from one Cango shale (Cg 1) and one Malmesbury shale (Mm 7), and the results are presented in Table 26A. As has been shown to be the case for the whole rocks, the clay fractions are also very similar in major element chemistry, and the total clay contents of the two rocks are notably high, 82% and 77% respectively.

10. NAMA SYSTEM

Sediments of the Nama System cover large portions of the southern part of South West Africa and Namaqualand, and are Pre-Devonian in age (Martin 1965). The system is divided into four series, as follows:-

(i) The Kuibis Series:- In the type area, the series consists of interbedded quartzites and shales overlying basal conglomerates, and reaches a maximum thickness of about 600 feet (Haughton 1969). Kröner (1968) believes that the Kuibis sediments were deposited under shallow marine conditions, a view supported by Nel (1967) on the basis of the high boron contents of the Kuibis shales.

(ii) Schwarzkalk Series:- This series consists of a maximum thickness of 1000 feet of well bedded, dark, bituminous limestones with a few intercalated shales.

(iii) Schwarzrand Series:- In the type area the series consists of about 1150 feet of soft greyish-green to bluish-grey shales with sandstone intercalations and some black limestones.

(iv) Fish River Series:- This series is typically developed between the Schwarzrand Escarpment and the Fish River Valley, and consists of a maximum of 2300 feet of quartzites and red and purple argillaceous sandstones and shales. Current bedding and ripple marks are common features of the Fish River sediments.

Martin (1965) believes that most of the sediments of the Nama System were deposited in shallow water, on a stable platform or shelf. Two Kuibis shales, and one siltstone have been analysed, and the results are presented in Table 5A, together with the mean values of five Kuibis shales analysed by Kröner (1968). The samples all contain illite as the dominant clay mineral together with traces of montmorillonite, and small quantities of K-feldspar. Plagioclase was not detected in any of the samples.

The shales are rather variable in composition, but one feature of importance is the high K_2O content of the Kuibis shales. Kröner found an average K_2O content of 5.68% in the five shales analysed by him, and the two analysed in

this work, Kui 2 and 4 contain 5.79% and 8.57% respectively. Further, less than 2μ fractions were separated from these two shales, and the separates were found to contain 9.58% and 10.25% K_2O, on a water free basis. The significance of these results will be discussed in the section dealing with major element variation with geological age.

Four Schwarzrand shales were analysed, and the results are presented in Table 5A. The samples are all illite-chlorite shales containing variable amounts of albitic plagioclase and K-feldspar. The K_2O contents of these samples vary between 1.92% and 5.83% (Ave. 3.20%). The remaining major elements show rather wide variations.

Fourteen samples from the Fish River Series were analysed, nine samples from various outcrop localities in South West Africa, and five from a borehole in the Gibeon District, and the results are given in Table 7A.

All the samples contain illite as the dominant clay mineral, together with occasional minor quantities of chlorite and traces of montmorillonite. Plagioclase is present in all the samples, as also is K-feldspar in lesser amounts. Diffraction lines of calcite were identified in several samples.

The average SiO_2 content of these sediments is 66.07%, σ = 6.75%, whereas the mean Al_2O_3 content is 12.77%, σ = 2.53%. The Si/Al ratios are therefore high, and average out at 4.44 , σ = 0.94 . In addition to the large proportion of detrital quartz, the samples contain abundant detrital plagioclase (Ave. Na_2O = 1.72%), and these features

together with the abundant cross bedding noted at several of the sampling points infer a fairly rapid rate of erosion and deposition. It is interesting that the Al/Ti ratios are slightly lower than for most other shales studied (Ave. 15.51), and as was the case for the Kunyas shales, it is suggested that the sediments contain minor quantities of detrital ilmenite.

Further, most samples contain moderate amounts of normative calcite (Ave. CaO = 2.77%), and several samples contain conspicuous quantities of P_2O_5, for example FR.4, whose P_2O_5 content is 0.39%. The mean P_2O_5 content is 0.22%. Sulphur is only present in trace quantities. These factors are suggestive of deposition in water where pH was probably in the range 7.2 - 8.0, and Eh $>$ 0.

11. CAPE SYSTEM

(a) Bokkeveld Series

The Lower Devonian Bokkeveld Series consists of five shale bands, separated one from the other by bands of sandstone. The thickness of the succession is difficult to ascertain, but apparently reaches about 5000 feet in the Gydo Pass (Haughton, 1969). Fossils are found in most beds of the series, but marine forms (predominantly brachiopods and lamellibranchs) are largely confined to the lower half of the sequence, from whence most of the samples discussed below are derived. A few marine forms have been recovered from the upper parts of the series, but these beds have yielded mainly plant fragments.

Major element analyses for 38 Bokkeveld shales are given in Table 8A. These shales contain illite and chlorite as the dominant clay minerals, and in several samples illite is the only clay present in abundance, and only traces of chlorite were detected. Most samples contain traces of montmorillonite and minor amounts of plagioclase. K-feldspar was only rarely detected.

The samples were taken from a series of widely separated localities in the Cape Folded Belt, and it is therefore of particular interest that variations both in the absolute abundances of the major elements, and in the inter-element ratios (Table 30A) are not large. SiO_2, for example, has an average abundance of 62.57%, the standard deviation being 3.92%. For Al_2O_3 the values are 17.55% and 2.22% respectively. Similarly ratios such as Al/K and Al/Mg do not vary greatly, the mean values being 3.25 and 8.71, and the standard deviations 0.33 and 2.10 respectively.

Further, samples from the first and second shale bands when compared with similar samples from other laterally separated localities showed no statistical differences either for the absolute abundances of the major elements or for various inter-element ratios such as Si/Al, Al/K, Al/Mg and Mg/K, thus further demonstrating the chemical homogeneity of these shales. Thus unlike other examples discussed earlier, in the case of the Bokkeveld Series it is unlikely that geochemical parameters could be used as indicators of source locality or sediment transport.

Figure 10 shows a plot of the Si/Al ratio against that of Na to K, and a strong positive correlation between the two ratios is illustrated. This suggests that the single most important factor affecting the Na/K ratio in these shales is the rate of supply of detritus to the basin of deposition, which is in turn related to the rate of erosion in the source area. In other words, during periods where the quartz/clay ratio of the material transported to the basin of deposition was high, so also was the quantity of detrital plagioclase being transported, and consequently the Na/K ratio. Since K-feldspar is rare in these rocks it follows that when the quartz/clay ratio was low, so also was the Na/K ratio, since most of the K entering the basin of deposition was present within the illite lattice. It would therefore appear that the effects of ion-exchange reactions during deposition on the Na/K ratio have been masked by the effect of varying rates of plagioclase inflow, which reached a maximum during periods of more rapid sedimentation.

A further notable feature of these shales is the close relationship between Al_2O_3 and TiO_2. (Fig. 11). The existence of an Al-Ti coherence in shales was first noted by Goldschmidt (1954), who suggested that very little Ti is chemically or physically bonded to clay minerals, but is probably present as finely divided TiO_2 (for example as anatase), and is deposited along with clay flakes. Hirst (1962) concluded that Ti is probably associated with the clay fraction during weathering and transportation, and suggests that very little Ti can be actually precipitated

from solution. Porrenga (1967) has attempted to relate the Al_2O_3 / TiO_2 ratios in modern marine sediments to those of the source areas, noting that granitic rocks have ratios in the range 37 to 46, while for gabbros and basalts the value is usually between 18.5 and 6.5.

In the South African shales the ratio is quite constant regardless of the nature of the source areas of the various shale groups. For example, the Fig Tree shales which are believed to have had a basic provenance have an average Al/Ti ratio of 20.3, $\sigma = 1.6$; while the shales from the Northern Facies of the Ecca Series of the Karroo System have ratios varying from 18.0, $\sigma = 2.3$, in the GB series boreholes to 21.4, $\sigma = 1.9$ in samples from the Somkele borehole. These rocks are believed to have been derived from a source area in which albite, orthoclase and muscovite were the dominant minerals.

It has been shown that in a few instances low ratios were recorded for sediments where the rate of deposition is believed to have been comparatively rapid, and small quantities of detrital ilmenite have been washed into the basin of deposition together with quartz, feldspar and clay detritus. In the case of the Kunyas shales, where the lowest average ratio was recorded (12.9) a basaltic provenance is most unlikely, as it has been shown that these shales contain only 2.21% total Fe_2O_3, and 0.66% MgO. These samples have the highest average Si/Al ratio of any group for which results are presented in this work.

It is particularly interesting that for the separated $< 2\mu$ fractions, variation of the ratio is wide,

and in addition the overall average value of the ratio in these clay fractions is considerably higher than in the shales themselves, that is to say 32.3, $\sigma = 15.3$. This means that the ultrasonic disaggregation-gravity settling treatment has removed some of the titanium relative to the aluminium, and renders extremely unlikely the suggestion that the bulk of the Ti in shales is present in six-fold co-ordination in the clay minerals (see Porrenga 1967). Also, no support can be found for the suggestion of Lebedev (1967) that Ti is enriched in shales deposited in a fresh-water environment.

It seems more likely that since the vast majority of the clay minerals are apparently detrital in origin, the relationship between Ti and Al which is closely maintained regardless of clay type has its origin during the processes of mineral breakdown and clay formation in the source area. The reasons for the quantitative nature of the coherence and the form of the titanium oxide or hydrate in the shales are nevertheless not fully understood, and require further study.

Further features of interest are the low concentrations of CaO and P_2O_5 in the Bokkeveld shales (0.21% and 0.14% respectively). In addition, sulphur rarely exceeds 0.1%, and carbon, which was determined in four samples, Bk1, 3, 20 and 23 is less than 0.5% in each case (Table 8A).

Less than 2μ fractions were separated from four samples, Bk 7, 14, 18 and 21, and the major element analyses are given in Table 26A. As was found to be the case for the whole rocks, the clay fractions are remarkably similar

in chemical composition, and the average mineralogical composition of the four samples is:-

Clay	62%
Quartz	33%
Feldspar	4%
Carbonate	1%

(b) Witteberg Series

Rocks of the Witteberg Series lie conformably above those of the Bokkeveld, and according to Theron (1962), the series reaches a maximum thickness of about 4,000 feet in the Willowmore District. It is divided into a Lower Stage, which comprises about 590 feet of ripple marked quartzites and shales, a Middle Stage, consisting of about 1900 feet of cross bedded sandstone with thin shale intercalations, and an Upper Stage consisting of about 1600 feet of dark shales with intercalated sandstones. The Upper shales carry plant and fish remains which have yet to be fully identified (Haughton, 1969). Du Toit (1939) considers the entire 4,000 feet to be non-marine in origin and to range in age from Middle Devonian to Lower Carboniferous.

Seven Witteberg shales were analysed, and the results are presented in Table 9A. As was the case for the underlying Bokkeveld shales, illite and chlorite are the dominant clay types, with occasional traces of montmorillonite. Diffraction lines of plagioclase were detected in only one sample, Wb 4, and K-feldspar was not

observed. Chemically the samples are very similar to those of the Bokkeveld Series as may be seen from the data given in Table 5 below.

Table 5.

Element	Bokkeveld	Witteberg
SiO_2	67.3 %	66.1 %
TiO_2	0.95%	0.90%
Al_2O_3	17.7 %	18.8 %
MgO	1.79%	1.46%
CaO	0.27%	0.26%
Na_2O	0.66%	0.56%
K_2O	3.47%	3.50%
Si/Ti	53.9	54.2
Al/K	3.25	3.54
Mg/Ti	1.89	1.70
Na/K	0.21	0.30
B (Nel 1967)	64 ppm	42 ppm

It is therefore highly probable that the Bokkeveld and Witteberg sediments were derived in a continuous period of sedimentation from the same source area. Small differences in the major element chemistry such as the increased Al and decreased Na contents of the Witteberg shales can be explained in terms of the slightly increased clay and decreased plagioclase contents which in turn are functions of the rate of erosion and deposition. A less than 2μ

fraction was separated from Wb 6, and the mineralogical composition of this shale is 69% clay, 27% quartz, 3% feldspar and less than 1% carbonate. Differences in the salinity of the waters of deposition are discussed in the section devoted to the trace elements.

12. KARROO SYSTEM

(a) Dwyka Series

Rocks of the Dwyka Series are divided into the Tillite Stage and the Upper Stage (Haughton 1969). Along the Southern belt of the Karroo System the Tillite Stage has an estimated thickness of 2,000 feet, and is followed conformably by a succession of about 500 feet of olive green shales whose upper part consists of a zone of persistent carbonaceous shale, generally between 50 and 100 feet thick, which weathers white on exposure, and is known as the "White Band".

Several Upper Dwyka sediments were sampled at various localities in the Cape Province and South West Africa, and in the field the samples appeared to be very fine grained and clay rich. Chemical analyses of these samples, (Table 9A), however, showed that many of them, Dw 1, 4 and 5 for example, contain very high SiO_2 contents ($>$ 70%), and that they were generally clay poor and very variable in chemical composition. Two samples from the "White Band", LDw 3 and LDw 4 were analysed, and the results are also given in Table 9A. Organic carbon was determined in both samples, and found to be 4.18% and 3.71%

respectively corresponding to losses on ignition of 10.3% and 8.9%. These samples have very low total iron contents (Ave. 1.60%), as well as CaO and P_2O_5 contents (0.22% and 0.15% respectively). Several authors (Du Toit, 1939, and Haughton, 1969, for example) report variable occurrences of pyrite and carbonate nodules within the "White Band", and in view of the results given above, it would appear that chemical conditions varied widely during the deposition of this carbonaceous shale, and thus renders it highly suitable for further, more detailed geochemical studies.

Ecca Series

The rocks of the Ecca Series follow conformably on the Dwyka Series, and have been subdivided by Ryan (1967) into four facies - the Northern, Central, Western and Southern Facies. Shales from the Northern Facies have already been discussed in some detail, and now the geological nature of the remaining three facies as described by Ryan will be reviewed.

(b) The Southern Facies

The Southern Facies is confined to the Karroo Trough, and reaches a maximum thickness of 10,500 feet north of Grahamstown. The rocks outcrop along the southern structural margins of the basin and form an outcrop belt 10 to 15 miles wide, extending from Matjiesfontein in the west to the Indian Ocean in the east. Ryan has subdivided the facies into the Lower, Middle and Upper Groups. The Lower Group consists of a succession of green and blue shales containing plant fragments and invertebrate tracks, followed by

a more arenaceous group of sandstones with thin intercalated shale bands. Ryan believes that turbidity currents played an important role during the deposition of these sediments. The Middle Group consists of 2,000 to 4,000 feet of bluish-black shale, and the Upper Group comprises a succession of sandstones and shales commonly displaying ripple marks and cross bedding. The thickness of the group varies from about 2,000 to 4,000 feet.

Ryan believes that the Middle and Lower Groups of this facies were deposited in a deep water environment, since the sediments show abundant turbidite structures, and shallow water structures are generally absent. He points out, however, that no marine fossils have been found in the Southern Ecca Facies. In Upper Ecca times, uplift in the source area to the south resulted in an influx of coarser clastic material, and fluvial-deltaic conditions are thought to have prevailed.

(c) Central Ecca Facies

As the name implies, the sediments of the Central Facies occupy the central portions of the Karroo Basin, and are composed almost entirely of bluish-black shales and flagstones. The facies reaches an estimated maximum thickness of 4,000 feet along the northern margins of the Karroo Trough and thin out to the north to a minimum thickness of about 1,300 feet. Ryan points out that sandstone formations within the other three facies grade into shale in the Central Facies, and he believes that fairly deep water conditions prevailed throughout most of Ecca times, shallow

water structures only being found in the very uppermost beds. Marine fossils have not been found in these sediments, and Ryan believes they were deposited in a vast "continental sea".

(d) Western Ecca Facies

Rocks constituting the Western Facies outcrop along a belt five to twenty miles wide between Matjiesfontein in the south and Calvinia in the north. Ryan has divided the facies on lithological grounds into the Lower, Middle and Upper Groups. The Lower Group comprises a thick argillaceous formation, overlain by more arenaceous members which thin out towards the north west. About 60% of the Middle Group is a bluish-grey shale, the remainder being made up of siltstones and sandstones. The Upper Group is composed of shales, siltstones and sandstones in which ripple marks are commonly observed.

Ryan suggests that the Lower Group was deposited in relatively deep water, but that during Middle and Upper Ecca times tectonic uplift in the source areas to the west and south caused a rapid influx of coarser clastic material, and that the sediments of these groups are predominantly fluvial-deltaic in origin.

Apart from the shales of the Northern Facies, a total of forty four samples from different localities in the remaining three facies were analysed, and the results are given in Tables 20A, 21A and 22A. Sample localities are given in Table 1A.

Nine samples from the Southern Ecca Facies were studied, (Table 20A), five of these being from boreholes in the Fraserburg and Laingsburg Districts, and the remaining four are outcrop specimens, three from near Laingsburg, and one from the Ecca Pass near Grahamstown. The samples all contain illite as the dominant clay mineral, together with lesser quantities of chlorite in some instances, and occasional traces of kaolinite. X-ray diffraction analysis revealed the presence of plagioclase in eight of the nine samples, and K-feldspar in only one.

The Central Facies is represented by 24 samples from widely spaced localities, ten being obtained from boreholes in the Victoria West and Sutherland Districts, and the remainder are outcrop samples (Table 1A). With two exceptions the samples all contain illite as the dominant clay with lesser amounts of chlorite and occasional traces of kaolinite and montmorillonite. Two samples, WEc 5p and CV 71 contain kaolinite as the dominant clay. The presence of plagioclase was confirmed for most samples, and K-feldspar was detected in trace amounts in four instances.

The Western Ecca Facies is represented by 10 samples, seven from borehole No. 1 in the Gibeon District of South West Africa, and the remaining three are outcrop samples, one from the Calvinia District; and two from west of Sutherland. The clay mineralogy of these samples is variable (Table 1A), and each of the four clay types is represented. Both plagioclase and K-feldspar were detected in all ten samples.

In addition, eight Lower Ecca shales and six Upper Ecca shales from the Northern Facies were analysed and the results are given in Tables 10A and 19A. The Lower Ecca representatives are all illite bearing shales from outcrop localities in the Greytown and Vryheid Districts, while those from the Upper Group were selected from Borehole VB/85/65 in the Bothaville District. The clay mineralogy of these carbonaceous shales is dominated by montmorillonite with lesser quantities of kaolinite and illite. Small amounts of plagioclase and K-feldspar were detected in all six samples.

Shales from the Southern, Central and Western Facies show remarkably little variation in their chemical compositions, and differ in several important respects from those of the Northern Facies. Some relevant data illustrating these features have been extracted from Tables 28A and 30A, and are reproduced below as Table 6.

Table 6

Sample	* TiO_2	* Al_2O_3	* MgO	* CaO	* K_2O	* Na_2O	Si/Al	Al/Mg	Al/K	Mg/Ti	Mg/K	Na/K	K/Ti
Upper Group - Northern Facies (6)	0.97	21.10	1.61	0.66	2.23	1.31	2.65	11.87	6.23	1.66	0.53	0.49	3.17
Middle Group - Northern Facies (115)	1.06	21.77	1.25	0.64	3.01	0.92	2.74	17.44	5.41	1.47	0.35	0.24	4.57
Lower Group - Northern Facies (8)	0.84	20.64	0.90	0.56	2.49	0.89	2.88	21.89	5.60	1.11	0.27	0.33	4.13
Southern Facies (9)	0.66	17.94	1.90	1.22	4.03	1.29	3.72	7.74	2.96	2.68	0.38	0.45	6.97
Central Facies (24)	0.70	17.96	1.93	0.74	3.80	1.38	3.19	8.09	3.04	2.94	0.39	0.37	7.63
Western Facies (10)	0.79	16.94	1.92	0.83	3.47	1.29	3.42	8.28	3.41	2.84	0.53	0.38	6.08
Beaufort Series (11)	0.71	17.01	1.85	0.83	3.84	1.32	3.38	8.21	2.89	2.71	0.35	0.34	7.72

* Abundances given in weight percent, volatile free.

Values in parentheses indicate number of samples studied.

Two factors of importance emerge from these data. First, although the number of samples studied is relatively small, it would appear that the shales of the Southern, Central and Western Facies are notably homogeneous in their major element compositions. It will be remembered that the samples were taken from widely spaced localities, both laterally and vertically in each of the three facies. It is therefore probable that these sediments were all produced in areas of similar climatic conditions from rocks not widely different in chemical composition, and that the clay detritus has been further homogenised during transportation and deposition.

Second, shales from the Northern Facies contain significantly more Al, and less K and Mg than those from the other three facies. This is principally because of the dominance of kaolinite in the former instance, and illite and chlorite in the latter, although it is interesting that the six Lower Group shales from the Northern Facies contain illite as the dominant clay, and in spite of this contain significantly more Al_2O_3 than illite rich shales from the Central, Southern and Western parts of the basin. The separated clay fraction of one of these samples, Ec 18, also contains more Al_2O_3 than clays from shales in the other facies (Table 26A).

Although it has been shown that the bulk of the material of which most shales are constituted is detrital in origin, it is distinctly possible, but does not necessarily follow that the shales of the Northern Facies were

derived from source rocks whose chemical compositions differed markedly from those of the other three facies. Several other extremely important factors operative during the processes of mineral breakdown and clay formation can drastically affect the ultimate composition of the resultant shale. Particularly significant in this respect is the nature of weathering to which the source rocks were subjected, which in turn is primarily dependent on prevailing climatic conditions and the nature and extent of the vegetation in the source area. In addition, factors such as the rate of erosion, distance from the source, and the presence or absence of diagenetic minerals all contribute to the ultimate chemical composition of the resultant shale.

In the case of the Northern Facies shales, particularly those from the Middle Group climatic conditions in the source area probably played an important role in this respect. In view of the abundant coal seams and deciduous plant fossils (Haughton, 1969) which are found in these shales it is probable that a moist, cool climate prevailed, and that weathering conditions generally were quite acid, thus favouring the formation of kaolinite rather than illite and chlorite. Further, in the depositional environments themselves where vast quantities of organic matter accumulated, the pH has been shown with few exceptions to have been low, thus further favouring the stability of kaolinite.

In this respect, two samples from the western flank of the Central Facies, WEc 5b and 5p, are of interest. Both samples are black shales containing abundant calcite, the CaO contents being 12.95% and 34.09% respectively. In addition WEc 5p contains abundant phosphate (1.57% P_2O_5) and normative pyrite (1.30% S). This sample contains very little clay, and has only 5.2% Al_2O_3, whereas WEc 5b contains illite as the dominant clay and has a K_2O content of 4.16%. Unlike the black shales of the Northern Facies these sediments appear to have been deposited in water of considerably higher pH (> 7.8), as evidenced by the high normative calcite and apatite contents.

Also of interest are the six upper Ecca shales from the Bothaville District, from borehole VB 85/65. Chemical analyses of these black shales are given in Table 10A, and as may be seen from the compilations of average inter-element ratios, they are similar in composition to the shales from neighbouring Vierfontein Collieries. Organic carbon was determined in two of the samples, BEc 4269 and 4270, and they were found to contain 3.5% and 5.8% C respectively. As was the case for several of the Vierfontein shales, those from Bothaville contain moderate amounts of normative pyrite, four of them having greater than one weight percent, and one sample BEc 4265 has 6.31% S. In addition, three of the samples, BEc 4268, 4269 and 4270 contain more than two percent normative siderite. The samples contain an average of 0.56% CaO, and 0.11% P_2O_5. Unfortunately these samples were not analysed by Nel (1967) for boron, but in view of the diagenetic mineral assemblage, and the remarks made previously in connection with the work

of Williams and Keith (1963), it is emphasized that this sector of the Karroo Basin merits further close study.

(e) Beaufort Series

Within the main Karroo Basin the sediments of the Beaufort series follow conformably on those of the Ecca Series (Haughton, 1969). The series makes a huge oval, covering an area some 800 miles long and 300 miles wide, and the Beaufort beds are exposed over the whole of the Great Karroo, most of the Orange Free State, western Natal, the Transkei and the Eastern Province. The total thickness of the series is probably in excess of 12,000 feet in the southern part of the basin, and the entire sequence is made up of alternating feldspathic sandstones, and blue, purple, green and red mudstones and shales. In many areas, particularly in the central portion of the basin it is impossible to differentiate between the Upper Ecca shales, and those of the Lowermost Beaufort Beds (Ryan, 1967). The outstanding feature of the Beaufort Series as a whole is its abundance of vertebrate fossil remains, the lower beds contain reptiles, and these give place largely to mammal-like reptiles and amphibians. Ryan (1967) believes that shallow water continental conditions prevailed during the deposition of most of the Beaufort Series.

The major elements were determined in eleven Beaufort shales and the results are given in Table 24A. The samples were taken from widely spaced localities (Table 1A), ranging from Coffee Bay in the Transkei to

Bloemfontein, Richmond, Carnarvon and Victoria West. In each case illite is the dominant clay mineral, together with traces of kaolinite and montmorillonite. The presence of plagioclase was confirmed in all eleven samples, and traces of K-feldspar were observed in samples Bf 1 and Bf 5.

The dispersion of the major elements in these shales is very small, and the samples have extremely similar chemical compositions. For example SiO_2 has a mean concentration of 63.04%, the standard deviation being 2.04%. For Al_2O_3 and TiO_2 the values are 16.25% and 0.68% with standard deviations of 1.15% and 0.04% respectively. Reference to Table 6 in this text shows that in terms of both the absolute abundances of the major components, and also the inter-element ratios, the shales are statistically indistinguishable from those of the underlying Southern, Central and Western Facies of the Ecca Series. This suggests that conditions in the source area showed very little change during the formation of this entire sequence.

13. SHALES DREDGED FROM THE AGULHAS BANK

An example of the application of accurate major element analysis of fine-grained sediments is afforded by a series of submarine shales dredged from the Agulhas Bank, and supplied by R. Gentle of the Department of Oceanography, U.C.T. The offshore locality of the Bokkeveld-Malmesbury contact is not known with any degree of certainty in this area; and it was hoped that chemical treatment would provide information as to whether the samples were derived

from the Bokkeveld Series or the Malmesbury Formation.

Eight samples were studied, and in each case illite and chlorite were found to be the dominant clay minerals, together with minor amounts of plagioclase and occasional traces of K-feldspar. Complete major element analyses are given in Table 25A, and mean values for 24 inter-element ratios are presented in Table 30A. Some more pertinent data have been extracted from these Tables, and are reproduced in this text as Table 7.

It is seen that the dredged Agulhas Bank shales and those from the Bokkeveld Series contain significantly more Al_2O_3 and TiO_2, and less CaO, MgO and K_2O than do those of the Malmesbury Formation. Two sets of data are given for the Malmesbury sediments, in the first case all analyses including both the argillaceous and arenaceous varieties are included, and in the second only the more fine grained types have been considered.

Table 7.

	Dredged shales	Bokkeveld Series	All Malmesbury sediments	Malmesbury shales
SiO_2	62.91	62.57 (3.92)	66.10	60.90
TiO_2	0.87	0.94 (0.90)	0.68	0.80
Al_2O_3	17.63	17.55 (2.22)	15.25	16.94
MgO	1.89	1.53 (0.48)	2.82	3.58
CaO	0.19	0.21 (0.25)	0.67	0.65
K_2O	3.49	3.12 (0.69)	3.78	4.50
P_2O_5	0.15.	0.14 (0.05)	0.14	0.15
Al/Mg	9.14 (1.62)	8.71 (2.10)	5.20	4.27
Al/K	3.21 (0.33)	3.25 (0.33)	2.65	2.38
Fe/Mg	4.12 (0.58)	4.38 (1.50)	2.68	2.74
Mg/Ti	2.08 (0.70)	1.89 (0.53)	3.83	3,34
Ca/P	2.12 (0.71)	2.41 (2.48)	7.47	7.53

Figures in parentheses are the standard deviations on the means.

The similarities between the dredged shales and those of the Bokkeveld Series are particularly well illustrated when the ratios Al/Mg, Al/K, Fe/Mg, Mg/Ti and Ca/P are considered, and it is seen that in each case the mean values recorded for the Malmesbury sediments fall outside of the range of two standard deviations from the mean of both the Bokkeveld and dredged shale values. These data suggest

very strongly that these submarine samples are members of the Bokkeveld Series of the Cape System.

E. VARIATION OF THE MAJOR ELEMENTS WITH GEOLOGICAL AGE

Age variation studies of the major elements in fine grained sediments are of particular importance to a number of geological and chemical disciplines, and are pertinent to discussions concerning the chemical evolution of the world's oceans and continents. Unfortunately, data are scarce and of variable quality. The most comprehensive studies to date are those of Vinogradov and Ronov (1956 a, b), who analysed some 250 composite samples comprising over 6,000 individual argillaceous rocks from the Russian Platform. The samples ranged in age from Precambrian (580 million years) to Tertiary (30 million years).

Debate concerning possible chemical variations of the composition of the oceans has, on the other hand, been profuse. Goldschmidt (1933) was the first to perform a series of geochemical balance calculations in which he attempted to prove that the oceans had formed by continuous and additive weathering processes. He found that geochemical balance was particularly poor for most volatile elements, as well as some involatile elements. Barth (1961) suggested that the situation is in fact more complex, and that consideration must be given to the fact that most sediments have experienced a number of cycles of weathering, deposition and metamorphism. He visualised the oceans as being extensive reservoir systems where addition by inflow is balanced by subtraction effected during sedimentation.

Current opinion favours the idea that the composition of the oceans at the present time may be explained in terms of well defined equilibria in which the clay minerals play a dominant role (Sillén 1961, 1963, 1967a, b; Kramer 1965, Holland 1965). The models propose that the oceans are effectively bufferred and that constancy of composition is maintained by equilibria reactions such as:

$$1.5\ Al_2\ Si_2\ O_5\ (OH)_4\ (s) + K^+ \leftrightharpoons KAl_3\ Si_3\ O_{10}\ (OH)_2 + H^+ + 5H_2O \quad \text{---------- (1)}$$

This reaction would apply to a simplified system containing only water, HCl, KOH, Al $(OH)_3$ and SiO_2, and the equilibrium constant for this reaction, K, may be written as:

$$K = \left[H^+\right] / \left[K+\right] \quad \text{----- (2)}$$

Sillén (1967b) developed this model to accommodate the phases quartz, kaolinite, illite (hydromica), Mg-rich chlorite, Na-montmorillonite, calcite and phillipsite, in addition to the aqueous and gas phases. Sillén noted the difficulties in comparing this system with those occurring in nature, but nevertheless pointed out that the value of the equilibrium constant in equation (2) above for sea-water, is very close to a value extrapolated to the temperature of sea-water from those determined in the laboratory by Hemley (1959).

These models have been criticized on a number of scores, the principal objection being that the majority of silicates present in the ocean are detrital, and coarse grained, and would not have time to reach equilibrium with the sea-water before burial and lithification. Sillen, however, feels that sufficient $< 2\mu$ material is available to react with the ocean water prior to its removal from

the system. In this respect it is interesting to note the work of Garrels and Mackenzie (1966), who calculated that only 7% of the detritus entering the ocean would be required to react fully with the sea-water in order that equilibrium be maintained. Helgeson et al. (1969) have noted that these models make no allowance for irreversible reactions in the ocean, and variations of equilibrium assemblages in different parts of the ocean. The chemical composition of the ancient oceans is clearly also a critical factor.

In this respect, results from the present work are plotted in Fig. 12, which shows the variation with decreasing geological age of Al_2O_3, K_2O, MgO, Na_2O and CaO in the South African shales. The range covered is from the three billion year Precambrian Fig Tree Shales to the Triassic Beaufort shales. The age sequence as given in Fig. 12 was arranged by J. de Villiers (personal communication). The values are given on a volatile free basis so that the Permian organic rich shales of the Ecca Series may be viewed more realistically. Since for all other shales the ignition loss is of the order of 5% or less, the results are not significantly changed. In addition, samples containing more than 70% SiO_2 (siltstones) or 20% total Fe_2O_3 (ironstones) have been excluded. It will be remembered that for all shales older than the Permian, illite and chlorite were the dominant clay minerals, whereas beginning in the Permian, kaolinite, and later montmorillonite are more extensively developed. No significant variation trends could be detected for Al_2O_3, CaO

or Na_2O.

In the case of potassium, however, the abundance increases from the early Precambrian shales to values in excess of 5% K_2O for shales of the later Precambrian and Cambrian whereafter it drops to about 3% in the Silurian and Devonian shales. In spite of rather wide fluctuations in a few of the sample groups, it is believed that this trend is real for the following reasons.

The average K_2O content of the Fig Tree shales is 2.85%, and this may be considered as being close to an upper limit for these sediments since the low potassium graywackes have been excluded. Nevertheless the potassium contents are somewhat higher than might have been expected if they were derived from predominantly basic and ultrabasic rocks as suggested by their Cr and Ni contents. The graywackes contain abundant plagioclase of intermediate composition and only small amounts of K-feldspar and it appears possible that the K_2O contents are not a true reflection of the source area, and have been somewhat upgraded to various degrees during and after deopsition. The average K_2O content of the ten Witwatersrand shales is of the order of 2%, the maximum value recorded being 4.02% for Jp 3, but these samples are not of great significance in the present discussion since it has been shown that they were probably deposited in a fresh-water continental sea of low salinity.

The remaining Precambrian shales have K_2O contents significantly in excess of these values. The average value for the five Kunyas shales examined is 4.61%, the range being

from 3.7% to 5.4%. The single Damara shale, Dm 1, believed by H. Martin to be of marine origin has 5.06% K_2O. The three argillaceous Malmesbury shales all have K_2O contents in excess of 4%. A. Erlank (personal communication) has determined the potash contents of over thirty Malmesbury argillites, and he found that in each case the K_2O content exceeded 4%.

All four Cango shales studied have K_2O contents in excess of 4.5%. Kröner (1968) recorded a mean K_2O content of 5.68% for five Kuibis shales analysed by him, and the two studied in this work have K_2O contents of 6.02% and 8.91%. $< 2\mu$ fractions separated from these shales contain 8.93% and 9.63% K_2O respectively. On a water free basis these values are 9.58% and 10.25% the highest recorded for any of the separated clays analysed. The data for the four Schwarzrand shales are inconclusive, and the values range from 1.9% to 6.2% and more samples from this series will have to be analysed to clarify the position. The Fish River sediments studied are not true shales in that they contain abundant quartz (Ave. 69% SiO_2) and detrital feldspar.

There would therefore appear to be a definite increase of K_2O from the Ancient Fig Tree shales through the late Precambrian- early Cambrian Kunyas, Malmesbury, Cango and Kuibis shales. Shales from the lower Devonian Bokkeveld Series on the other hand have an average K_2O content of 3.47%. These are true marine shales, and it has been shown that the dominant clay minerals in these samples

are also illite and chlorite. Of the 38 samples analysed from this group, only four have K_2O contents in excess of 4.5%. The average K_2O content of the Witteberg shales is also lower, being 3.50%. Similarly, the mean K_2O contents of the illite bearing shales from the Southern, Central and Western Facies of the Ecca Series rarely exceed 4%, although the possibility of deposition of many of these samples in fresh or brack water must be borne in mind. In their study, Vinogradov and Ronov (1956a) noted a steady decrease in the K_2O contents of their composite samples from Precambrian through to Tertiary. Unfortunately, these authors only record single averages for the Precambrian and Cambrian composites. Nevertheless there is an increase of K_2O from 3.96% in the 580 million year Precambrian shales to 4.82% in the Cambrian composite. These authors make no comment as to the possible reasons for this increase. They attribute the general enrichment of potassium in the ancient shales to the terrestrial weathering of biotite and K-feldspar to hydromicas, a process they believe to have been more operative during Precambrian times. Further, they regarded the Na_2O content throughout the section as "virtually unchanged".

In a re-interpretation of this work, Weaver (1967) suggested that there was an abrupt decrease in the K_2O content, and a corresponding increase in the Na_2O content between the Carboniferous and the Permian. Weaver noted that this corresponded to a decrease in the abundance of illite, and an increase in the kaolinite and mixed-layer clay contents of North American shales over the same time interval. Weaver (1959) first attributed this change in mineralogy to differences in the respective source rocks of the Pre and Post-Upper Mississippian sediments.

In the later paper (Weaver, 1967), however, he felt that chemical conditions prevailing during weathering were of more fundamental importance. He believed that the prolific growth of land plants in Devonian and Carboniferous times caused an upsurge in the amount of humus, CO_2 and S, and by implication generally more acid conditions. He suggested that these conditions would favour the formation of kaolinite and montmorillonite.

In the South African sediments the decrease of K_2O after the Precambrian does not appear to be principally dependent on clay mineralogy, since the Lower Devonian Bokkeveld shales, like those from older sequences contain illite and chlorite as the dominant clays. Abundant kaolinite first makes its appearance in the Permian coal-bearing shales of the Northern Ecca Facies of the Karroo System.

Conway (1945) in a series of material balance calculations based mainly on the data of Clarke (1904, 1924) argued that K has not been removed from the ocean at a constant rate throughout, but at a steadily increasing rate reaching a peak in the late Precambrian or Cambrian. The K_2O abundances in the South African shales appear to be in accord with this prediction. Conway (1945) visualised large scale development of primitive living organisms during this time, which he believed aided the fixing of K in glauconite and illite. He also pointed out that second and third cycle clays will not readily yield the bulk of their potassium during weathering and transportation.

The theory has much to commend it. Barghoorn and Schopf (1966) found bacterium-like fossils in the Fig Tree Shale, and similar evidence of multi-cellular and algal plant life has been recorded in Precambrian sediments from numerous localities (Oro et al. 1965, Cloud et al. 1965 for example). Weaver (1967) has reviewed the literature dealing with the association of primitive life forms and plants with potassium. He notes that the ash of most marine algae contains between 20% and 40% K_2O, and considerably lesser amounts of Na_2O. Similarly yeast ash contains between 28% and 48% K_2O. (Eddy, 1958). Weaver also notes that some algae and bacteria concentrate potassium by a factor of over 1000 relative to their nutrient solutions.*

The presence of simple life forms in the Fig Tree shale, and the proliferation of these forms are therefore likely to have influenced the K_2O contents of the sediments accummulating over this period. It seems likely that an ever increasing quantity of these dead organisms were buried with the sediments, and that their preservation during burial was made possible by the lack of oxygen in the primitive oceans. This explanation would account for the apparent slight over-abundance of potash in the Fig Tree shales, and the steadily increasing K_2O contents of shales accummulating in Precambrian and early Cambrian times.

Conway (1945) believed that in the younger oceans K^+ continued to be extracted at a faster rate than it was supplied, and Weaver (1967) has noted that as land plants proliferated, so also would the degree of weathering due to

* See page 115

the increased acidity of the soils. He feels that under these conditions a considerable portion of the available potassium instead of flowing to the sea would be retained by these plants and be continually recycled on land. It is difficult to assess the relative importance of marine and terrestrial organisms, but it seems likely that various life forms have played an important role in controlling the distribution of potassium over geological time.

The data presented here for the South African shales confirm the findings of Conway (1945), Nanz (1953), and Vinogradov et al. (1956a,b) and suggest that on a world-wide basis Precambrian shales contain more potassium than those from younger formations. The chemical composition of the source rocks of these shales does not appear to have been the major controlling factor in this respect, but rather the alkaline weathering conditions which would favour the formation of illite in the source areas, and particularly the effects of various life forms as outlined above. It is therefore highly unlikely that the overall potassium concentration in the ocean has remained constant over geological time, and appears to have attained a maximum value during late Precambrian or early Cambrian times.

MgO behaves differently. Reference to Fig. 12 shows that there is a somewhat erratic decrease in abundance from the Precambrian to the Permian shales, the largest fluctuations being observed in the oldest shales. The average MgO content of the Fig Tree shales is 6.0%. It was explained in an earlier section that trace element studies led the author to believe that these shales were

derived from source areas of predominantly basic or ultrabasic rocks. The MgO contents of the shales are in agreement with this postulate. It has also been mentioned that the Fig Tree graywackes contain higher than average MgO contents. A further factor is that weathering conditions during the early Precambrian were almost certainly highly alkaline (Perelmen, 1962) and these conditions would favour the formation of Fe-Mg chlorites, such as are found in the Fig Tree Shales.

Samples from the Jeppestown and Government Reef Series of the Witwatersrand System were also shown to have high Cr, Ni and Mg contents, and again, these features were related to the basic nature of the source rocks from which these shales were derived.

The MgO contents of the remaining Precambrian and Cambrian shales show rather wide fluctuations. The Kunyas shales are low in MgO (Ave. 0.7%) as also is the single shale from the Kheis System (0.49%). It is probable that these values reflect derivation from low Mg granitic source areas. The argillaceous Malmesbury shales have a mean MgO content of 3.7%, and shales from the Cango Formation vary between 1.5 and 4.3% (Ave. 2.8%). Kröner (1968) records an average MgO content of 4.6% for five Kuibis shales, the samples studied in this work being somewhat lower. Thereafter there is a steady decrease in the mean MgO contents to the shales of the Lower Ecca Series, whereafter values are once again more variable.

It is suggested that the MgO contents of the argillaceous rocks under discussion have been dominated by their source rocks, and to a lesser extent by the nature of the weathering processes experienced by these rocks. It would appear that during Precambrian times the exposed crustal rocks were sufficiently inhomogeneous that in some areas the terrains consisted of predominantly basic rocks, whereas, less commonly, in others, granitic rocks were more abundant. With progressive weathering, recycling and metamorphism the source areas became generally more homogeneous and intermediate in chemical composition. In addition climatic conditions probably became less alkaline, and consequently less favourable for the formation of chlorites high in Mg. Furthermore, these effects have been sufficiently dominant as to mask any possible ion-exchange relationship between Mg and K as suggested by Conway (1945), and there is no apparent interdependence between these two elements.

* Note added in press : Borovic - Romanova (1969) has determined alkali metal abundances in a variety of marine algae, and found that the K/Rb ratios in these algae are the same as in normal sea water, i.e. 2000. The enrichment factors of the alkali elements in the algae over sea water were found to be Na - 0.78, Li - 0.95, K - 19, Rb - 18 and Cs - 45.

F. THE AVERAGE SOUTH AFRICAN SHALE

The average chemical composition of all South African shales analysed in this study is presented in column (1) of Table 8. Since the sample population is biased by the large number of shales rich in organic matter from the Coal Measures of the Karroo System, the data are also presented in column (2) on a volatile free basis for more realistic comparison. The average values are generally in good agreement with those available in the literature, particularly the mean concentrations in 51 Palaeozoic shales (Clarke, 1924) and the average shale of Degens (1965). The latter author recalculated the average shale analysis on a carbonate free basis assuming a CaO/MgO ratio of six in the carbonate fraction.

Table 8.

	(1) This work (a)	(2) This work (B)+	(3) Average shale Clarke (1924)	(4) Average Pelite Shaw (1956)	(5) Average shale Wedepohl (1969)	(6) Average shale Degens++ (1965)	(7) 51 Palaeozoic shales Clarke(1924
SiO_2	60.7	66.2	62.2	60.8	58.9	65.0	60.2
Al_2O_3	16.5	18.8	16.5	19.7	16.7	17.2	16.4
Fe_2O_3	3.1	6.18*	4.3	1.9	2.8	4.5	4.04
FeO	3.3	-	2.6	3.2	3.7	2.7	2.90
MnO	0.1	0.1	Tr	0.1	0.1	Tr	Tr
MgO	1.8	1.9	2.6	3.7	2.6	2.24	2.3
CaO	0.8	0.8	3.3	1.9	2.2	0.52	1.4
Na_2O	1.0	1.1	1.4	3.5	1.6	1.4	1.0
K_2O	3.0	3.3	3.5	4.3	3.6	3.6	3.6
TiO_2	0.8	0.9	0.7	0.6	0.8	0.7	0.8
P_2O_5	0.2	0.2	0.2	0.1	0.2	0.2	0.2

* Total Fe expressed as Fe_2O_3

\+ Volatile free

++ Recalculated on a carbonate-free basis.

Frequency distribution diagrams for SiO_2, CaO, Al_2O_3, TiO_2, total Fe_2O_3, K_2O, Na_2O and MgO in the entire sample population are given in Figs. 13 to 20 respectively. The frequency plot of SiO_2 is positively skewed, and this is due to the presence in the samples of variable amounts

of detrital quartz. Most clay minerals have SiO_2 contents in the range 45-50% (Table 26A, and Grim 1968), and additional SiO_2 in shales is contributed mainly by admixtures of detrital quartz. Shaw and Weaver (1965) found that the distribution of quartz itself in 300 North American shales was similarly positively skewed, but when only samples containing less than 50% quartz were considered they found that the quartz of the "true shales" was normally distributed.

These authors also showed that the distribution plot of carbonate minerals in the shales was positively skewed, and apparently lognormal, as compared to the plot of total clay distribution which was found to be normal. The frequency distribution diagram of CaO in the South African shales is strongly positively skewed, while that of Al_2O_3 closely approaches normality. TiO_2 on the other hand has a slight positive skew, probably as a result of Ti contributions from detrital ilmenite grains in the more silty sediments, in excess of the Ti more intimately associated with the clay fraction. K_2O and Fe_2O_3 have negatively skewed distributions whereas that for Na_2O is bimodal in the sense that a disproportionate number of carbonaceous shales whose mineralogy consists almost exclusively of kaolinite and quartz are represented. A further, smaller number have apparently been affected by surface weathering and some of the sodium originally present has probably been lost through leaching.

G. THE ALKALI METALS - A DISCUSSION

The trace alkali metals (Li, Rb and Cs) have been determined in the South African shales and separated clay fractions, and the results for the individual samples are given in Tables 31A to 54A in which the sample groups are arranged in order of decreasing geological age. Rb was determined by X-ray fluorescence spectrometry, and an optical emission technique was employed for Li and Cs. Full details of the analytical methods are recorded in Chapter I. In Table 9 of this text average abundances for each of the sample groups studied are presented for comparison, and Table 10 gives overall averages for the entire sample population together with values for shales determined by other workers. In addition abundance data are given for natural waters as well as estimates of crustal abundances.

Consideration of the data in Table 10 shows that the average Rb content of the South African shales is in excellent agreement with values recorded for shales from other localities. The average Cs abundance (7.2 ppm) is slightly higher than the value recommended by Wedepohl (1970), (5.5 ppm), and slightly lower than the value given by Canney (1952) for 94 North American shales (8.4 ppm).

Table 9

The Alkali and Alkaline Earth elements in some South African shale sequences

Sample Group	Li (ppm)	Rb (ppm)	K/Rb	Cs (ppm)	K/Cs	Ba (ppm)	K/Ba	Sr (ppm)
Fig Tree shales	44	121	198	6.0	4025	481	47	28
Fig Tree graywackes	31	57	224	3.1	4393	285	46	47
Jeppestown and Government Reef Series	46	83	194	4.6	3693	542	30	168
Kunyas Series	10	228	162	4.9	8468	584	66	85
Malmesbury Formation	45	175	173	12.5	2848	436	72	110
Cango Formation	44	216	198	7.0	7282	675	64	48
Fish River Series	33	138	176	5.8	4848	483	52	122
Bokkeveld Series	67	155	177	7.0	3816	700	39	113
Witteberg Series	49	153	175	8.0	3653	711	38	70
Dwyka Series	13	147	162	8.0	2957	689	34	245
Bothaville Boreholes (Ecca Series)	90	115	175	6.9	4053	520	39	164
Borehole GB 45/64	42	153	185	5.5	6032	998	28	185
Borehole GB 47/64	54	161	178	6.8	4696	1004	28	168
Borehole GB 48/65	69	160	179	6.7	5033	890	32	182
Borehole A78	66	84	166	5.7	2348	546	23	119
Borehole A76	70	65	156	4.9	2136	532	20	278
Borehole A62	68	64	161	5.3	2052	454	22	190
Somkele Borehole	34	159	164	9.1	2992	832	32	168
Dannhauser Borehole	72	143	164	7.0	4470	858	31	158
Springbok Colliery	109	106	148	6.7	2444	727	22	208
Vierfontein Colliery	94	65	143	-	-	394	21	101
Lower Ecca, Northern Facies	40	125	166	6.4	3245	804	26	130
Southern Ecca Facies	34	171	185	9.5	4109	697	45	134
Central Ecca Facies	52	161	174	8.4	3380	729	40	216
Western Ecca Facies	49	133	188	8.5	3384	427	52	212
Beaufort Series	40	180	168	9.2	3788	600	53	144
Ave. S.A. shale	55	141	172	7.2	3666	681	37	150
Ave. Separated clay	63	240	175	16	3170	932	50	162

Table 10

	Na	K	Na/K	Rb	K/Rb	Cs	K/Cs	Li
Average S.A. Shale	0.90%	2.40%	0.4	141 ppm	172	7.2 ppm	4066	55 ppm
Average Shale (1)	1.19%	3.00%	0.4	140 ppm	-	5.5 ppm	-	66 ppm
Average Shale (2)	-	3.80%	-	140 ppm	280	6.3 ppm	5555	66 ppm
Average Shale (3)	-	2.11%	-	130 ppm	170	8.4 ppm	2611	-
Black Shales (4)	-	3.40%	-	262 ppm	130	11 ppm	3200	44 ppm
Sea Water	◊ 1.056%	+ 380 mg/l	28	125 µg/l*	3050	0.30 µg/l*	1,250,000	0.2 ppm◊
River Water	◊ 6.0 ppm	■ 2.90mg/l	2.1	1.1 µg/l□	2650	0.02 µg/l□	145,000	0.0016 ppm◊
Crustal abundances (5)	2.36%	2.09%	1.1	91 ppm	230	3.0 ppm	7,000	25 ppm
Field Function (6)	1.83	2.27	-	2.31	-	2.33	-	1.47
Enrichment Factor	0.42	1.15	-	1.55	-	2.40	-	2.20
Residence Time (my)	210	5.7	-	3.0	-	0.89	-	0.069

(1) Wedepohl (1970)

(2) Horstman (1957)

(3) Canney (1952) (Corrected by Heier and Adams (1964).

(4) Spencer (1957)

(5) Taylor (1964)

(6) Welby (1958)

■ Sreekumaran et al. (1968)

◊ Wedepohl (1970)

\+ Goldberg (1963)

* Bolter et al. (1964)

□ Kharkar et al. (1968)

The Li average (55 ppm) is slightly lower than the average value for shales recommended by Horstman (1957) (66 ppm), and somewhat higher than the value of 44 ppm recorded by Spencer (1957) for a series of black shales.

Although it is generally accepted that a large proportion of the trace alkali metal content of shales is intimately associated with their constituent clay minerals, the factors governing the incorporation of these elements into argillaceous sediments are not fully understood. Recent suggestions that the chemical composition of ocean water is maintained in a steady state of equilibrium (Rubey, 1951; Sillén, 1961; 1963; 1967 a,b; Kramer, 1965; Holland, 1965) have emphasized the importance of a more complete knowledge of these factors, particularly for elements such as the alkali metals whose residence times are long relative to the age of the oceans (Table 10). Of vital significance in this respect is the problem concerning the origin of the clay minerals themselves, which has already been discussed at some length.

It was pointed out that following the work of Hurley et al. (1959, 1961, 1963), Biscaye (1965) and others, there is a strong body of opinion which favours a detrital origin for the vast majority of the clays found in sediments, and that these clays are not markedly affected upon entering the marine environment. In the discussion to follow, this concept will be investigated in the light of previously published data, and the data presented here for the South African argillites.

Canney (1952) has pointed out that the alkali elements can be transported from the site of weathering to the site of deposition in a number of ways:

1) In true ionic solution.
2) In structural sites of unweathered minerals.
3) In structural sites of minerals formed during weathering.
4) In organic matter.
5) As adsorbed ions on the clay minerals and other colloidal material.

Furthermore, in an earlier section dealing with major element abundances it was pointed out that the alkali metal contents of sediments accummulating in the basin of deposition could conceivably be modified by one or more of the following processes:

1) By ion exchange and adsorption reactions with sea water.
2) By the formation of authigenic minerals in the ocean.
3) By the incorporation in the accummulating sediment of organic debris (algae, fungi, etc.) rich in alkali metals.

An attempt will now be made to assess the relative importance of these processes.

In the source area, prevailing climatic conditions and the chemical composition of the source rocks themselves are clearly of fundamental importance, since the type of clay mineral formed in the first instance is largely dependent on these factors. In alkaline environments where the formation of micaceous clay minerals is favoured

(Weaver, 1967), the alkali elements are incorporated in the interlayer positions of these minerals. In more acid soils, on the other hand, where kaolinite tends to be the dominant clay mineral, no suitable structure site exists for the accommodation of the alkali elements. Furthermore, cation exchange capacities of the different clay minerals vary considerably. According to Carroll (1959), exchange capacity is lowest in kaolinite, and increases in the order kaolinite < chlorite < illite < montmorillonite < vermiculite.

The importance of ion-exchange reactions in the oceanic environment with respect to the alkali metals has been questioned by several authors. Although data on the uptake of the alkalis is rather limited, it would appear from the work of Potts (1959) and Carroll and Starkey (1960) that more Mg and Na are adsorbed than K. The latter authors found the replaceability of H+ ions from clay minerals follows the order $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$. Potts (1959) treated clays from the Missouri River with sea water for various lengths of time, and found that Na^{+} and K^{+} were only marginally affected compared to the much larger changes recorded for Ca^{2+} and Mg^{2+}. Weaver (1967) suggested that the K^{+} ion may only be adsorbed in cases where the lattice charge is sufficiently high as to overcome the effects of Na^{+} and Mg^{2+}, and although "stripped" illites may contain numerous such sites, Weaver (1967) feels that these clays satisfy much of their demand for K^{+} in the rivers during transportation to the ocean.

The behaviour of the alkali elements during weathering and soil formation has been studied by several authors, for example Goldschmidt, (1954); McLaughlin, (1955, 1958, 1959); Lebedev, (1957) and Horstman (1957). McLaughlin (1955) showed that Na is readily lost during leaching processes and is almost invariably lower in abundance in clays than in silts. This author emphasized the importance of organic agents and mineralogy in controlling alkali element variation during weathering. Horstman (1957) showed that a number of features of alkali element distribution in shales manifest themselves during the early stages of weathering. Particularly important in this respect is the enrichment of Rb relative to potassium, resulting in the lower K/Rb ratios of argillites compared to igneous rocks. Goldich and Gast (1966) showed that during the weathering of biotite Rb is preferentially adsorbed over K prior to transportation from the site of weathering. Dasch (1969) noted that the weathering of crustal rocks results in a marked partitioning of Rb and Sr, and that the marked increase of the Rb/Sr ratio in the weathered material is almost entirely due to the loss of Sr during weathering.

Canney (1952) and Welby (1958) have attempted to explain the distributional features of the alkali elements in sediments in terms of their relative adsorptive capacities. These authors have noted that the adsorption of ions is largely controlled by electrostatic forces, and for ions of equivalent charge the one having the greatest positive electrostatic potential at the surface will be relatively enriched. Ahrens (1953) suggested that a measure of the

electrostatic potential is given by the field function, F,

$$\text{where } F = \frac{\text{Ionization potential}}{\text{Ionic radius}}$$

Welby (1958) calculated F values for each of the alkali metals using hydrated radii (Gedroiz, 1918), and his values for this function are reported in Table 10. Also given in Table 10 are a series of enrichment factors, E.F.,

$$\text{where E.F.} = \frac{\text{Average abundance in shale}}{\text{Average crustal abundance}}$$

It is seen that the predicted order of enrichment is Cs $>$ Rb $>$ K $>$ Na $>$ Li, and that with the exception of Li which has an E.F. intermediate between Cs and Rb, this sequence is obeyed. It therefore may be inferred that whether the alkali elements become associated with the clay minerals during the weathering process, as suggested above, or alternatively during transportation and deposition, electrostatic attraction between the clay particles and the hydrated ions play an important role in controlling the distribution of these elements in sediments.

In this respect it is essential to consider the partitioning of the alkali elements between clay particles and natural waters in the world's rivers and oceans. Harriss (1967) has studied the effect of ion exchange reactions on the Na/K ratio of the sea by constructing influx-removal budgets for these elements using the data of Potts (1959) and Carroll and Starkey (1960) and these may be examined in Table 11.

Table 11

Annual sodium and potassium budget in the Ocean

Na influx from continental waters (corrected for cycling)	1.1×10^{17} mg/yr.
Na removed by ion exchange	5.9×10^{14} mg/yr.
K influx from continental waters (corrected for cycling)	6.6×10^{16} mg/yr.
K removed by ion exchange	3.6×10^{14} mg/yr.

It is evident from these data that the total quantities of Na and K involved in ion exchange reactions are negligible compared to the annual amounts flowing into the oceans from continental drainage. Harriss (1967) explains the high Na/K ratio of ocean water (28 compared to a value of 2.7 for river water) by variation in the input from different water sources. He suggests that the Na/K ratio of ocean water was adjusted to a value of forty to fifty by the extensive diagenesis of natural waters. As the oceanic volume reached its present value the input of metamorphic and deep subsurface waters became small relative to the amount of water involved in terrestrial weathering and continental drainage, and that the evolution of alkali metal ratios in the sea has been controlled by mixing with continental drainage water whose chemistry is determined by reactions in the soil zone involving the weathering of igneous rocks and the formation of clay minerals. In other words, he suggests that oceanic sedi-

ments are essentially non-reactive and that the composition of ocean water is primarily a function of parent water types.

Consider now the distribution coefficient data

$$\left(K_D = \frac{\text{concentration in clay}}{\text{concentration in solution}}\right)$$

for Cs produced by Wahlberg and Fishman (1962). It is found that the ratio decreases at least five times for a ten-fold increase of the Na concentration of the solution. Unfortunately no distribution coefficient data for Rb have been published.

The ratio $\frac{\text{Na in the sea}}{\text{Na in streams}}$

has a value of 1760 (Wedepohl, 1970), and on this basis one would predict a difference of at least 880 (i.e. 5 x 176) in the distribution coefficient, K_D, between the two environments.

Sreekumaran et al. (1968) measured Cs concentrations in river sediments and suspended matter, and recorded an average abundance of 1.8 ppm. The Cs level in river water (Table 10) is of the order of 0.02 µg/l. and therefore

$$K_D \text{ fresh water} = \frac{\text{Cs in clay}}{\text{Cs in solution}} = 90{,}000$$

There is very little data for Cs in deep sea sediments. Sreekumaran et al. (1968) recorded an average value of 1.5 ppm for samples from the central Pacific, and Turekian and Wedepohl (1961) recommend a value of 6 ppm for deep sea clays. On the basis of these data, K_D for sea water is in

the range 5000 - 20,000.

Therefore $\frac{K_D \text{ fresh water}}{K_D \text{ sea water}}$ is of the

order of 4.5 to 18. In other words there is a gross disagreement between the predicted and observed values of the ratio. Although analytical error can be considered as possibly being contributory to this discrepancy, the differences involved are sufficiently large as to render this unlikely, and it would seem that in order to alter this ratio in the direction predicted above, Cs would have to be desorbed from detrital clays on entering the oceanic environment. In other words, it is highly unlikely that detrital clays could act as a sink for oceanic Cs (and possibly also Rb) and the possibility that detrital clays do not equilibrate with the marine environment for these elements must be seriously considered.

In the opinion of the author it would be most productive to study the exchange equilibria for the relevant clay-water systems for both Rb and Cs and investigate these possibilities more fully. These results seem to confirm the suggestion of Bolter et al. (1964) that the Cs and Rb contents of marine clays are relict from their terrestrial sources and weathering environments, and it is therefore highly unlikely that these elements could be used as indicators of paleosalinity (Degens et al. 1957, 1958), Nicholls (1963).

In an attempt to simulate river transportation conditions, and also to confirm that the alkali and alkaline earth elements were not leached from the shale samples during the clay mineral separation procedure, twelve assorted shale samples were vigorously and continuously agitated for four weeks in stoppered polythene bottles with artificial river water (pH = 6) kindly supplied by Dr M. Orren, Department of Geochemistry, U.C.T. In addition the samples were placed for seven hours in an ultrasonic cleaning tank. The shales were then washed five times with distilled water, dried and re-analysed for Li, Rb, Cs, Sr and Ba; the results are given in Table 12. For Rb, Sr and Ba, which were determined by X-ray fluorescence techniques the precisions of which are considerably less than 5%, correspondence between the two sets of data is extremely good. The precision of the optical spectrographic technique employed for the determination of Li and Cs is in the range 5 - 10%, and accordingly the results are slightly more erratic. However with the exception of two samples, FR2 and BK1, which appear to have lost appreciable quantities of Li, the correspondence is within the precision of the analytical procedure.

Sreekumaran et al.(1968) conducted similar experiments using sea water and sediments from the Colorado River, and found that after four hours less than 2% of the K and Rb were leached from the sediment, and less than 1% of the Cs was lost after 72 hours. These experiments indicate that Cs, Rb, K and probably also Li are quite firmly bound by the clay minerals, probably at their sites of

formation, and once installed are not easily removed. If the postulated movement of alkali metals from the sediments to the sea is to be quantitatively studied, precise and sensitive analytical techniques will have to be employed.

Table 12

Sample	Rb (a)	Rb (b)	Cs (a)	Cs (b)	Li (a)	Li (b)	Ba (a)	Ba (b)	Sr (a)	Sr (a)
Fg 14	170	174	9.9	9.2	40	32	604	606	19	20
Fg 17	190	193	10.4	10.0	29	29	654	655	63	62
JP 7	82	81	3.8	3.5	62	60	608	611	120	119
Kun 4B	223	221	5.1	4.7	6.0	5.5	503	494	61	60
Cg 2	242	239	4.7	4.4	18	13	733	728	30	30
FR 2	130	129	5.9	5.2	35	24	365	362	107	108
BK 1	211	202	13	11.5	88	58	884	886	115	103
Ec 14	26	20	n.d.	n.d.	n.d.	n.d.	166	157	48	48
Ec 30	192	187	7.1	6.9	23	20	1053	1048	141	138
Sec 25	51	50	n.d.	n.d.	n.d.	n.d.	281	270	121	111
GB45/64/3	171	160	8.1	7.6	51	51	949	947	123	113
Ec Dan 3	154	153	7.7	8.0	107	95	743	732	177	155

(a) Concentration in untreated shale. (ppm).

(b) Concentration after treatment. (ppm).

H. THE ALKALI AND ALKALINE EARTH TRACE METALS IN SEDIMENTS FROM THE SOUTH AFRICAN STRATIGRAPHIC SEQUENCE

(a) Rubidium

Rubidium abundances and K/Rb ratios for the various South African sediments and separated clay fractions are given in Tables 31A to 54A which are arranged in order of decreasing geological age. Consideration of the K/Rb ratios shows that Rb follows K very closely in the external cycle; in fact the coherence appears to be even closer than in the igneous environment where the K/Rb ratio varies between less than a hundred and greater than a thousand (Erlank 1967). In the entire sample population for which results are presented here, less than 5% of the sediments have K/Rb ratios falling outside the range 120-230. The overall average Rb content is 141 ppm, corresponding to an average K/Rb of 172. The average Rb content of the 33 separated clay fractions is 240 ppm, and the K/Rb 175.

Fig. 21 is a frequency distribution diagram of the K/Rb ratios in the sediments studied, and it is seen that the oldest rocks, those from the Fig Tree Series, have the highest average K/Rb ratio. The average value for the ratio in the shales is 198, while in the graywackes it is 224. The Precambrian Witwatersrand System shales also have a high average K/Rb ratio of 194. Two alternative explanations are offered.

First, it is highly likely that these ancient shales, particularly those of the Fig Tree Series, are first

cycle sediments derived directly from basic igneous parent rocks, and that their slightly higher than average K/Rb ratios are possibly relict features, and indicative of a non-attainment of equilibrium during the weathering process in which rocks of high K/Rb were broken down to form the clays chlorite and illite.

Alternatively it is possible that compared to shales of younger age those of the Fig Tree Series have incorporated relatively more K than Rb in the basin of deposition during sediment accumulation and burial. One possible mechanism for the K enrichment of ancient shales is the inclusion of organic debris rich in K, and relatively impoverished in Rb, as suggested by Conway (1945) and Weaver (1967). This process has been discussed at some length in an earlier section of the work.

With few exceptions the remaining younger shale samples have K/Rb ratios very close to the overall average of 172, regardless of their geological age or mineralogy. The enrichment of Rb relative to K in shales as compared to igneous rock types, and the extremely close coherence between the two elements are well demonstrated by the shales of the marine Bokkeveld Series of the Cape System (Table 37A). The average K/Rb ratio of these 38 shales is 177 and the standard deviation is 9.5. The coefficient of variation is 5.3%. Further, there is no variation of the K/Rb ratio with either K content or mineralogy. It will be remembered, in addition, that large distances, both vertical and horizontal, separate

the individual sample localities. The rocks of the overlying, fresh-water Witteberg Series have identical average Rb contents and K/Rb ratios.

No support can therefore be found from these data to support the suggestions of Degens et al. (1957 , 1958), that Rb may be utilised as an indicator of fresh water as opposed to marine deposition. It might be pointed out in this respect, that in a later paper (Keith and Degens 1959), these authors noted that their previous Rb data were to be considered as unreliable due to experimental difficulties. Wedepohl (1970) in a study of 30 European Carboniferous shales arrived at a similar conclusion, in that he found the marine shales to contain higher boron contents than their fresh-water counterparts, but that the two sets were indistinguishable in terms of their Rb abundances.

(b) Cesium

Cesium abundances together with the K/Cs ratios of the various shales and separated clay fractions studied are given in detail in Tables 31A to 54A, and summarized in Table 9 of this text. The average Cs content of the South African shales is 7.2 ppm, while for the separated clays the value is 16 ppm. The average K/Cs ratios are 3666 and 3170 respectively. Figure 22 is a frequency distribution diagram of the K/Cs ratios for the total sample population.

Figure 23 is a plot of K versus Cs in the shales of the Bokkeveld Series, and it is seen that although there

is a well developed relationship between the two elements, the coherence is not as close as was found to be the case for K and Rb. The average K/Cs ratio for these shales is 3816 and the standard deviation is 880. The coefficient of variation for the 38 samples is 23% compared to 5% for the K/Rb ratio in the same shales. It is likely that some of the observed spread is the direct consequence of analytical error, since the Cs level in shales is considerably lower than is the case for Rb, and, further, the optical spectrographic technique used to determine Cs has a precision in the range 5 - 10% compared to values in the range 1 - 2% attained in the X-ray fluorescence method used to determine Rb. As was found to be the case for Rb, the marine Bokkeveld shales are indistinguishable from the overlying fresh-water Witteberg shales both in terms of their absolute Cs abundances, and their K/Cs ratios.

The distribution of Cs in sediments from the Northern Ecca Facies of the Karroo System is more complex. Consider first the samples from the Somkele Borehole. It will be remembered that these shales contain kaolinite and illite as the dominant clay minerals, and that the presence of K-feldspar was only rarely confirmed. The K/Cs ratios of these samples are reasonably constant (Table 45A), and since there is only one major potassium phase present, illite, it is safe to assume that the bulk of the Cs in these sediments is associated with the contained illite. The average Cs content of the 26 samples is 9.1 ppm, and the average K/Cs ratio is 3000. Further, the average K/Cs ratio of four separated clay fractions from samples

Sec 2, 3, 22 and 23 is 2400, while the value for the four whole rock samples in question is 2700.

Sediments from the GB series boreholes, the Dannhauser borehole and the Bothaville borehole, on the other hand, frequently contain significant quantities of K-feldspar in addition to kaolinite and illite. For these rocks there is a positive relationship between the K/Cs and Si/Al ratios(Fig. 24). It has been shown that the latter ratio may be effectively used as an indicator of the sedimentation rate in these sediments, and also that during periods of rapid sedimentation there was an increase in the amount of quartz and K-feldspar entering the basin of deposition. During periods of less profuse sediment influx the clay minerals were supplied in greater abundance, and there was a corresponding decrease in the amounts of both quartz and K-feldspar entering the basin.

K-feldspars from igneous rocks other than pegmatites normally contain considerably less than 5 ppm Cs, and Heier and Adams (1964) quote an average value of 1.5 ppm. Consequently, the effect of adding significant quantities of such a mineral plus quartz at the expense of illite, which contains a minimum of 20 ppm Cs (Table 53A), would be to reduce the absolute Cs content of the total rock without drastically affecting the K abundance, since K-feldspar contains of the order of 8 - 12% potassium (Heier and Adams, 1964). The overall effect of such a process would be a sharp increase in the K/Cs ratio while leaving the K/Rb ratio relatively unchanged. Consider for

example two sediments, A and B, containing 80% and 50% illite respectively. If sample A contains 5% K-feldspar and sample B contains 20%, the K contents will be 6.2% and 5.9% respectively, assuming that normal illite contains about 7% K, and K-feldspar about 12%. If the K/Rb ratio of the illite is 170 (Table 53A), then the Rb content is 400 ppm, which is also the average Rb content for K-feldspars reported by Heier and Adams (1964). If the Cs contents are 20 ppm and 2 ppm respectively, then sample A has a K/Rb ratio of 183 and a K/Cs ratio of 3750. For sample B the values are 210 and 5700 respectively.

These data are consistent with the trend depicted in Fig. 24, and infer that the Cs contents and the K/Cs ratios of the rocks under consideration are principally affected by the nature of the detritus entering the basin of deposition.

The highly carbonaceous shales of the A series boreholes as well as those from the Springbok and Vierfontein Collieries (Ec4-16) unlike those considered above, contain only minor amounts of illite and/or K-feldspar, and the dominant mineral in these samples is kaolinite. Reference to Table 47A shows that these shales are slightly enriched in Cs relative to K compared to those previously discussed, and the average K/Cs ratio is of the order of 2200 in each case. The K/Cs ratio in these samples also appears to be related to the sedimentation rate in a general way, as evidenced by Fig. 25 where the carbon dioxide corrected loss on ignition is plotted against the K/Cs ratio. It is unlikely that the slight Cs enrichment in these samples

is directly related to the organic matter itself, as there is no evidence of a relationship between the absolute Cs contents either in the rocks themselves or in the ash and the organic matter contents. It is more likely that due to the extremely slow rates of deposition of these samples, sufficient time was available for a minor amount of Cs adsorption to take place prior to burial.

The average Cs contents of rocks from the Central, Southern and Western Ecca Facies are 8.4 ppm, 9.5 ppm and 8.5 ppm respectively, and the average K/Cs ratios for these sediments are 3,900, 4100 and 3400 respectively.

(c) LITHIUM

It is well known (Goldschmidt, 1937; Horstman, 1957; Heier and Adams, 1964) that in the igneous environment, unlike Rb and Cs, Li does not display a coherent relationship with K, but rather substitutes for Mg^{2+} and Fe^{2+} in the femic silicate minerals on the basis of similar ionic radii. According to Horstman (1957), Mg^{2+} exerts a dominating influence during the early stages of differentiation, while Fe^{2+} plays an important role in the later differentiates. Strock (1936) showed that with progressive differentiation, the absolute Li content and also the Li/Mg ratio increase systematically. Howie (1955) demonstrated a regular increase in the Li concentration and the Li/Mg ratio in the sequence orthopyroxene - clinopyroxene - amphibole - mica, the mica lattice being the most favourable for the Li^{+} ion. Table 13 gives average Li abundances for the common igneous rock types (Heier and Adams, 1964).

Table 13

Rock	Li (ppm)
Dunite	< 0.3
Basalt	7
Gabbro	10
Diorite	20
Granodiorite	20
Granite	30
Rhyolite	50
Nepheline Syenite	20

Horstman (1957) studied the behaviour of Li during the weathering of a variety of rock-types and concluded that the greater part of the Li present in shales enters the clay minerals at the weathering site, and is retained by these minerals during transportation and diagenesis. Goldich (1938) showed that the weathering of Li rich micas is coincident with the formation of clay minerals which concentrate Li in their structures due to the small size of the Li^{+} ions. This conclusion was supported by Hirst (1962), and Nicholls and Loring (1962).

Horstman (1957) also showed that the constituent mineralogy of shales is an important factor in controlling the distribution of Li in the sedimentary environment. He found the Li abundance in kaolinite (Ave. 120 ppm) to be the highest of all the clay minerals and suggested that in kaolinite some Mg is present in the octahedral layer in place of Al, resulting in a charge deficiency. In addition, Horstman pointed out that only four of the six octahedral positions are occupied in the unit cell, and these two factors render the kaolinite structure suitable to accept significant quantities of Li. Ohrdorf (1968) found 180 ppm Li in a sample of Westerwald kaolinite. Another clay which frequently contains relatively large amounts of Li is montmorillonite. Horstman (1957) noted that montmorillonites contain appreciable amounts of Mg in the octahedral layer, and found the average Li content of three montmorillonites to be 56 ppm. Hirst (1962) showed that montmorillonite concentrates Li more strongly than does illite. Ohrdorf (1968) reported Li values of 66, 37

and 24 ppm (Ave. 42 ppm) for three North American illites. Nicholls and Loring (1962) on the other hand, found in their study of British Carboniferous sediments that some illite rich shales contained appreciable amounts of Li.

Li data for the South African sediments and separated less than 2μ fractions are given in detail in Table 31A to 54A, and summarized in Table 9 of this text. The Li abundances for the individual samples, and for the various stratigraphic groups show considerably more variation than was found to be the case for Rb or Cs. The average Li content for the entire sample population is 55 ppm, and in accord with the findings of other workers, Li was not observed to vary coherently with K.

Figure 26 demonstrates the close relationship displayed by Li and MgO in the Bokkeveld shales of the Cape System. Also shown is the Li-MgO plot for the ancient Fig Tree shales and graywackes. It is interesting that while both sets of sediments show a close coherence between the two elements, the Mg/Li ratios are greatly different. It will be remembered that both the Bokkeveld and Fig Tree shales have clay assemblages dominated by chlorite and illite. For the majority of the remaining sequences studied, similar relationships are observed. That is to say, in each case there is a coherent relationship between Mg and Li, but there is no evidence for a single Mg/Li ratio applicable to the shales as a whole as is the case for example with K and Rb. A similar, but less well defined, relationship is observed for the Bokkeveld shales between Li and total iron expressed as Fe_2O_3. The FeO results could not

be used for this purpose since the samples are all outcrop specimens and in many cases sufficiently weathered, such that some of the original ferrous iron has been oxidized.

If as suggested by Goldich (1938), Horstman (1957), and Hirst (1962), the Li content of a shale is primarily acquired at the site of weathering, then the high Mg/Li ratios of the Fig Tree shales may be explained in terms of their presumed basic or ultrabasic provenance (Danchin 1967), since these rock types contain low Li contents compared to more acid varieties (Table 13).

Keith and Degens (1959), on the other hand, made use of Li to differentiate between marine and fresh-water Pennsylvanian shales, and suggested that in the marine environment Li is adsorbed by the clay minerals and ultimately incorporated into the clay lattice positions. Similarly Ohrdorf (1968) analysed 16 marine and 9 fresh-water European Carboniferous shales and found the average Li abundances to be 117 ppm and 72 ppm respectively. When these results were plotted against the boron contents of the shales it was possible to successfully distinguish between the two sample populations.

Accordingly, the boron concentrations for the marine Bokkeveld shales and the non-marine, overlying Witteberg shales (Nel, 1967) were plotted against the Li abundances (Fig. 27). It is seen that the average B and Li values for the two sets of samples are marginally different, those for the Bokkeveld Series being higher in each case. Unfortunately, insufficient Witteberg shales were studied to allow any firm conclusions to be drawn. The

average Li content of the four separated Bokkeveld "clay" fractions is 79 ppm while one Witteberg separate, Wb6, has 58 ppm Li.

Although the differences are not extreme, it is suggested that the Bokkeveld-Witteberg sequence is suitable for future research in this connection, since the major element data presented earlier indicate that the two series have shared the same provenance area, and it is one of the few known South African fresh-water - marine sequences containing adequate fossil documentation.

Sediments rich in kaolinite from the Northern Facies of the Ecca Series contain considerably more Li than those from the Central, Western and Southern Facies. Particularly significant in this respect are the shales from the Springbok and Vierfontein Collieries (Ec 4-16) whose combined average Li abundance is 101 ppm, the Dannhauser borehole sediments (Ec Dan 1-10, Ave. 72 ppm Li), the A series boreholes (Ave.68 ppm Li), and the GB series boreholes which contain somewhat more illite than those enumerated above (Ave. 58 ppm Li). The sediments of the Somkele borehole contain illite as the dominant clay mineral and have an average Li content of 34 ppm. The average Li abundances of the shales from the Central, Western and Southern Ecca Facies are 52 ppm, 49 ppm and 34 ppm respectively. Samples from the Bothaville District (BEc series) contain significant quantities of montmorillonite and the average Li content of these shales is 90 ppm.

It is possible that some of the Li in these carbonaceous shales is associated with the contained organic matter since Goldschmidt (1937) found approximately 500 ppm Li in coal ash, but no definite correlation could be established in any of these samples with the organic content as expressed by the CO_2 corrected losses on ignition. Careful study of the Mg - Li and Fe - Li relationships in these carbonaceous shales is inhibited by virtue of the irregular presence of diagenetic sulphide and carbonate minerals in them. For one of these sequences, the Somkele borehole sediments, the Li abundances have been plotted against total non-diagenetic iron (i.e. iron remaining after suitable corrections have been made for normative pyrite and siderite) and the results are shown in Fig. 28. It is seen that there is a reasonably well-developed positive correlation between the two parameters for these sediments, and it is evident from the preceding discussion that Mg-Li and Fe-Li relationships are not restricted to the igneous environment, but continue to play a part in controlling the distribution of Li in the external cycle.

Evidence from the remaining less than 2 μ separates is inconclusive, since insufficient samples from any one sequence were treated, and in addition the exact mineralogical composition of these clay separates in terms of clay mineralogy, iron oxides and hydroxides and clay sized feldspar is unknown. It is clear however that much further work is needed to define more exactly the factors controlling the distribution of Li in sedimentary rocks, particularly if, as suggested by Keith and Degens (1959) and Wedepohl (1970), the element is to be useful in dif-

ferentiating between fresh-water and marine shales.

From the data presented here it would seem that source rock chemistry and clay mineralogy play important, if not dominating roles, and these factors would have to be taken into account if it were to be shown conclusively that Li sorption and installation into clay lattice sites takes place in the marine environment during deposition and burial.

(d) BARIUM

In igneous rocks barium and potassium show a close coherence since the ionic radii of the divalent Ba^{2+} ion (1.34 A) and the univalent K^{+} ion (1.33 A) are very similar. It is also well known that Ba shows a preference for the potassium feldspar structure (Von Engelhardt, 1936; Goldschmidt, 1954), and its abundance in this mineral is frequently in excess of several thousand parts per million (Berlin and Henderson, 1969). Similarly, Ba can often reach extremely high abundances in micas (Goldschmidt, 1954; Kolbe, 1965). The Ba contents of plagioclases are extremely variable, and although in some cases values of 1000 ppm are exceeded, the levels are usually considerably lower (Berlin and Henderson, 1969).

During the weathering process Ba is sometimes lost with K, but generally it is preferentially adsorbed on the surfaces of the clay minerals (Short, 1961). Cameron (1957) has suggested that Ba, like K is incorporated into the clay minerals at or near the site of

weathering, Ba in all probability being preferentially adsorbed due to its greater charge. Carroll (1959) showed that the alkaline earths are adsorbed on colloidal clay minerals from aqueous solutions in the same order as the alkalis, that is in order of increasing atomic weight - Ba > Sr > Ca > Mg. Rankama and Sahama (1950) suggested that in addition to Ba included in the lattice structures, clay minerals also adsorb moderate quantities of Ba from overlying waters during deposition and burial. Nicholls and Loring (1962) in their study of British Carboniferous shales suggested that Ba might in addition be adsorbed by the negatively charged ion monosulphide colloid. In addition, the association of Ba with the biogenous components of oceanic sediments has been noted by several authors (Revelle et al. 1955; Goldberg and Arrhenius, 1958; and Turekian and Tausch, 1964, for example).

Turekian (1968) has studied the accumulation rate of Ba in a core from the Mid-Atlantic Ridge and has shown that the material balance of Ba may be explained in terms of continental supply and inhomogeneous removal in the ocean. The areas of high Ba concentration in the deep-sea sediments are related to the major ocean ridge areas as well as areas of high biological productivity. Turekian (1968) pointed out that in the accumulation of pelagic muds the detrital fraction makes up 95% of the total Ba being deposited.

Ba data for the South African sediments and separated clay fractions are given in detail in Tables 31A

to 54A, and summarized in Table 9 of this text. The average Ba contents of the individual stratigraphic units do not vary greatly on either side of the mean value of 680 ppm for the entire sample population. The overall average compares well with the value of 600 ppm recommended by Turekian and Wedepohl (1961) for shales. The frequency distribution diagram of Ba in the samples studied shows a distinct negative skew (Fig. 29).

Examination of the K/Ba ratios of the individual sample groups (Tables 31A to 54A) reveals that the coherence displayed by these two elements in the igneous environment is maintained in the external cycle. Fig.30 is a plot of K versus Ba for the shales and graywackes of the Fig Tree Series, as well as the shales of the Bokkeveld and Witteberg Series of the Cape System. Of particular interest is the fact that although the Fig Tree shales contain more Ba than the graywackes (481 ppm and 285 ppm respectively), the average K/Ba ratios for the two types are identical (Ave. = 46). In addition, the marine Bokkeveld shales and the non-marine Witteberg shales have equivalent absolute Ba abundances (700 ppm) and K/Ba ratios (38). It is suggested that Ba in these samples has been incorporated in the clay minerals during the weathering process, and as such the Ba distributional features are indicative of their respective source areas, and that post depositional changes have been minimal. The average K/Ba ratio of the separated clay fractions of the single Witteberg and four Bokkeveld shales is 50, and thus slightly higher than the

average value for the whole rocks from which they were separated (41). This suggests that the plagioclase present in these samples contains a small amount of Ba, and that this plagioclase was not collected together with the clay fraction during the separation procedure.

The Ba distribution in the sediments of the Northern Ecca Facies of the Karroo System is more complex. The average Ba contents of samples from the GB series boreholes, the Somkele borehole, and the Dannhauser borehole are somewhat higher than those observed for shales from elsewhere in the Karroo Basin, the respective averages being 960 ppm, 830 ppm and 860 ppm respectively. The K/Ba ratios are very similar in each case (29, 32, and 31 respectively), and lower than values recorded for other Ecca shales. These samples all contain significant quantities of K-feldspar or illite or both, and reference to Tables 40A, 41A, 42A, 45A, and 46A shows that the K/Ba relationship is maintained within reasonably close limits regardless of whether illite alone (Somkele Borehole) or illite and K-feldspar are the dominant potassium phases present.

This would infer that the K/Ba ratios of the illite and K-feldspar present in these sediments are not greatly dissimilar, and that the Ba abundances in these sediments are controlled by the total amounts of the two main Ba hosts - illite and potassium feldspar. The average K/Ba ratio of the nine clay fractions separated from these rocks (Table 54A) is 39. This suggests that

the K/Ba ratio of the illite is slightly greater than that of the K-feldspar, which is in accord with bariums known preference for the K-feldspar structure.

In the highly carbonaceous kaolinite rich shales of the A series boreholes, as well as those from the Springbok and Vierfontein Collieries (Ec 4-16), Ba is enriched relative to potassium and the K/Ba ratios of these sediments, are somewhat lower than their less carbonaceous counterparts discussed above. The average K/Ba ratios are 22, 22, and 21 respectively, corresponding to average Ba abundances of 530 ppm, 727 ppm and 394 ppm respectively. Moreover, there is an inverse relationship between the K/Ba ratios and the carbon dioxide corrected losses on ignition, depicted in Fig. 31.

Goldschmidt (1954) noted that Ba is often concentrated in coal ashes, and amounts of up to 1% BaO were recorded for such ashes by Von Engelhardt (1936). It therefore seems likely, that either sufficient Ba entered the basins of deposition associated with the organic material to produce the observed lowering of the K/Ba ratios, or that Ba was adsorbed during deposition. In each case samples containing the most organic material would be expected to show the lowest K/Ba ratios, since it has been demonstrated that for these samples the organic matter content is closely related to the sedimentation rate.

Samples from the Bothaville District (BEc Series) show the highest K/Ba ratios of any of the Northern Ecca

Facies sediments (Ave. = 39), and reference to Table 39A shows that this ratio is very closely maintained in all but one of the ten samples studied. It seems likely that the Ba abundances of these sediments are almost exclusively controlled by their K-feldspar contents, since the four samples containing abundant K-feldspar (BEc 4286, 87, 88 and 92) also contain the highest absolute amounts of Ba. It will be remembered that illite is only present in minor or trace amounts in these samples. This being the case, it is difficult to explain the higher K/Ba ratios, since the K-feldspar present in sediments from other regions is believed to have a characteristically low K/Ba ratio. It is therefore possible that this extreme South-western sector of the Facies was supplied with K-feldspar from a different source to those localities described above.

The combined average K/Ba ratio of sediments from the Central, Western and Southern Ecca Facies is 44, which is somewhat higher than for the rocks of the Northern Facies discussed above. This is in accord with a view put forward in an earlier section that the source area, from which the bulk of the Northern Facies was derived showed distinct chemical differences from those supplying the remaining three facies.

(e) STRONTIUM

Opinion on the distribution of Sr in igneous rocks is divided, and its precise location would appear to vary from one rock type to another. The ionic radius of Sr^{2+} is intermediate between those of Ca^{2+} and K^{+}, and its ability to replace both these elements in the feldspar lattice has been discussed by Heier and Taylor (1959). Turekian and Kulp (1956) found a sympathetic variation between Sr and Ca in granites but an inverse relationship in basaltic rocks. Gerasimovsky and Lebedev (1958) remarked on the absence of any direct interdependence between Sr and Ca in the alkali intrusives of the Lovozero Massif, which they attributed to the isomorphous replacement of both Ca and K by Sr.

Short (1961) found that during the weathering of igneous rocks, Sr displays no strong preference for substitution in either the Ca or K sites, and remarked that it is more tightly held on the clays than is Ca. Goldschmidt (1954) suggested that in hydrolysate sediments Sr may be fixed on a very moderate scale by base exchange, while Turekian and Kulp (1956) indicated that the situation is complicated in most instances by the presence of Sr bearing calcites.

Dasch et al. (1966) studied the behaviour of Sr during weathering and noted that to a first approximation, whereas Rb behaves like K, so Sr follows Ca which is lost significantly in incipiently weathered

rocks, and continues to be lost during the later stages of weathering. This results in a partitioning of Rb and Sr between the weathered residue and the ground water and causes a marked increase in the Rb/Sr ratio. Dasch (1969) concluded that Sr in even the finest fraction of aluminosilicate detritus deposited in the ocean does not equilibrate isotopically with marine Sr. This is a particularly important conclusion since it lends considerable substance to the view which has been stressed here that geological provenance is the major factor controlling the composition of argillaceous sediments, and that there is a very strong possibility that ion exchange reactions between the clays and the waters of the depositional environment are not as important as was previously believed. It also follows from the work of Dasch (1969) that the factors affecting the $Sr^{87}/86$ ratios of carbonate free deep-sea sediments are the ages and Rb/Sr ratios of the source rocks.

Strontium data for the South African sediments and separated clay fractions are given in Tables 31A to 54A, and summarized in Table 9 of this text. Fig. 32 is a frequency distribution diagram of Sr in the samples studied. The average Sr abundance for the shales is 150 ppm which is significantly lower than the value of 300 ppm recommended by Turekian and Wedepohl (1961). Keith and Degens (1959) found that the average Sr contents of a series of marine and fresh-water shales of Pennsylvanian age were 250 ppm and 205 ppm respectively. Dasch (1969) recorded an average value of 154 ppm for 130 deep-sea sediments on

a carbonate free basis which is in accord with the findings of Wedepohl (1960) who gave an average of 120 ppm for sediments of the Atlantic Ocean. The average Sr/Ca ratio for the South African sediments is 0.03, which is somewhat lower than the value of 0.06 derived by Turekian and Kulp (1956) for "pure" shale.

The average Sr contents of the individual stratigraphic units vary erratically, the lowest value recorded being 28 ppm for the ancient Fig Tree shales. Moreover, Ca and Sr in the shales do not display a well developed coherence, and no evidence for a positive K-Sr relationship could be found. Finally, the data presented here endorse the findings of Keith & Degens (1959) and Wedepohl (1970) that the Sr contents of shales or their separated clay fractions cannot be used as indicators of paleosalinity.

I. ANALYTICAL PROCEDURE

a. (i) The Major Elements - SiO_2, TiO_2, Al_2O_3, MnO, CaO, MgO, K_2O, P_2O_5 and total iron as Fe_2O_3.

In an attempt to find the best method of sample preparation for the major element analysis of rocks by X-ray fluorescence spectrometry, seven published methods were examined in collaboration with colleagues at the Geochemistry Department, U.C.T. The results of this study were combined in a joint paper (Willis, Danchin, Fesq and Berg, 1968) which was read by the author at the fifth meeting of the South African C.S.I.R. Spectroscopic Discussion Group held in Pretoria in February, 1968. Since these results have not yet been published elsewhere, the main conclusions reached will be summarized here.

Important factors considered in this work were that the method should be usable on a routine basis, sample preparation should be both simple and rapid, and the results should be both precise and accurate to within 1% relative, where counting statistics permit. The seven sample preparation techniques investigated were as follows:-

1. Welday et al. (1964)

(Silicate sample preparation for light element analyses by X-ray spectrography).

A sample of -120 # rock powder was heated at 850°C for ten minutes and cooled in a dessicator to deter-

mine the loss on ignition. The pre-heated sample was mixed with $Li_2B_4O_7$ (35 : 65), total weight 2.4 gm, and fused in a furnace for 20 minutes at 1050°C in graphite crucibles. Ten crucibles were placed in the furnace at one time. The fused bead, allowed to cool in the crucible, was fine ground and briquetted.

2. Pb_3O_4 - G. Hornung (1965)

(Sample preparation for X-ray fluorescence analysis)

One gram of -300 # rock powder was mixed with 1 gm. Pb_3O_4 containing 5% cellulose powder as a binder in a Spex Mixer Mill for 10 minutes. The mixture was then briquetted under a load of 15 tons with a backing of bakelite-boric acid (1 : 1).

3. Whole Rock - A. Volborth (1963)

(Total instrumental analysis of rocks).

1 - 4 gm. of -300 # rock powder were briquetted under a load of 15 tons with a bakelite-boric acid (1 : 1) backing. In specimens of high SiO_2 content 1 drop per gram sample of de-ionised water or of a 2.5% sample solution of Mowiol (a water-soluble plastic) was added to prevent shearing of the briquette.

4. Rose - H.J. Rose et al. (1963)

(X-ray fluorescence analysis of the light elements in rocks and minerals).

0.125 gm. sample -120 # powder, 0.125 gm. La_2O_3 and

1.000 gm. $Li_2B_4O_7$ were mixed by shaking in a vial, heated to 750°C in a graphite crucible to remove CO_2 and H_2O, fused in a furnace at 1100°C for about 10 minutes and allowed to cool in the crucible. The bead was weighed and boric acid added to bring the weight to 1.300 gm, thus compensating for different ignition losses from sample to sample. The bead and powder were ground to -300# and briquetted under 15 tons load with a bakelite-boric acid (1 : 1) backing.

5. Lithium tetraborate method (Willis et al. 1968)

The sample -120 # powder, preheated at 950°C to constant weight (approx. 1 hour), was mixed with $Li_2B_4O_7$ (11.5 : 88.5) total weight 14 gm, and fused in Pt crucibles at 1050°C for 20 - 25 minutes, swirling the melt every 5 minutes. A disc was cast on a hot-plate inside a brass ring and the bottom surface ground flat and washed with water and acetone. The temperature of the hot-plate was empirically determined to prevent the surface of the disc either sticking or rippling. Subsequently 5 gm. total weight samples were fused in Pt - $Au_{5\%}$ crucibles and poured into a red-hot shallow Pt - $Au_{5\%}$ dish heated over a bunsen. The dish was removed from the flame and allowed to cool on an asbestos pad, placed on a hot-plate at ~ 200°C. The resultant disc fell free from the dish after a few minutes and was annealled on the asbestos pad for ~ 30 minutes.

The Pt - $Au_{5\%}$ alloy is not wetted by the fusion mixture, and any melt left behind in the crucible falls free soon after cooling.

6. $Na_2B_4O_7$ - $Li_2B_4O_7$ - A. Strasheim and M.P. Brandt (1967)

(A quantitative X-ray fluorescence method of analysis for geological samples using a correction technique for the matrix effects).

Two fused, cast discs were prepared for each sample from -120 # powder preheated at 950°C, one being made with $Na_2B_4O_7$ and the other with $Li_2B_4O_7$. A sample to flux ratio of 11.5 : 88.5 was used, total weight being 14 gm. The fusion was carried out in Pt crucibles, although Pt - $Au_{5\%}$ would be more suitable, and the melt cast inside a brass ring on a hot-plate as in the $Li_2B_4O_7$ method. The bottom surface was ground flat and washed with water and acetone.

7. Norrish and Hutton (1969)

(An accurate X-ray spectrographic method for the analysis of a wide range of geological samples).

0.28 gm. of -120 # rock powder, preheated to constant weight at 950°C, was mixed with 1.50 gm. borate flux and 0.02 gm. sodium nitrate, and fused for ~ 10 mins. in a Pt - $Au_{5\%}$ crucible over a Meaker burner at 980°C (the melting point of NaF). The flux consisted of 47% $Li_2B_4O_7$, 36.6% Li_2CO_3 and 16.3% La_2O_3, which had

been prefused and crushed to ~ 80 #. The melt was poured onto a shallow (~ 1 mm. deep) graphite dish placed inside a brass ring on a hot-plate at 230°C and stamped flat with an aluminium plunger. The resulting disc was annealled on another hot-plate for about 15 minutes at 200°C.

It is well known (Jenkins and de Vries, 1967, for example) that the controlling factors in accurate major element analysis of samples differing widely in chemical composition are absorption, enhancement and particle size effects, and each of the preparation techniques enumerated above aims to a greater or lesser extent to eliminate or correct for absorption and particle size effects. None of the methods make any allowance for errors caused by enhancement effects which are thought to be slight. Fourteen International rock standards were employed in this study and the adopted values for these standards are given in Table 14. Since this work was commenced some of these recommended values have altered very slightly (Fleischer, 1969; Flanagan, 1969; Sine et al, 1969; Roubalt et al, 1968), and all the analytical data for the shales and clays presented in this work have been calculated on the basis of these new, updated values.

For each of the methods some or all of these fourteen standards, depending on how many were available at the time, were analysed. The determinations were carried out on single samples, each counted once only. In

order to allow for machine drift, a reference sample was always counted before and after each set of three samples and the intensities for each element were normalised to a fixed reference count rate.

Table 14

Adopted Values for Rock Standards

Element	G-1	W-1	T-1	S-1	GA	GH	GR	BR	G-2	GSP-1	AGV-1	BCR-1	PCC-1	DTS-1
Fe_2O_3	1.96	11.13	6.03	8.24	2.81	1.31	4.05	12.87	2.66	4.24	6.72	13.29	8.25	8.55
MnO	0.03	0.175	0.11	0.40	0.09	0.05	0.06	0.20	0.04	0.05	0.10	0.19	0.12	0.12
TiO_2	0.26	1.07	0.59	0.48	0.37	0.08	0.65	2.61	0.47	0.65	1.05	2.25	0.01	0.00
CaO	1.39	10.98	5.19	10.10	2.48	0.68	2.50	13.89	2.00	2.10	4.90	6.90	0.50	0.10
K_2O	5.52	0.64	1.23	2.70	4.03	4.78	4.50	1.38	4.50	5.50	2.90	1.70	0.00	0.00
P_2O_5	0.09	0.14	0.14	0.21	0.12	0.01	0.28	1.02	0.15	0.30	0.50	0.40	0.01	0.00
SiO_2	72.45	52.54	62.65	59.50	69.71	75.58	65.90	38.49	69.20	67.30	59.00	54.20	41.90	40.60
Al_2O_3	14.29	15.05	16.52	9.30	14.61	12.63	14.75	10.31	15.40	15.30	17.10	13.60	0.70	0.20
MgO	0.41	6.64	1.89	4.06	0.97	0.07	2.40	13.21	0.75	1.00	1.50	3.50	43.20	49.70
Na_2O	3.32	2.07	4.39	3.36	3.57	3.83	3.80	3.07	4.10	2.80	4.20	3.30	0.00	0.00
Total	99.72	100.44	98.74	98.35	98.76	99.02	98.89	97.05	99.27	99.24	97.97	99.33	94.69	99.27

The mean absolute errors and their range, together with the mean relative errors (without regard to sign) are shown for each of these methods in Table 15. With the exception of the Norrish and Hutton (1969) method, these data were calculated as follows:

Where blank samples were measured, the intensities were blank corrected, following which regression lines were calculated for percent versus intensity, or intensity times mass absorption coefficient (M.A.C.). Values for each element in each standard were then read off this regression line and compared with the adopted values, the difference between the two values being the absolute error. The relative error was then calculated as being

$$\frac{\text{Absolute Error}}{\text{Adopted Value}} \times 100\%$$

Relative errors were not calculated for those concentrations below 0.5%, since for these low concentrations the absolute errors are much more informative. At these levels where the adopted values themselves could be in error by as much as the absolute errors, and ver high and rather meaningless relative errors result.

For the Norrish and Hutton (1969) method, the procedure adopted was to subtract the blank from the measured intensities and calculate the regression line through the origin. The apparent concentrations for all samples and the blank were calculated from the equation of this line, and therefore high by the amount present in the blank. These apparent concentrations were then

corrected for interelement effects, after which, the blank, itself corrected, was subtracted to give the corrected concentrations according to the equation:

$$\text{Actual \%} = \text{Apparent \%} \times A_1 - \text{Apparent blank} \times A_2$$

where A is a function of the absorption coefficient of the disc. A is calculated in the normal way on the basis of weight fractions multiplied by M.A.C.s. For each element, therefore,

$$A = X + FeY_1 + Mn\,Y_2 + \text{--------} + NaY_{10}$$

where Fe, Mn, Ti etc. are the weight fractions of the corresponding oxides, X is the mass absorption coefficient of the flux, and Y_1, Y_2, Y_3 etc. are the correction coefficients of the oxides at the wavelength for which the matrix factor A is calculated.

Norrish and Hutton (1969) have provided tables of correction coefficients applicable to fused discs where the sample - flux formula described above is employed. Willis (1969) has devised a sophisticated one-step computer program for the calculation of major element analyses by this method. In this procedure computer input consists of the relevant loss on ignition and counting data for samples, standards and blanks, the adopted values of the standards, and suitable dead-time and instrument corrections. Output consists of apparent and actual percentages for each element as well as the pertinent matrix correction coefficients used for each sample.

Table 15

Comparative accuracies of some sample preparation techniques

Element	Range	Welday		Pb_3O_4		Range	Whole Rock		Rose		$Li_2B_4O_7$		Norrish (uncorrected)		Norrish (corrected)	
	(%)	mean absolute error and range	mean relative error and range	mean absolute error and range	mean relative error and range	(%)	mean absolute error and range	mean relative error and range	mean absolute error and range	mean relative error and range	mean absolute error and range	mean relative error and range	Mean absolute error and range	mean relative error and range	mean absolute error and range	mean relative error and range
Fe_2O_3	0 - 13	0.22 0.09 - 0.35	5.59 0.81 - 14.70	0.18 0.02 - 0.41	3.48 0.71 - 12.76	0 - 13	0.16 0.01 - 0.46	3.00 0.24 - 12.24	0.13 0.02 - 0.38	2.30 0.23 - 4.44	0.08 0.00 - 0.26	1.64 0.00 - 6.12	0.13 0.01 - 0.45	2.02 0.08 - 6.09	0.06 0.0 - 0.23	1.34 0.07 - 4.57
MnO	0.0 - 0.4	0.0 0.00 - 0.01	- -	0.00 0.00 - 0.01	- -	0.0 - 0.4	0.00 0.00 - 0.01	- -	0.00 0.00 - 0.02	- -	0.005 0.00 - 0.01	- -	0.004 0.00 - 0.01	- -	0.005 0.00 - 0.02	- -
TiO_2	0 - 2.6	0.01 0.00 - 0.02	- -	0.02 0.00 - 0.04	- -	0 - 2.6	0.01 0.00 - 0.04	- -	0.03 0.00 - 0.09	- -	0.01 0.00 - 0.03	- -	0.02 0.01 - 0.03	- -	0.02 0.00 - 0.11	- -
CaO	0 - 14	0.11 0.03 - 0.21	2.01 1.18 - 2.67	0.11 0.01 - 0.20	3.59 0.10 - 11.51	0 - 14	0.15 0.01 - 0.45	3.43 0.05 - 8.28	0.11 0.00 - 0.31	2.97 0.00 - 7.35	0.07 0.00 - 0.23	2.42 0.00 - 8.63	0.11 0.01 - 0.27	6.21 0.01 - 37.73	0.08 0.02 - 0.12	3.30 0.43 - 8.57
K_2O	0 - 5.5	0.05 0.03 - 0.09	2.55 1.10 - 4.69	0.10 0.00 - 0.29	3.17 0.00 - 7.81	0 - 5.5	0.03 0.00 - 0.07	1.19 0.00 - 3.62	0.02 0.00 - 0.08	0.93 0.00 - 2.17	0.03 0.00 - 0.09	0.93 0.00 - 3.25	0.03 0.00 - 0.07	1.26 0.0 - 3.13	0.04 0.00 - 0.13	1.39 0.22 - 3.68
P_2O_5	-	- -	- -	- -	- -	0 - 1.0	0.04 0.01 - 0.08	- -	- -	- -	0.02 0.00 - 0.04	- -	0.02 0.0 - 0.04	- -	0.02 0.00 - 0.05	- -
SiO_2	38 - 76	0.44 0.21 - 0.90	0.71 0.26 - 1.50	1.91 0.53 - 3.33	3.11 0.85 - 4.70	38 - 76	1.26 0.15 - 3.12	2.28 0.22 - 5.76	0.31 0.04 - 0.71	0.57 0.07 - 1.79	0.80 0.02 - 2.91	1.45 0.03 - 4.21	0.44 0.03 - 0.89	0.75 0.07 - 1.36	0.50 0.01 - 0.95	0.84 0.01 - 1.50
Al_2O_3	9 - 17	0.36 0.03 - 0.84	2.52 0.18 - 5.57	0.53 0.04 - 1.28	4.25 0.27 - 10.13	0 - 17	0.80 0.08 - 1.98	6.98 0.47 - 19.20	0.23 0.01 - 0.50	1.96 0.33 - 4.85	0.29 0.04 - 0.83	2.89 0.46 - 7.14	0.19 0.02 - 0.51	1.73 0.18 - 3.55	0.16 0.01 - 0.32	1.70 0.30 - 5.41
MgO	0 - 13	- -	- -	0.17 0.01 - 0.41	9.00 0.53 - 29.0	0 - 50	0.36 0.03 - 1.44	7.53 0.74 - 22.00	- -	- -	0.13 0.00 - 0.54	5.54 0.00 - 19.00	0.08 0.00 - 0.15	2.40 0.0 - 7.14	0.16 0.02 - 0.85	2.86 0.51 - 7.18
Na_2O	-	- -	- -	- -	- -	0 - 45	0.23 0.00 - 0.73	8.43 0.23 - 23.78	- -	- -	0.12 0.05 - 0.21	3.97 1.21 - 8.17	- -	- -	- -	- -
Standards used:		G-1, W-1, T-1, S-1, GR		G-1, W-1, GH, GR, BR.	T-1, S-1, GA		All standards						All standards except GR.			

Results obtained by the Different Methods

1. Welday et al. (1964)

Sample preparation by this method is time consuming, and contamination of the sample may occur during grinding. Dissolution problems can occur at these very high sample/flux ratios, especially for minerals such as chromite and rutile. The results, especially for iron (Table 15) are poor because no mass absorption corrections were made. The five standards used (Table 15) are the best known, and it is safe to assume that if all 14 standards have been employed the results would have been considerably worse.

2. Hornung (1965)

Unless great care is taken to obtain the same particle size for samples and standards very poor results are obtained by this method and totals of only 85% are not uncommon. It was concluded that any advantages gained by adding lead oxide as a heavy absorber are more than offset due to the particle size errors incurred.

3. Volborth (1963)

In this method the M.A.C.s. of the samples were calculated from the adopted values using the tables of Heinrich (1966). It was found that for a wide range of rock types the whole rock method does not give good results, mainly due to particle size effects as it is almost impossible to grind different types of rocks to the same particle size. It was found that individual

rock types (e.g. granites, basalts, shales etc.), tended to fall on their own working curves, and since, for strict comparison with the other methods, the results were calculated from a single working curve, serious errors resulted for some elements (Table 15). The whole rock method is, however, used for the determination of Na, S and Cl in our laboratories since for these elements the chromium X-ray tube gives too low a count rate for determinations to be made on diluted samples. Detailed descriptions of the techniques employed for these elements are given immediately after this section on major elements.

4. Rose et al. (1963)

This was found to be a good method, and results for all elements except iron, where a M.A.C. correction is necessary, were found to be satisfactory.

5. Lithium tetraborate fusion method

This method is iterative in that concentration values were read off Intensity (I) versus concentration (C) plots, and these concentration values were used to calculate the relevant M.A.C.s. These values were then used to derive new concentrations from μI versus C working curves, where μ is the M.A.C. One iterative cycle was generally found to be sufficient but the results may be recycled as many times as required to give constant values, with the exception of Al and Mg, the results (Table 15) were found to be quite satis-

factory. One sample, G-2, gave poor results being consistently low by about 5%, and this was presumed to be due to poor sample preparation. The results for this sample have however, been included for completeness in calculating errors.

6. Strasheim and Brandt (1967)

In this method the sample is dissolved separately in two fluxes, yielding two intensity values for each element. It is therefore possible to calculate the M.A.C. of the sample independently for each element. The intensities for all elements heavier than Si are then corrected for M.A.C. calculated from the two intensities. This method was only investigated for a series of artificial standards, and therefore the results are not included in Table 15. The disadvantages of this technique are that preparation time, cost and counting time are all doubled. In addition it was found that mass absorption corrections should be made for Si, Al and Mg, as even in a 1 : 9 sample to flux mix the M.A.C.s of the discs differ by as much as 3% for Al, 4% for Mg, and 8% for Si in the standards used here. The main advantage of the method is that the M.A.C.s can be determined without resort to tables (except for the flux coefficient), and one can therefore determine a single element in each sample without having to know the total composition of the rock. This is a big advantage over all other methods where the M.A.C. must be calculated from the overall composition of the sample.

7. Norrish and Hutton (1969)

This method was found to be superior in almost all respects to those discussed so far. In the first instance the amount of sample required is small (0.28 g. or less), and the discs are speedily and easily made over a bunsen burner due to the high reactivity of the flux. Non-wettable Au-Pt alloy crucibles are used and time wasting cleaning of the crucibles is avoided. In addition the discs once cast are stable, and immediately suitable for analysis without further grinding, polishing, etc.

If results for individual elements only are required straight intensity versus concentration plots may be used, but generally, all elements are determined, and the results corrected for mass absorption as described earlier. All the major element analyses presented in this study were carried out using this method, and the results calculated using the previously described computer handling scheme of Willis (1969). In order to estimate the precision attained using this method, eleven discs were made from one sample of a Malmesbury Formation shale (Mm 7), and the standard deviations and percent coefficients of variation for each of the major elements determined, were calculated, and the results presented in Table 16. Also given in Table 16 are the instrumental settings used for the determination of these elements. A further indication of the precision and accuracy of this technique may be found by referring to the work of Von Michaelis et al. (1969).

Table 16

X-Ray Fluorescence Instrumental conditions for the major elements

Element	Tube	kV	mA	Analysing Crystal	Collimator μm	Detector	Peak Position $^{o}_{2\theta}$	Peak Counting time (secs)	Background Position $^{o}_{2\theta}$	Background counting time (secs)	Concentration in Mm 7 (%)	Standard Deviation	Precision C.V. %
Fe	Cr	50	32	LiF (200)	160	F	57.45	60	-	-	5.72	0.040	0.69
Mn	Au	50	32	LiF (220)	160	F	95.13	120	-	-	0.05	0.001	1.06
Ti	Cr	50	12	LiF (200)	480	F	86.88	30	-	-	0.48	0.002	0.41
Ca	Cr	50	32	LiF (200)	160	F	112.98	30	-	-	0.46	0.005	0.97
K	Cr	50	32	LiF (200)	480	F	136.48	60	-	-	4.00	0.025	0.63
P	Cr	50	32	Germanium	480	F	140.70	180	-	-	0.05	0.001	0.77
Si	Cr	50	32	PET	480	F	108.94	120	-	-	27.75	0.133	0.48
Al	Cr	50	32	PET	480	F	144.77	180	-	-	9.31	0.071	0.76
Mg	Cr	50	32	ADP	480	F	136.49	300	-	-	2.27	0.020	0.88
Na	Cr	50	32	Gypsum	480	F	102.95	300	96.00	300	0.95*	0.019*	1.97*
S	Cr	50	32	Germanium	480	F	110.58	180	113.50	180	100 ppm*	4.4 ppm*	4.36*
Cl	Cr	50	32	Germanium	480	F	92.67	180	95.00	180	150 ppm*	3.5 ppm*	9.31*

F = Flow Proportional

S = Scintillation

* Willis (1969)

(ii) Na_2O, S and Cl.

It has been explained that Na, S and Cl were determined using a Philips semi-automatic PW 1220 X-ray spectrometer, and instrumental conditions are set out in Table 16. Sample preparation consisted of briquetting 4g. of -300 # rock powder under a load of 15 tons with a bakelite-boric acid (1 : 1) backing, according to the method of Volborth (1963).

In the case of sodium, 23 shale samples were also analysed by flame photometry, using a procedure similar to that described by Taylor (1960), who used the same instrument. The precision of this technique was found to be of the order of 2-3%, and the agreement between the X-ray and flame photometrically determined values was good, the data pairs being within 6% of each other for all 23 samples.

The sulphur and chlorine calibration curves were constructed with the additional aid of a series of carefully prepared addition standards. In order to further confirm the reliability of the sulphur analyses by the whole-rock method, the S contents of 12 shale samples were determined by Prof. Carleton B. Moore (Arizona State University, U.S.A.). The method used was an automatic iodometric titration of SO_2 produced by the combustion of 100 mg of sample in an oxygen atmosphere. For samples containing more than 0.10% S the agreement between the data pairs was good, and values were found to be within 15-25% of each other at this level. Although the chlorine values were not used in the interpretative work discussed here, they are included in the major element data tables for the sake of completeness.

(iii) Ferrous Iron

The ferrous iron contents of the shales were determined by the method of Nicholls (1960). This technique was specially devised to cater for carbonaceous shales, and involves the reaction of ferrous iron with iodine monochloride, and the subsequent titration of the liberated iodine against standard potassium iodate solution. Prior to this treatment the samples were broken down in a covered platinum dish with a mixture of sulphuric and hydrofluoric acids.

Nicholls (1960) reports satisfactory accuracy and precision for this method, and in this study two shales, Fg 14 and GB 47/64/1 were analysed ten times each and the mean coefficient of variation was found to be 1.87%. The accuracy was tested by determining FeO in International Standards T-1 and BR, and in each case the observed FeO content was within 2% of the recommended value. Nicholls (1960) found the method to be less reliable in shales of high carbon equivalent (greater than 4%), and for this reason FeO values are not given for highly carbonaceous shales (e.g. the A series boreholes) in this study.

Although FeO values are given for all other samples, it is probable that in a few instances where the content of organic matter is high, the FeO contents have been somewhat overestimated.

(iv) Carbon Dioxide:

The carbon dioxide contents of the samples were determined using a technique similar to that described by Shapiro and Brannock (1956). In this method, the volume of CO_2 released by acid attack on a fixed weight of sample is collected in a specially constructed apparatus and measured at room temperature and pressure. The instrument is calibrated against standard samples of known CO_2 content, and for this study several apparatuses of the type described by Shapiro and Brannock (1956) were constructed to cater for samples having CO_2 contents in the range 0.1 - 10%. These were calibrated using a series of dilutions of the U.S.B.S. argillaceous limestone standard, as well as pure natural calcite. The method is well suited to studies where large numbers of samples are involved, and according to Siedner, Porrenga, 1967 (personal comm.) is not markedly inferior to the standard gravimetric absorption methods.

All samples from the Northern Ecca Facies of the Karroo System were determined in duplicate. It was found that if due caution was exercised with these determinations the results obtained were easily reproducible, and eleven determinations on one sample (GB 48/65/10) yielded a coefficient of variation of 4.7%.

Table 17

X-Ray Fluorescence Instrumental Settings for Trace Element Analyses

Element	Tube	kV	mA	Analysing Crystal	Collimator /um	Detector	Peak Position $^{o}_{2\theta}$	Peak counting Time (secs)	Background Positions $^{o}_{2\theta}$	Background Counting time
Rb	W	65	30	LiF (220)	160	Scintillation	37.93	120	35.00, 37.00, 41.00, 41.80	60 secs each
Sr	W	65	30	LiF (220)	160	Scintillation	35.78	120	As for Rb	60 secs each
Ba	Cr	50	20	LiF (220)	160	Flow	154.31	90	TiK$_{\alpha}$, 149.76 Bg, 132.00	Tik$_{\alpha}$, 30 secs Bg, 90 secs
/u 0.9A	Mo	48	20	Topaz	160	Scintillation	31.64	32,000 counts	-	-

(v) Loss on Ignition

The loss on ignition for all the shale and clay samples was determined by ashing the dry samples in vitreosil crucibles in a muffle furnace at 950°C to constant weight.

(vi) Carbon

The total carbon contents of 50 samples were determined by Prof. Carleton B. Moore. (Centre for Meteorite Studies, Arizona State University, U.S.A.) For samples low in organic carbon a gas chromographic technique on 100 mg samples was employed, while for those from the Ecca Series, a modified Orstat technique was used. (Moore, Personal comm.).

(b) TRACE ELEMENTS

(i) Rubidium and Strontium

Rb and Sr were determined using a Philips PW 1220 semi-automatic X-ray spectrometer, and the instrumental conditions are set out in Table 17. The background intensities for each sample were plotted on an intensity versus ^{o} 2θ graph, the points then being fitted by means of a spline curve. The background intensities were interpolated at the peak positions.

The results were calculated by the method of Reynolds (1963) as follows:

$$C_{sample} = C_{standard} \times \frac{In_{sample}}{In_{standard}} \times \frac{\mu_{sample}}{\mu_{standard}}$$

where C is the concentration in ppm, In is the nett intensity at the respective K_α peak positions, and μ the mass absorption coefficient measured at 0.9Å. For the determination of the M.A.C.s the time taken to record 32,000 counts at the molybdenum compton Peak was measured for the unknowns, and for G-1, W-1, K_2SO_4, CaF_2 and U.S.B.S. sample No. 99 which were used as standards. A calibration curve relating μ to time in seconds was constructed, and the M.A.C.s of the unknown samples read off. Each sample was run twice.

For the calculation of the Rb and Sr results G-1 (220 ppm Rb and 250 ppm Sr) was used as the standard. A

measure of the accuracy of this technique for Rb is given in Table 18 where values determined in the Fig Tree shales by isotope dilution mass spectrometry (Allsopp et al. 1968) are compared with the X-ray fluorescence results of this study. The agreement is found to be excellent. Further details regarding the precision and accuracy of this technique, and values derived thereby for a series of International Standards were described by Cherry et al. (1970). These authors found counting errors for Rb and Sr to be of the order of 1% or better.

Table 18

A comparison of Rb abundances in shales of the Fig Tree Series determined (a) by X-ray fluorescence spectrometry (this work) and (b) by isotope dilution mass spectrometry. Allsopp et al. (1968)

Sample	Rb (ppm) X.R.F.	Rb (ppm) I.D.
SF 2	31	31
SF 3	64	54
SF 4A	177	187
SF 4B	88	88
SF 5	147	151
SF 6	42	43
SH 7	49	52

(ii) Barium

Barium was determined in the shales and clays using a Philips PW 1540 X-ray spectrometer under vacuum by the method of Willis et al. (1969). In this technique the analytical line used is that of $BaL_{\alpha 1}$, and a correction for tailing, from TiK_{α} is made, as well as a correction for background contribution. The Ti tailing correction was made by adding varying amounts of TiO_2 to Ba-free quartz, and these mixtures were then used to set up a correction curve relating intensity at the TiK_{α} position to that at the $BaL_{\alpha 1}$, position. Since the mass absorption coefficient measured using the MoK_{α} Compton peak cannot be used in this instance (Reynolds, 1963), this parameter was calculated from the major element composition at $BaL_{\alpha 1}$, from the tables of Birks (1963), with the aid of a computer.

A calibration curve was then drawn up using G-1 (1075 ppm Ba, M.A.C. = 209.7) W-1 (181 ppm Ba, M.A.C. = 225.0), and GA (845 ppm Ba, M.A.C. = 206.5) as standards. Willis et al. (1969) found the precision of this technique for a sample containing 147 ppm Ba to be 2.3%.

(iii) Lithium and Cesium

A dc arc spectrographic technique (Gurney and Erlank, 1966) was used for the determination of Li and Cs in the sediments and separated clay fractions. In this method a Jarrell-Ash 3.4 meter plane grating spectrograph is used, and a red filter removes second and third order

interferences on the alkali element emission lines. Potassium which had previously been determined by X-ray fluorescence was used as an internal standard. Full analytical details are set out in Table 19.

Table 19.

Analytical details for the optical spectrographic technique used for the determination of Li and Cs.

Spectrograph	-	Jaco 3.4 meter plane grating spectrograph. Dispersion 5Å/mm.
Filter	-	Spex Industries 9023R.
Excitation	-	Anode.
Wave length	-	6400 to 8900Å.
Current	-	7.5 amperes d.c.
Slit	-	25 microns
Plate	-	Kodak 1-N backed, cut in two pieces.
Electrodes	-	Anode, National Carbon Co. regular graphite (L 4306). Cavity 3mm x 2.5mm. Cathode, Morganite carbon.
Buffer	-	20% CaF_2 (B.D.H. extra pure).
Sample	-	Sample powders were ashed at 950°C and mixed with the CaF_2 in an automatic pestle and mortar

Table 19 (continued)

Arcings	-	shales arced in duplicate
	-	separated clays arced in triplicate
	-	standards - one per plate, each arced at least eleven times.
Sectoring	-	Hilger sevenstep sector (2 : 1).
Internal Standard	-	K6939Å
Analysis lines	-	Li 8126 Å.
	-	Cs 8521 Å.
Developer	-	Kodak D 19b developer (4½ minutes)
Fixer	-	Amfix ultrarapid fixer (5 minutes)
Calibration	-	Self-calibration method of Ahrens and Taylor (1962).

The reasons for choosing optical spectroscopy for these determinations were twofold. First, it allows the simultaneous determination of both Li and Cs with reasonable precision and accuracy, provided satisfactory standards are available. Second, the number of samples to be analysed motivated against the use of atomic absorption for the lithium determinations, even though the precision of this latter technique is unquestionably superior. Atomic absorption analysis for Li requires that the samples be digested and analysed in platinum crucibles, and since the amount of platinum ware available to the author is very limited, this method would have proved excessively time consuming.

Because of the lack of satisfactory natural rock standards at the abundance levels of Li and Cs commonly found in shales and clays, the working curves were calibrated by isotope dilution mass spectrometry in the case of Cs, and atomic absorption spectrophotometry for Li. Four samples from the Malmesbury Formation - Cape Granite contact were used for this purpose. M38 and M39 are Malmesbury Argillites, and M60 and M63 are granitized xenoliths. The Cs abundances of these four samples were determined by A.J. Erlank at the Department of Terrestrial Magnetism, Washington D.C. using a mixed K-Rb-Cs spike (Hart 1969). The adopted values for these standards are given in Table 20, and it is emphasized that the high Cs contents of M60 and M63 are due to the fact that these samples have been metasomatized, and were selected because they anchor the working curve (Fig. 33) at its upper extremity. Each of these four samples were arced at least eleven times, and the intensity error bars in Fig. 33 represent the measured precisions of these determinations. These precisions are also shown in Table 20. The concentration error bars were estimated by Erlank (1970, personal comm.) to be 3% in the case of M39 and 5% for each of the other three standards.

Table 20

Adopted values for standards used in the optical spectrographic determination of Li and Cs.

Sample	ppm Cs	% C.V.	ppm Li	% C.V.
M38	12.06	10.3	72	5.9
M39	5.92	7.9	30	8.0
M60	17.04	7.2	155	6.2
M63	40.18	6.1	196	6.8
G-1	1.5	11.7	21.3	8.3
W-1	1.0	12.2	12	7.9
BCR	-	-	15	12.4

The lithium working curve (Fig. 34) was calibrated by atomic absorption spectrophotometry. In this technique the four samples together with a blank were treated with 10 ml. HF and 10ml. $HClO_4$ in platinum crucibles and the mixtures were heated to dryness in a fume cupboard. Each sample was then made up with double distilled water, in the platinum crucibles to a constant volume of 25 ml. Gurney (1969) found that serious contamination resulted if this procedure was carried out in glass volumetric flasks, hence the use of platinum crucibles for this purpose.

Artificial standards were prepared with the utmost caution using spec-pure Li_2CO_3, and two sets of determinations were made. In the first instance a working curve

was prepared using the set of artificial standards, and the results were read directly from this curve. A second set of results was obtained by addition using the same set of standards. Instrumental conditions are given in Table 21.

Table 21

Instrumental conditions for the determination of Li by atomic absorption spectrophotometry.

Instrument	-	Perkin-Elmer 303 Atomic absorption Spectrophotometer.
Air pressure	-	30 lb/sq. inch.
Air flow	-	8 arbitrary units.
C_2H_2 pressure	-	8 lb/sq. inch.
C_2H_2 flow	-	6 arbitrary units.
Li lamp	-	Analysis line Li6707.
Slit	-	3

The intensity error bars on the Li working curve (Fig. 34) represent the precisions calculated from at least eleven arcings of each of the standards, and the concentration error bars are twice the difference between the two sets of atomic absorption results described above.

(c) SAMPLE PREPARATION

The rock samples were reduced to half inch chips by means of a core splitter. Weathered surfaces were removed, and these chips were in turn reduced in a hardened

steel jaw crusher to less than $\frac{1}{8}$" in size. The samples were then further reduced by pulverising them in a carbon steel ball mill, and finally a powder of fineness in the range 300-400 mesh was produced by grinding in an automatic pestle and mortar. Four grams of this powder was then briquetted for X-ray analysis by the method of Volborth (1963).

(d) SEPARATION OF THE LESS THAN TWO MICRON FRACTION

Approximately 15 - 20 g of 120 mesh rock powder was placed in a beaker of double distilled water to which had been added a few drops of ammonia. Disaggregation of the clay minerals was then effected by placing the beakers in a Dawe automatic ultrasonic cleaning tank for seven hours. The samples were stirred frequently during this period. After testing a number of different separation techniques, Hofmeyr (1968) showed that the most reproducible results were produced by decanting the disaggregated slurry into two litre beakers of distilled water which were made up to the mark and stirred vigorously. After standing for 25 hours the less than 2 micron fraction was removed, by decantation, and evaporated to dryness over a hot-plate in a fume cupboard. The procedure was repeated as often as was necessary to obtain more than 6 grams of clay from each sample. The dried clays were then ashed at 950°C in a muffle furnace prior to X-ray and optical spectrographic analysis.

(e) X-RAY DIFFRACTION

For the X-ray diffraction studies of the sediments, a procedure adapted by Fesq (1967) was employed. A Philips PW 1050-30/1054 diffractometer and generator was used, and the instrumental settings are laid out in Table 22.

Table 22

Instrumental conditions for the X-ray diffraction analysis of shales and clays.

Tube	-	Copper
Filter	-	Nickel (over scatter slit)
Slits	-	Divergent - 1^{o}
	-	Collimating - 0.2^{o}
	-	Scatter - 1^{o}
Generator	-	48 kV, 20 mA.
Counter	-	Proportional counter (with discrimination).
Goniometer speed	-	2^{o}/minute
Chart speed	-	800 mm/hour.
Rate meter	-	16
Time constant	-	2
Multiplier	-	1
Range (2θ)	-	2^{o} - 64^{o}

Initially the four gram whole rock birquettes prepared for trace element studies were used, and for further detailed examination of the clay minerals involving routine procedures such as heat treatment, glycolation and acid leaching, a modified Philips sample holder was used (Fesq. 1967). Clay mineral identifications were carried out using the scheme described by Weaver (1967).

J. STATEMENT

The Anglo American Research Unit in Sedimentary Geochemistry commenced its activities at the University of Cape Town in 1965. The author was appointed as sole member of the Research Unit, under the direction of Prof. L.H. Ahrens, at the time of its inception, and the results presented here represent part of his contribution to the work of the Unit. In 1966 he was joined by Mr. P.K. Hofmeyr, the only other permanent appointment, who is at present studying the distribution of a variety of trace elements, including the transition elements, gallium, uranium, thorium and lead in the Units' collection of shales. In 1967 Mr W.A. Nel began a project in which he studied the distribution of boron in the shales, and he presented the results of this work in the form of a Master's thesis at the end of 1968. In 1969 a second Master's student, Mr J. Marchant embarked on a project in which several techniques were devised for the separation of organic fractions from the carbonaceous shales of the collection, and the determination of a number of metallic trace elements in these fractions. His work is still in progress. In

addition, several part-time personnel were employed at various times to assist with routine sample preparation and handling. Of these, Mr H.W. Fesq devised a technique for routine qualitative X-ray diffraction analysis of the shales. The clay mineral data given in Volume II was obtained by him, Mr Hofmeyr, and Mr K. Perry, using this technique. Mr R. Jakob and Mr A. Versveld were employed during University vacations and assisted with routine sample preparation.

Unless otherwise specified, all other work presented in this thesis is solely that of the author.

Signed

R. DANCHIN.

U.C.T.

6th October, 1970.

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ance in arranging the various sample groups studied in their presumed order of decreasing geological age.

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