

ALTERATION REACTIONS WHICH AFFECT THE GEOCHEMISTRY
OF KIMBERLITE AND ITS XENOLITHS,

AND THE SEARCH FOR UNALTERED MANTLE MATERIALS.

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Thesis submitted to the University of Cape Town
in fulfillment of the requirements of the degree of Doctor
of Philosophy.

Department of Geological Sciences, 1994.

Volume 1 (Text)

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ABSTRACT

This thesis records a series of attempts to elicit from bulk kimberlites and their xenoliths, geochemical and mineralogical information meaningful with respect to the primary composition of their source in the mantle. Some of these attempts were successful and some controversial, whilst others were modified significantly to cater for secondary alteration processes (metasomatic events) which took place either in the mantle, or during, or after the emplacement of the rocks in the crust. These secondary events document those stages of the history of the rocks which overwrite and disguise their primary state. It is important to understand the details of these secondary alteration processes so that their record is not erroneously attributed to the primary state of the rocks in the mantle.

The main observations made in the thesis may be summarised as follows:

Chapter 2 reports that the primary garnet and omphacite of eclogites do not account for their bulk concentrations of K, Rb and Cs. Potassium is located mainly in mica which may be late secondary. Rubidium in the bulk-rocks shows a close geochemical coherence with K and would therefore appear to be located also in the mica. Cs shows no geochemical coherence with K and Rb; it is located in an analcite type mineral.

Chapter 3 details the secondary mineralogy of the eclogites. It is suggested that the location of Cs in analcime explains the unusually high concentrations of Cs in the bulk rocks because analcite has a crystal-structure closely similar to that of polucite. The lack of any geochemical coherence between K and Cs, although both are alkali metals, is a consequence of their incorporation into different minerals which formed at different times: the mica formed in the mantle or en route to the surface, possibly by reaction with the kimberlite; the analcite probably formed after consolidation of the kimberlite host in the crust.

Chapter 4 reports an alkali metal study on peridotite xenoliths and their kimberlite hosts. It is shown that, if the bulk mineralogy of the peridotites represents a series ranging from relatively "fertile" mantle (garnet lherzolite) to residua of partial melting (harzburgite), the bulk rocks' K, which resides in mica, was introduced subsequent to the last partial melting event. In point of fact what was observed was partly the mineralogy of alkali metal metasomatism in the mantle. The first reported example of a primary mica in a mantle peridotite is illustrated in the appendix to this chapter.

In Chapter 5 the first low Sr-isotope ratios reported in kimberlite are considered; these were found in kimberlites selected on petrographic grounds as being exceptionally fresh. Higher ratios were found in altered kimberlites, and it was concluded that previously published high Sr-isotope ratios were from altered kimberlites. This was probably

correct in part, but in Chapter 6 high Sr-isotopic ratios are discussed which were discovered in fresh micaceous kimberlites; further fresh "basaltic" kimberlites were also analysed and these proved to have low ratios as before. The petrographic criteria used to classify fresh and altered kimberlites are given in the Appendix to Chapter 6; they are noted to be subjective, and this problem is re-addressed in Chapter 7.

Chapter 7 records an attempt to use stable isotope measurements on bulk kimberlite powders to put the assessments of freshness of kimberlites on a more quantitative footing; this approach proved unsuccessful, and the problem is again re-addressed in Chapter 8.

Chapter 8 reports an alternative approach to assessing the freshness of bulk kimberlites, by studying the detailed mineralogy of the serpentinising reaction. It is shown that fresh kimberlites generally carry brucite as a product of isochemical serpentinisation. In contrast, kimberlites previously assessed as altered, by independent petrographic study, were found devoid of brucite. It is concluded that this absence of brucite is a reflection of open-system serpentinisation in the altered kimberlites, which has also modified their isotopic ratios. The work reported in this chapter therefore succeeded in elucidating the different relative quantities of water involved in the serpentinisation reactions affecting fresh and altered kimberlites, but not the source of this water.

Chapter 9 is a study of the bulk Na₂O content of fresh and altered kimberlites, and a by-way in the mineralogy of altered kimberlites. It reports the first aegerine and aegerine-augite documented in the matrix of any kimberlite, as well as a new paragenesis of sphene.

Chapter 10 returns to the search for unaltered mantle materials; it documents and expands upon the first report of 20-micron calcite/brucite intergrowths which are interpreted to represent protoliths of dolomitic carbonate from the mantle. The intergrowths occur within lenticles of approximately 5mm, thus matching the grain size of the mineral assemblages of the host peridotite nodules. The few previous reports of carbonate from the mantle are as minute inclusions in single minerals. The discovery of the calcite/brucite intergrowths, derived partly from the analysis of bulk peridotite powders for brucite by thermal analysis, demonstrates that despite many difficulties, bulk-rock analysis does have a role to play in the investigation of kimberlites and their xenoliths.

In summary, the thesis commences by examining elements which were added by replacement reactions late in the history of the rocks; it ends by examining the potential loss of essential information due to other minerals being removed by these same late replacement reactions.

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PREFACE

This is an unusual thesis. The work was carried out on three continents over an extended time-span. This Preface gives a brief background to the evolution of the scientific philosophy which was followed; the scientific detail is given in the Introduction.

The thesis was first registered in 1963 in the Geochemistry Department of the University of Cape Town (UCT) under the supervision of the late Prof. L.H. Ahrens. The aim was to perform bulk-rock chemical analyses on a series of samples from the Earth's mantle in the form of xenoliths from kimberlite pipes; the purpose was to establish the geochemistry of the mantle and compare it with that of the meteorites. This would facilitate checking the internal consistency of the then competing models which sought to relate the chemistry of meteorites and the Earth. Implicit in these models were different theories on the origin of magmas in the mantle, and it was intended that the accurate establishment of the chemistry of the mantle should contribute to a better understanding of magma-forming processes. This phase at UCT continued for some seven years.

During these initial years the project proceeded on four broad fronts, in part identifiable only in retrospect. First, a large collection of mantle-derived xenoliths and their kimberlite host-rocks was assembled and prepared for analysis. Secondly and partly in concert with the expansion of the study-collection, exploratory chemical analyses were carried out. At that time only an optical spectrograph and a flame photometer were available for the chemical analysis of rocks in the relatively newly established Geochemistry Department at the University of Cape Town. Analyses made with these two instruments by John Gurney and myself led to the opening salvo of this project, a paper published by us jointly with Prof Ahrens in "Nature", and reproduced here as Appendix 2. It

became clear already at this stage that the research program originally envisaged was not viable, but the broad problem tackled remained of enormous interest: what was happening down there in the earth's mantle, now and in the past ?

The third activity in the beginning years was part of a joint effort by all members of the Geochemistry Department. Modern X-Ray fluorescence (XRF) equipment was being installed and analytical methods had to be implemented or developed. Part of the work on this front is reflected in a joint publication with my colleagues in "Canadian Spectroscopy", on the determination of Ba in rocks by X-ray fluorescence analysis, (Willis et al, 1969). In addition a joint paper was presented at the Spectroscopy Discussion Group at the CSIR, Pretoria, on the XRF analysis of major elements in rocks (Willis et al, 1968).

The fourth facet of the initial period of the research at UCT was the assembly of a data-base of major and trace element analyses for the collection of kimberlites and their xenoliths which I had assembled. These analyses were carried out as the analytical methods referred to above became viable, and the instrumental work was completed towards the end of 1969.

A further two papers were published in 1968 and 1969, as part of the initial phase of study at UCT (Appendices 3 and 4). In particular Appendix 3, which concerns secondary alteration in eclogites, reflects the evolution of the philosophy underlying the research. It is a cautionary note which attempts to explain why the problem originally envisaged for this thesis could not be resolved by the methods that were applied. In the light of these results, the research program unwittingly evolved into attempting to understand what really underlay the unforeseen complexities; what could be salvaged from the data that had already been obtained; and what alternative routes there might be to gain insight into the upper mantle.

As is demonstrated in Appendices 3 and 4, the nature of the complexities of secondary alteration which rendered the original research design for this thesis largely unviable, could easily be elucidated with the help of the XRF and X-Ray diffraction (XRD) techniques with which I was familiar at UCT. But at that stage these techniques did not appear to offer alternative routes to understanding the processes going on in the mantle. The first inkling of what new approaches might profitably be followed came with the milestone review article by O'Hara (1968). Here and in O'Hara (1970) was a critical appraisal of the disparate scientific philosophies which were being applied at the time in attempts to better understand the upper mantle. It appeared that more chemical data on samples of the mantle such as those I was working on could contribute to resolving aspects of the growing controversy. But at the time it was not altogether clear to me how, largely because the phase equilibria used by O'Hara were then all but incomprehensible to me. They are explained these days in texts such as Cox et al (1979) and Morse (1980), but the position in 1970 is very aptly reflected in the Preface of Morse (1980) who writes,

"...When I was a student the elegant use of phase diagrams was a closet speciality practiced by a few brilliant experimentallists and just a few clever teachers."

I moved to Britain in 1970 and was accepted as a research associate at the Grant Institute of Geology of the University of Edinburgh. My prime purpose was to learn the phase equilibria of mantle petrology and this was undertaken by attending undergraduate and post graduate courses in both igneous and metamorphic petrology. This program was enhanced by the opportunity of doing some exploratory high pressure experimental petrology on my kimberlite samples. It proved possible also to refine the analytical data-base started at UCT by doing ferrous iron and low-level sodium analyses.

Two papers were published on Sr isotopic relations in kimberlites on the basis of work done during the Edinburgh tenure (Appendices 5 and 6). This Sr isotope work was done independently of the program of learning phase-petrology, but reflects the continuity of the theme of this thesis: to see through the secondary overprints that hide the primary geochemical information in our rocks.

The Edinburgh environment was ideal for entering the new area of isotope geochemistry referred to above, although no facilities for actually making Sr isotopic measurements were available in Edinburgh; the catalyst was a stream of scientific visitors to local meetings or symposia, as well as the opportunity to attend scientific meetings elsewhere in Britain. Thus, during a discussion at a chance meeting with the late Prof Hugh Allsopp (of the Bernard Price Institute for Geophysics, University of the Witwatersrand) at the Symposium on African Geology held in Leicester in 1971, I contended that existing Sr isotope data for kimberlites probably reflected secondary alteration in poorly selected samples. At my request Prof Allsopp consented to carry out a limited number of measurements of Sr isotope ratios to help test this contention. K and Rb data for the rocks were already available from Appendix 4, and Sr abundances were available from my data-base referred to above. Consequently only five Sr isotope ratio measurements on carefully selected samples were required to assemble Appendix 5.

Appendix 5 was submitted as a manuscript in 1972 to Prof S Moorbath in his capacity as Editor of Earth and Planetary Science Letters. In his response Moorbath cautioned against publishing this paper. The conclusions of the work appeared to him so important and far-reaching, but were based on so little data, that Moorbath suggested I consider waiting until I could assemble further data and publish a more substantial work. Against his better judgement, however, he said that he would accept the paper if I adequately responded

to the referees comments, urging me nevertheless to think the matter over carefully. After careful consideration and revision of the manuscript I took the opportunity to publish, but would like to acknowledge Moorbath's profound positive influence on the decision to expand this line of investigation, which led to Chapter 6; he seems to have foreseen intuitively the complications which lay ahead. And there seems to be a broader lesson in this episode, which is surely how the old cats nurture the kittens of science!

In addition to the Sr isotope work (Chapters 5 and 6), the Edinburgh sodium analyses in turn form an essential part of Chapter 9 of this thesis, on the geochemistry of sodium in kimberlites.

The penultimate chapter of the thesis is equally, if less directly, related to the period of work in Edinburgh. The decarbonation reaction suggested in Chapter 10 was taught by Dr Ben Harte in the Edinburgh 3rd-year metamorphic petrology course. Without that background I would probably never have realised the importance of the brucite/calcite intergrowths illustrated in Appendix 10.

Efforts initiated together with O'Hara in Edinburgh to understand partial melting relations in the mantle are outside the scope of this thesis. However, the general background in mantle petrology which was developed in the process is pertinent to aspects of the phase of the research reported in Chapter 7, as enlarged upon below.

O'Hara and Yoder (1962) postulated that kimberlites might be residual fluids formed in deep-seated magmatic systems precipitating eclogite. Oxygen isotopic data published for eclogites by Garlick et al (1971) suggested complications to this model, however, and there was no matching isotopic data for kimberlites. On the other hand, it seemed possible that instead of conflicting with the model of O'Hara and Yoder

(1962) the data of Garlick et al (1971) might reflect secondary alteration processes. I wished to check their data on minerals separated with special care from eclogites already examined for secondary alteration (Appendix 3). Furthermore, it seemed worth investigating whether the hypothesis for the formation of kimberlite by eclogite fractionation stood up to a check of the total oxygen isotopic budget of the combined eclogite and kimberlite rocks.

The Edinburgh initiative into Sr isotope measurements on kimberlites also warranted testing by stable isotope measurements. The reasons are implied in Appendix 5 with reference to the work of Taylor and Forrester (1971) and amplified in Chapter 6.

A proposal whereby I would carry out the stable isotope measurements was accepted by Prof R.N. Clayton, and study continued at the Enrico Fermi Institute of the University of Chicago. The results of this segment are partly reported in Chapter 7, and discussed further in the Epilogue. No evidence was found that the earlier published oxygen isotope measurements on eclogites reflected secondary alteration processes. Furthermore, the quest for a more quantitative tool than the petrographic microscope with which to categorise the fresh and altered kimberlites on which Sr isotopes had been measured was thwarted: no unequivocal distinctions could be found in terms of the bulk-rock hydrogen isotopic compositions, or in the oxygen isotopic composition of the kimberlites' carbonates. The disappointment in these results is to some extent tempered by the reasonableness of the measurements undertaken: Carmichael et al (1974, p 525) independently suggested that stable isotope measurements of hydrogen and oxygen might clarify the role of meteoric water in the alteration of the kimberlites analysed by Berg and Allsopp (1972), as discussed further in Chapters 6 and 7. The disappointing stable isotope results also highlight the general complexity of our kimberlites.

The First International Kimberlite Conference took place in 1973 while I was working at the Enrico Fermi Institute in Chicago. During the conference I resolved to continue the study reported in this thesis in South Africa, and negotiated a position in Johannesburg at the National Institute of Metallurgy (NIM) as the Council for Mineral Technology was then known. The practice of trouble-shooting mineralogy required in this position unfortunately had little in common with academic research and NIM could not sponsor research on kimberlites. These were the "lean years" of this thesis; they continued into 1979.

The assumption of my current lecturing position on the academic staff of the University of Port Elizabeth allowed the revitalisation of the work reported in this thesis. The status quo which remained after the equivocal results obtained from stable isotope measurements was re-attacked via study of the serpentinitisation reactions which have to a greater or lesser extent affected all of the kimberlites examined here. Preliminary results were reported as part of a contribution to the 3rd International Kimberlite Conference in France in 1982 (Appendix 8a). The final results of the study of serpentinitisation in kimberlites, with particular reference to the presence of brucite, were presented at the 4th International Kimberlite Conference (IKC4) in Australia in 1986 together with the results of a preliminary investigation of the serpentinitisation of peridotite xenoliths. The latter investigation had led to the discovery of sub-microscopic calcite/brucite intergrowths, interpreted by the writer as a metamorphosed dolomitic solid solution. The combined presentation is outlined in Appendix 8b. The first half of the IKC4 presentation is fully documented as Appendix 8c, while the second half was published in 1986 in *Nature* (Appendix 10).

The most gratifying realisation whilst writing this preface is that this project has remained very much alive! Citations to Appendix 5, by Berg and Allsopp (1972) extend over a fifteen-

year time-span to Kirkley et al (1989); these writers use the criteria of freshness first set up in 1972 and amplified in Barret and Berg (1975). They also find that aspects of their results concur with some interpretations made by the writer on kimberlite/water interaction in 1972 as part of this thesis. Again, Egglar (1989) accepts at least the plausibility that protoliths of carbonate in the mantle may be observable in peridotite xenoliths from kimberlites (Chapter 10).

This "minor" odyssey, of attempting to elucidate the nature of the mantle while clarifying some events which obscure the evidence, ends where it began, at UCT and in the journal Nature. The journey would have been impossible but for the incredible fellowship of other scientists on many continents, acknowledged in more detail elsewhere. Its place in the hard science of the 1960's is outlined in Chapter 1, which follows.

CHAPTER 1**Introduction****1.1 FORMAT OF THE THESIS****1.1.1 General overview**

This thesis is presented in two volumes. Volume 1 serves primarily to illustrate how the bulk of the work, which has already been published, forms part of a unified theme. The work that has already been published is assembled in Volume 2. The two volumes have to be read in conjunction. This format is designed to avoid repetition of material which has already appeared in the press, but the brevity thus gained may introduce a need to guide the reader through the twin-format. An outline of the presentation-structure of the thesis is therefore given in the following sub-section (1.1.2), ending with a summary guide to where in the text specific contributions can be located in either Volume 1 or Volume 2.

Under the next two sub-headings (1.1.3 and 1.1.4), a resume is written of the scientific background against which the work here reported was conceived and commenced.

1.1.2 Structure of presentation

Chapters 2 to 6 are reviews of papers which have been published under the joint or sole authorship of the writer. These reviews have to be read together with the papers referred to in Volume 2.

Chapter 7 is a logical bridge between Chapters 6 and 8. The stable isotope measurements considered in Chapter 7 have, however, not been published. The measurements themselves, as well as the diagrams, are therefore presented in Volume 2 for convenient reference, but all discussion is in Volume 1. Where applicable this practice is followed in further chapters.

The presentation of Chapter 8, which discusses the mineral brucite in kimberlites, reverts to the format of Chapters 2 to 6. The results obtained in the brucite study, and their significance, are discussed comprehensively in a publication reproduced in Volume 2 as Appendix 8, which is briefly reviewed in Chapter 8.

Chapter 9 discusses work on the geochemistry of sodium which has not been published. Like Chapter 7 it is therefore presented entirely in Volume 1, except for data and diagrams in Volume 2.

Chapter 10 again follows the main format of the thesis. It discusses the shortest paper of the thesis, a single-page note to Nature on carbonate in the mantle. The brevity of the publication is in this case balanced by a more comprehensive presentation in Chapter 10, supported by further diagrams in Volume 2.

The writer's specific attempts to contribute to the knowledge of the geochemistry and mineralogy of kimberlites and their xenoliths may be located as outlined below:

Chapters 2 and 3

The first systematic study of the effects of alteration reactions on the bulk-rock geochemistry of kimberlitic eclogites.

The first report of the presence of analcite, and the relation of this mineral's crystal structure to the enrichment of caesium in kimberlitic eclogites.

Chapter 4

The first report of both primary and secondary micas in peridotite xenoliths in kimberlite.

The first report of an association of high concentrations of potassium, that is, high mica contents, with **lherzolite** xenoliths in kimberlite.

Chapters 5 and 6

The first low Sr isotope ratios reported in kimberlites, which were selected on petrographic criteria as being minimally altered by secondary reactions.

The first suggestion that high Sr isotope ratios in kimberlites may be a consequence of alteration reactions which were recognised by petrographic study.

The first report of high Sr isotope ratios in fresh micaceous kimberlites, acknowledged by Smith (1983) to represent, as they do, the Type II kimberlites which he defines by combined Pb, Sr and Nd isotope criteria.

Chapter 7

The first and only study to date directed to the relation of hydrogen isotope ratios in fresh as compared to altered bulk kimberlites. Concomitant measurement of O isotope ratios in carbonate phase.

Chapter 8

The first report of the presence of brucite in South African kimberlites. The first low-level estimates of the brucite-contents of kimberlites.

Chapter 9

The first suggestion that high-Na kimberlites reflect alteration reactions.

The first systematic study of the geochemistry of sodium in kimberlite.

The first report of the presence of aegirine and aegirine-augite in kimberlite, located in country-rock xenoliths, probably as alteration products.

Chapter 10

The first report of brucite/calcite intergrowths in peridotite nodules from kimberlite, and the suggestion that they may represent metamorphosed protoliths of carbonate from the mantle.

In summary, the above outline reflects an attempt to establish some of the limits of what can be achieved with bulk-rock analyses of kimberlites and their xenoliths.

Although the emphasis is on the understanding of secondary reactions, some fundamental data such as the real Sr isotope ratios in kimberlite, the significance of brucite in kimberlite, and perhaps carbonate in the mantle, were revealed in the process.

1.1.3 Historical background to the thesis

1.1.3.1 The upsurge of interest in the upper mantle--- The Upper Mantle Project

Towards the early 1960's the international geological community had developed a profound interest in the Earth's upper mantle. Haughton (1969) records how in 1960 the International Union of Geodesy and Geophysics made the initial decision to further an international co-operative research project to focus on a better understanding of the upper mantle and its relation to the crust. This decision led to the formation of a joint committee together with the International Union of Geological Sciences in 1963. The joint committee initiated the International Upper Mantle Project. This project laid the foundation to many studies of the earth's mantle which have evolved in time into work continuing today. The present thesis represents a geochemical facet of this Upper Mantle Project era. The Project was very much alive in South Africa, culminating in the publication of the Upper Mantle Project, Geological Society of South Africa Special Publication No 2. (Appendix No 4 of the present thesis is reproduced from the above-mentioned volume).

The Upper Mantle Project involved many aspects of the earth sciences which are outside the scope of even an introduction to this thesis. An example of this is the background knowledge of geophysics (eg Brown and Musset, 1981) on which all geochemical models of the upper mantle ultimately rest. This background must here be taken for granted. It is pertinent, however, to begin the background to this thesis with a brief overview of the divergent views on the probable mineralogical and chemical

constitution of the mantle which were argued at the time of the Upper Mantle Project. It will not be necessary to evaluate the merits or detailed development of the models because this thesis ultimately contributed in a different manner. Scientific projects generally build on a long line of previous effort, and the short review below is meant merely to explain the roots of the work which constitutes this thesis.

1.1.3.2 Two competing models for the upper mantle

The most profound differences between the two models for the upper mantle which were in vogue when this research commenced were the assumptions made regarding which type of meteorite best represents the Earth's core, its mantle, or the whole earth.

In 1958, Lovering considered the iron meteorites to represent the Earth's core; and the achondritic meteorites, which have a broadly basaltic composition, to be the extra-terrestrial analogues of the Earth's mantle (Lovering 1958). This went together with the model that the earth's upper mantle is made of eclogite, that is to say, the high-pressure mineralogy of basalt. Samples of such eclogites were known to Lovering, from the literature, to be found as inclusions in volcanic rocks such as kimberlites. Lovering also studied eclogites from the Delegate diatreme in Australia (Lovering and White, 1969).

An alternative model was being developed for the upper mantle by Ringwood and his co-workers in Canberra. This group of scientists considered chondritic meteorites to represent either the earth's mantle, or the bulk composition of the whole earth (Ringwood, 1975 and references therein). Because the chondritic meteorites are of broadly peridotitic composition, it followed that Ringwood and his co-workers favoured a mantle model constituted of peridotite of some kind. Details of the complexities concerning which class of chondritic meteorite

should be considered in evaluating the composition of the whole Earth or its mantle are irrelevant to the present discussion. It is important, however, to outline two different approaches which developed with respect to the peridotite mantle model in general. The approach of the Canberra school of Ringwood will be discussed first. This will be followed by a comparison with a peridotite model for the mantle developed in Edinburgh by O'Hara and his co-workers. These two scientists adopted extreme positions in what became a celebrated controversy.

One of the fundamental tenets in the first approach, of the peridotitic "pyrolite" model for the mantle developed by the Ringwood school, was that no samples of the mantle available for study on the earth's surface, be they tectonically or volcanologically emplaced, represented material capable of yielding basalt by partial melting. In other words, there is no possibility of gaining access to samples of the mantle in the state it was and indeed is still, before melting partially to produce the basaltic lavas extruded on the earth's surface. Ringwood argued that we have access only to samples of the residua of partial melting (hereafter termed "residual mantle"); in this case we can only derive the composition of the pristine mantle as it was before partial melting by adding, arithmetically, the correct proportion of the already extracted melt composition, to the known chemistry of residual mantle. The summation thus derived yielded the chemical composition of model "pyrolite", an acronym for pyroxene-olivine rock. This model, or limiting condition, was based on the assumption that continental tholeiitic basalt represented a primary melt from the mantle. Given this precept it was shown that the elements constituting tholeite (and later in the development of the pyrolite model other magmatic rocks), could not be derived in plausible amounts from a common parent represented by any sample of peridotite from the mantle for which analytical data were then available.

The pyrolite concept, then, developed as a chemically

defined composition (eg Ringwood, 1962) with an implied mineralogy (Green and Ringwood, 1963). A number of chemistries were modelled (see Ringwood, 1975 and references therein; O'Hara, 1970; O'Hara et al, 1975; and Wyllie, 1971, for discussion.)

In general, a "depleted" natural peridotite had added to it about 20% of tholeiite to calculate the assumed parent pyrolite composition thought to exist in the mantle and to yield the copious amounts of tholeiite extruded on the earth's surface. The details of these pyrolite chemistries are of little importance to the present discussion. What is important is the potential contribution to the development of petrological science envisaged in planning the work reported here. This will become clearer in Section 1.3.3 after the pertinent facets of the alternative approach to the peridotite mantle model, developed by O'Hara and his co-workers, have been outlined very briefly below.

O'Hara and his co-workers, (evolving from O'Hara and Yoder, (1962), O'Hara (1965 and other works) to O'Hara et al (1975)), argued that the compositions of natural samples available from the mantle had not been investigated sufficiently thoroughly to justify the need to add conceptually such radical components as 20% tholeiite to any mantle peridotite in order to derive fertile mantle compositions. Ultimately O'Hara et al (1975) suggested that both fertile and depleted mantle, of different mineralogy, were actually to be found in the suite of peridotites which occur as xenoliths in kimberlite pipes. This development took place during the same period of time that the work reported here was carried out; but it had not yet been reached when the present study was started because the necessary data had not yet been assembled.

1.1.3.3 The need for more geochemical data

In summary of Section 1.3.2, we must note that at the time of the inception of the present work the two main models being developed for the the composition of the mantle embraced three clearly identifiable schools of thought: on the one hand there was an eclogite model (Lovering) and on the other peridotite, adherents to the latter having two very different philosophical slants (Ringwood as opposed to O'Hara); progress of each model required more geochemical data than was at hand.

To test the eclogite mantle model of Lovering, an equivalence of bulk compositions could to be shown or disproven between the theoretical chemical composition of the model achondritic earth's mantle, and the composition of the eclogite nodules in kimberlite postulated to represent this mantle directly.

To contribute to the debate on the pyrolite model the internal consistency of the chondritic earth mantle model could be tested, by ascertaining how closely (or otherwise) the peridotite nodules in kimberlite chemically matched the theoretical chondritic upper mantle. Was it really necessary to invoke the addition of tholeite to reach the composition of "pyrolite"? Furthermore, the assumption that no fertile mantle samples were available for study on the earth's surface could be tested by ascertaining the range of chemical composition actually represented in the peridotite nodule suite found in kimberlite.

The potential contribution with respect to the more pragmatic mantle model being developed by O'Hara and his co-workers again required more accurate chemical data about the range of bulk compositions and its relation to mineralogy of the peridotite nodule suite. Relations with meteorites were not involved. The approach was simply to look more closely at what the terrestrial rocks were telling us.

1.1.4 Evolution of the research design

When the research reported in this thesis was first launched in 1963, the object was to gather data pertinent to the geochemistry of the upper mantle by analysing bulk-rock powders of eclogite and peridotite xenoliths from kimberlite pipes. At the time one or the other of eclogite or peridotite were considered to be representative of the bulk of the Earth's upper mantle, by the two opposing schools of thought reviewed above. It was therefore planned that concentrations of elements such as the alkali metals would be determined, in the expectation that these data would first help to test between the hypotheses underlying the competing models of upper mantle petrology. It was the intention to then refine the most promising model for the upper mantle as the work progressed.

Given the availability of kimberlitic materials in the form of the famed Williams Collection at the University of Cape Town, a logical way of testing Lovering's eclogite-mantle model was to compare the bulk-compositions of kimberlitic eclogites and achondritic meteorites. It was necessary, as already implied above, to consider bulk and not mineral compositions because the two populations which were to be compared are of different metamorphic facies. Thus the achondrites which consist in the broadest sense of plagioclase and diopsidic or augitic pyroxene, have for the same bulk chemistry a mineralogy of broadly omphacite and calcic garnet in the eclogite (high-pressure) facies of the upper mantle. In this metamorphic transition elements become decoupled. For example, Na coupled with Al in meteoritic plagioclase largely separates in the eclogite facies; here Al is concentrated in garnet and Na in omphacitic pyroxene (plagioclase being absent in the kimberlitic eclogites of interest). This renders comparative mineral chemistries irrelevant, but the bulk compositions in the two facies may be the same. This point is re-emphasised to stress the fundamental validity of the tests originally visualised in the research undertaken here under the guidance of the late Prof. L.H. Ahrens.

After three years the program had to be modified drastically, because it had by then emerged that the original goals could not be achieved (see pp 1, 2 and 3). This renders superfluous a detailed examination of the resolution of the fundamental problems which were addressed initially. It is necessary instead to focus on how the work reported in this thesis may have contributed to that specific facet of upper mantle research exemplified by Ringwood (1975) in his text "Composition and Petrology of the Earth's Mantle", when he states on p183:

"...Detailed studies (Heier, 1963; Berg, 1968; Allsopp et al 1968 (sic¹)) have shown that xenoliths from kimberlites have usually been contaminated by trace components introduced from the surrounding kimberlites so that the proportions and composition of the complimentary differentiate needed for calculation of the model pyrolite composition are not readily estimated. Nevertheless...."

This reflects an on-going problem in geochemistry; for the first contribution to the problem made in the present thesis we must move to Chapter 2.

¹ The reference is erroneously recorded as 1968 in Ringwood (1975); a different but correct date (1969) is therefore recorded in the reference list of the present thesis.

CHAPTER 2

Observations on cesium enrichment and the
potassium/rubidium/cesium relationship in eclogites
from the Roberts Victor Mine, South Africa.

2.1 INTRODUCTION

As both eclogite and peridotite mantle models were to be investigated as part of this thesis, there was no particular precedence as to whether eclogite or peridotite xenoliths should first be analysed when the program commenced. The choice of eclogites as the subject of the initial investigation reported in this Chapter was based partly on the availability at UCT of the internationally renowned Williams Collection of eclogites, peridotites and kimberlites (See Ch 1, p19). It is noteworthy that three eclogites from Roberts Victor and one each from Jagersfontein and Tanzania out of this collection had already been analysed in one of the only two previous studies on the concentration of alkali metals in eclogites, by Heier (1963). An additional reason for investigation of the eclogites at an early stage was the preliminary discovery by J.J. Gurney (UCT), that some Roberts Victor eclogites carried unusually high concentrations of Cs.

As noted in the Preface, analytical facilities at UCT in 1963 did not allow for the complete analysis of major and trace elements in rocks. It was therefore decided to commence with analysis for the alkali metals, for which the analytical facilities were already available. An understanding of the geochemical behaviour of K and Rb in particular was a field of special interest in the UCT Geochemistry Department. The relative abundances of these elements offered to give some insight into petrological processes such as differentiation (eg Ahrens et al, 1952; Taylor et al, 1956; Taubeneck, 1965). Furthermore, their absolute abundances in eclogites, when compared to meteorites, appeared capable of contributing to

mass balance tests between the different models for the mantle reviewed in Chapter 1.

2.2 PREVIOUS WORK

Previous work on the alkali metals in eclogites by Heier (1963) and Faure and Hurley (1963) was on relatively few specimens, and no systematic study of both K and Rb in the same eclogites had previously been undertaken at all. Cs had never been studied. Heier (1963) had studied U, Th and K abundances, while Faure and Hurley (1963) studied Sr isotopes and report a single Rb value.

2.3 METHODS AND RESULTS

The program commenced with the analysis of 20 samples of eclogite for Na and K by flame-photometry, and Rb by X-ray Fluorescence (XRF) by the writer, concomitantly with the simultaneous analysis of Rb and Cs by means of the optical spectrograph by J.J. Gurney. The combined results were published by Gurney, Berg and Ahrens (1966) in *Nature* (See Vol 2, Appendix 2). The main discoveries reported in this paper are: the surprisingly high concentrations of Cs in some of the eclogites; the close coherence between K and Rb; and the lack of any coherence between Cs and the other alkali metals studied.

2.4 IMPACT

The paper by Gurney, Berg and Ahrens (1966) is cited together with Berg (1968) in the specialised text-book on kimberlite by Dawson (1980, pp155-156). Dawson (1980) refers particularly to disparities between bulk analyses for Rb and Cs compared to concentrations of these elements in the primary minerals of eclogites. Dawson further notes the large ranges in the K/Rb ratios of eclogites from Roberts Victor reported by Heier and Compston (1966), who report K/Rb = 176 to 349; Gurney

Berg and Ahrens (1966), who report $K/Rb = 257$ to 534; and Griffin and Murthy (1968), who found K/Rb ratios of 210 to 407. Dawson (1980) notes by contrast how K/Rb ratios in eclogites from localities other than Roberts Victor have a much more restricted range of K/Rb ratios from 240 to 286. He ascribes the large range of K/Rb ratios in Roberts Victor eclogites to varying degrees of alkali metasomatism.

In summary, the data in the the paper by Gurney Berg and Ahrens (1966) first indicated the unusual alkali metasomatism undergone by Roberts Victor eclogites for K and Rb, simultaneously with and independently of Heier and Compston (1966). Gurney Berg and Ahrens (1966) completely independently established the Cs enrichment in Roberts Victor eclogites. Initially the high bulk-rock Cs content of these eclogites was a mystery; only when the rocks were "taken apart" by separating and analysing their mineral constituents, was the real meaning of the high Cs contents revealed. For details of this phase of the study we must proceed to Chapter 3.

CHAPTER 3

Secondary alteration in eclogites from kimberlite pipes.

3.1 INTRODUCTION

Following the work reported in Chapter 2, the next step was to try and explain the unusual abundance of Cs in Roberts Victor eclogites. This involved a detailed mineralogical study of which only preliminary results had thus far been reported in Gurney, Berg and Ahrens (1966). The full details are reported by Berg (1968); see Appendix 3.

The prime requirement for understanding the high concentrations of Cs in the bulk eclogites was to locate where the Cs resided. The possibility that a zeolite, acting as a molecular sieve, was responsible for the high concentrations of Cs in the eclogites, was speculated upon on the basis of fundamental principles. A rapid check of this speculation was attempted, but it failed to reveal that the host for Cs had an analcime structure.

The rapid check sought to find out whether bulk-rock diffractograms of high-Cs eclogites exhibited X-ray reflections consistent with the d-spacings of any zeolite listed by Deer, Howie and Zussman (1963, Vol 4) (DHS 4). No match was found and the mineral carrying Cs had to be sleuthed out systematically by mineral separation combined with X-ray diffraction and chemical analysis as described in Section 3.2.

Analcime escaped identification in the first rapid check because while Deer, Howie and Zussman (1963, Vol 4, p338) consider it to be a valid member of the zeolite group, they write when discussing analcime that,

"...in structure, chemistry and paragenesis it has close affinities with the feldspathoids."

Analcime is therefore not discussed by these authors under the heading of "Zeolite Group", but in a separate section headed "Analcite" which precedes the zeolites; consequently, the analcime diffraction pattern was omitted from the first rapid search for zeolites based on the list in DHS4, p 351. There was little excuse for omitting the analcime X-ray pattern in the initial check for zeolite, inasmuch as Deer, Howie and Zussman (1963, Vol. 4, p351) state under the heading of zeolites,

"Analcite is commonly included as a member of the zeolite group", but "...is here treated separately..."

In the event, analcime was later identified by the more systematic methods outlined below.

3.2 METHODS

To determine where Cs resided in the eclogites the constituent minerals of two rocks (RV 372 and RV 378), were systematically separated. These two rocks were selected for detailed study on the basis that first, they carried amongst the highest bulk-rock concentrations of Cs. Secondly, they were the minimally altered specimens within the high-Cs group and hence offered the best prospect of successful separation of all phases.

As a first step in the mineral separation the rock powders were run through a Franz magnetic separator. The current fed through the coil of the magnet was increased systematically in very small increments so that each pass collected a minimum of more magnetically susceptible powder. This was done to assure the maximum possible separation of phases. The magnetic fractions were then treated with heavy liquids to effect further separation. The separated fractions were analysed semi-quantitatively on the optical spectrograph to determine which one held the highest concentration of Cs; this powder was

then run as an unknown by X-Ray diffraction methods and found to have the diffraction pattern of analcime (See Appendix 3, Fig 1).

3.3 RESULTS AND DISCUSSION

3.3.1 Decoupling of alkali metal abundances

Analysis of the separated pyroxenes, when combined with petrographic study and K analyses for the bulk rocks (see Berg, 1968, Tables 1 and 2; Appendix 2), left no doubt that the K contents of the bulk rocks were controlled by phlogopite². Clearly, Rb was associated with K in the mica, and this mineral controlled the K/Rb coherence recorded by Gurney, Berg and Ahrens (1966, Fig 1). In contrast, Cs was found to reside independently of K and Rb, in the analcime. This was readily explained in that analcime has the same atomic structure as the Cs mineral pollucite, which gives it the propensity to collect Cs in the eclogites. Analcime, a Na hydroxy silicate, does not, however, preferentially concentrate the intermediate-sized alkali metals K and Rb (which in the eclogites reside mainly in phlogopite as noted above). This clarified the decoupling of Cs from K and Rb, which was commented upon by Gurney, Berg and Ahrens (1966, Fig 2).

The bulk-rock alkali element relations of the eclogites could thus be explained by determining in which minerals the elements of interest resided. Interpreting just how and when these minerals formed was a more speculative exercise, but it seems to have been done with reasonable success, as reviewed briefly below:

² "Phlogopite" or "mica" are used here to denote the general range of phlogopite and biotite encountered in kimberlitic eclogites.

3.3.2 Origin of phlogopite

Since in some of the eclogites studied phlogopite occurs in reaction rims around garnet, and in another (Jag 351) in veins **cross-cutting** the sample at about 3cm intervals, there could be little doubt that at least those micas post-dated the primary garnet and omphacite. Such micas could thus be termed "secondary", but their age in relation to that of their hosts was at that stage known only in a relative sense. Berg (1968) suggested that the phlogopite formed by metasomatic alteration of the eclogites while their host kimberlite was in a fluid state. This suggestion gave rise to some partly controversial discussion, outlined in the following paragraphs.

Barrett (1973) considered that the relation of phlogopite in eclogites to their host kimberlite as suggested by Berg (1968) was untenable. She argued that the Sr isotopic ratios of 0.7082 measured by her in the micas of eclogites from Roberts Victor were incompatible with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.704 then believed to characterise fresh kimberlites (and implicitly the Roberts Victor kimberlite); the value of 0.704 was based on the initial study by Berg and Allsopp (1972). Subsequent measurements of the Sr isotopic composition of fresh **micaceous** kimberlites, which yielded values of about 0.708, initially by Barrett and Berg (1975) and definitively by Smith (1983), partly resolve the Sr isotopic difficulty of relating the micas in Roberts Victor eclogites to their host kimberlite. This is because the Roberts Victor kimberlite itself is highly micaceous; however, the Sr isotopic constitution of this particular micaceous kimberlite remains to be determined. We will return to this gap in our data-base at the end of this section.

Meyer and Boctor (1975) became involved in the subject of phlogopite in eclogite during a study which primarily focussed on the sulphide/oxide minerals in an eclogite from Stockdale, Kansas. On the basis of their compositions the sulphides were

inferred to have at one stage been melted within their eclogite host; a temperature of 1100 to 1200°C was implied. The eclogite being studied (op cit) also contains, along grain boundaries, amphibole, biotite and rutile, which Meyer and Brookins (1971) considered might be related to the host kimberlite. In this context Meyer and Boctor (1975) wrote:

"The evidence from the sulphides indicating some heating of the xenoliths makes this interpretation for the origin of the mica more attractive, and is in agreement with the conclusion of Berg (1968) concerning the secondary nature of mica in eclogites from South African kimberlites."

The work which confirms the secondary nature of the micas discussed by Berg (1968) is the age determination of about 2.5 b.y. reported by Kramers (1979) for the Roberts Victor eclogites themselves.³ This, when combined with the age determinations of 120 to 140 my on micas separated from the eclogites by Barret (1975), both proved and quantified the **relative** ages of eclogites and (secondary) micas suggested by Berg (1968). However, the fact that the micas are secondary does not yet relate them to their kimberlite hosts and this aspect remains an equivocal question. Hatton (1978) had to conclude that the phlogopitisation of eclogites from Roberts Victor was a metasomatic event at about 120 to 130 my, which preceded eruption of the kimberlite according to the (then) only available age determination for the Roberts Victor kimberlite at 92.2 my. This 92.2 my date was determined by Davis (1977), on a zircon **reputed** to have come from Roberts Victor.

³ That is making the assumption that the linear array of data-points on the $^{207}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ diagram presented by Kramers (1979) does reflect an isochron, noting nevertheless the caveat made by Dawson (1980, p177) in this regard.

Smith (1983) found that micaceous (Type II) kimberlites in the broad Kimberley region have ages in the general range from 114 to 127 my (eg New Eland, Bellsbank and Newlands). In this general pattern the age of 92.2 my for Roberts Victor is out of character, insofar as it is a highly micaceous kimberlite. According to Gurney (1992, pers. comm.) doubts have been expressed by other kimberlite researchers as to the source of the "Roberts Victor" zircon analysed by Davis (1977). The age of 125 my suggested by Smith et al (1985) is considered unreliable, but to approximate the emplacement age of the Roberts Victor kimberlite (Gurney et al 1991). An age of 125 my for the Robert Victor kimberlite, when combined with the 120 - 140 my age for the micas in its eclogite xenoliths determined by Barrett (1975) would strongly support the relation of the mica in the eclogites with the kimberlite host, as suggested by Berg (1968). The original suggestion by Berg (1968) would of course remain no more than the working hypothesis that it was: a plausible model based on the then available evidence, which can be tested; and rejected or modified after further data are obtained, in the nature and methodology of our science.

Roberts Victor carries an abundance of eclogites which is unique. This combined with the general interest in metasomatism in the mantle (eg Menzies and Hawkesworth, 1987) would seem to justify doing a combined Rb/Sr and Sm/Nd age determination on the Roberts Victor kimberlite, to better establish the relation of mica in the eclogites to the kimberlite host, as discussed above.

3.3.3 Origin of the analcime

Barrett (1975, p 643) found that both the Sr abundances and the Sr isotopic ratios in her freshest available and slightly altered omphacite from the same eclogite were indistinguishable. On this basis she favoured the hypothesis of Whitfield (1971), that alteration of eclogitic pyroxenes proceeded isochemically upon pressure release, rather than the

suggestion of Berg (1968) that alteration of omphacites may occur during post-emplacement alteration by deep weathering. Barrett's preference (op cit) is perfectly plausible (but not necessarily correct) as an explanation for the the omphacite separates to which she referred. These contain about 200 to 500 ppm Sr. The host kimberlite contains about 1000 to 1500 ppm Sr (Berg, unpublished). Moderate alteration of the omphacites may therefore not change their Sr parameters grossly. Isochemical alteration by decompression cannot account for the formation of the Cs-rich analcimes in eclogites, however, for a number of reasons:

First, analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) is hydrous, and therefore cannot be the product of isochemical alteration of omphacite in the strict sense, because unlike kimberlite magmas, eclogites do not carry the necessary volatiles to supply the 8 wt% H_2O^+ present in analcime.⁴ Secondly, whereas the omphacite contains

⁴ Note added in proof:

Since this was written I have become aware of the remarkable amounts of water (in the form of H) in nominally anhydrous minerals (see for example Bell and Rossman, 1992 and references therein; especially Smyth, 1987, the significance of which escaped me initially). Smyth et al (1991) consider that as much as 0.5 wt% OH may be present in eclogitic omphacite, and suggest that "the H released from the pyroxenes on cooling from solidus temperatures provides a source of H for autometasomatism", thereby being responsible for at least some of the ubiquitous alteration which characterises kimberlitic eclogites. I express doubt in Chapter 3 above, whether the decompression-alteration model of Whitfield (1971) could adequately explain **both** the formation of analcime **and** its enrichment in Cs, partly on the supposition that omphacite is anhydrous. The water referred to by Smyth et al (1991) may indeed suffice to make some analcime on grain boundaries upon decompression, given appropriate diffusion rates to emplace 8 wt% H_2O in the alteration phase (analcime?); but it is difficult to envisage the enrichment of Cs in the same process with only "local" previously unsuspected water participating on a grain-size scale.

A number of lines of further investigation suggest themselves: For example, the maximum amount of OH possible (0.5 wt% OH ?), less the amount of OH now present in pyroxene RV 378, would yield the amount of water that **might** have diffused into the analcime in this rock; this could be compared with the volume of analcime present to test for plausible mass balance. The volume of analcime has not been measured, but it may be estimated as follows: 16.4 ppm Cs was determined on the bulk rock (Appendix 2) and 75 ppm Cs in an impure (est 75%) analcime (Appendix 3). Assuming 100 ppm Cs in the pure analcime would suggest that approximately 15% of analcime is present in the rock to account for its bulk Cs content of some 16 ppm. Diffractogram D, Fig 1 in Appendix 2 does not suggest that this is unreasonable; at 8 wt% H_2O this analcime would contribute roughly 1 wt% H_2O to the bulk rock. If half the rock were made of omphacite this would imply the impossibly large (?) amount of 2 wt% H_2O which would have to have resided in the omphacite and entered the analcime to form the analcime auto-metasomatically. For RV 372 an even larger amount of OH would be required. But these calculations are crude and this facet should be pursued. The formation of analcime auto-metasomatically, and its subsequent enrichment in Cs by post-emplacement ion exchange in the hydrothermally altering or weathering kimberlite is a model which warrants further testing. It should also be borne in mind that analcime is not the only alteration phase of eclogitic pyroxenes, and that it cannot in general be detected optically.

relatively abundant Sr which can carry over into secondary alteration minerals, Cs could not be detected in the omphacite at all⁵; yet the analcime contains about 100 ppm Cs. This is better explained by alteration of omphacite by groundwater percolating through the kimberlite; this process can both supply the water required to make analcime from the (sodic) omphacite, and further allow the analcime to scavenge Cs from the same circulating water. The 6ppm Cs determined in the Roberts Victor kimberlite by Gurney et al (1966) reflects a plausible source from which to dissolve Cs into the groundwater in question.

The finer details of possible syn- and post-emplacement alteration become increasingly superfluous to the main thesis of the present work, the main thrust of which is summarised below:

3.4 IMPACT AND CONTINUATION

At the time of publication, the study by Berg (1968) was the only work devoted to establishing the viability of using bulk analyses of eclogites in geochemical modelling. The work was accepted as a general caution against placing too much credence on bulk analyses of eclogite, in the main sense that it was intended originally (eg Ringwood 1975 p 183, as quoted in Chapter 1) .

Clearly secondary processes such as phlogopitisation and weathering had altered the eclogite inclusions in the Roberts Victor kimberlite to a significant extent. It therefore had to be concluded that the alkali metal analyses which had been undertaken on whole eclogite powders, could not be used as a basis of comparison between the earth's mantle possibly represented by such eclogites, and the calculated bulk

⁵ The detection limit for Cs is taken to have been better than 1 ppm, on the basis of the data given by Gurney (1966, p 34 and Table 7).

composition of the mantle derived in the achondritic earth model. This line of investigation was therefore discontinued because the original objectives⁶ could not be achieved.

Rather than considering whether data for other elements might more successfully elicit information from bulk eclogites, it was decided instead to broaden the alkali-metal study to include the peridotites, as discussed in Chapter 4 which follows:

⁶ (as outlined in the Preface,(p1) the Introduction (1.3.2, para 2 and 1.3.3, para 2)

CHAPTER 4

<u>Potassium, rubidium and cesium in South African kimberlites and their peridotites xenoliths</u>
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4.1 INTRODUCTION

The outcome of the study of alkali metal abundances in eclogites (Chapters 2 and 3) led to the anticipation that difficulties due to contamination might be encountered in the study of bulk peridotites as well. It seemed plausible, however, that the difficulties might be less severe; the Roberts Victor Mine from which the eclogite samples were obtained, is renowned for its deep development of yellow-ground (Melville, 1910; see ref by Berg, 1968, p1343: (Appendix 2)). Yellow ground is a product of surface weathering. The Roberts Victor Mine was not mined to great depth, so that much if not all of its stock of nodules might have been recovered from the zone of (deep) surface weathering. In contrast, the peridotite nodules studied were predominantly from the Kimberley mines and Jagersfontein; it could be hoped, therefore, that due to deeper mining at Kimberley than at Roberts Victor, at least the contamination reactions due to weathering would turn out to be less extreme. In any case, it would have been irrational to abandon the proposed bulk-rock analyses on peridotites merely on the basis of the results on the Roberts Victor eclogites. The philosophy of the thesis was beginning to evolve from its original unattainable objectives into the establishment of the limits of what **could** be achieved with bulk rock analyses, as outlined in the Introduction, (Section 1.2), and expanded below:

The prospects of achieving petrologically more useful results from the bulk analysis of alkalis in peridotites than eclogites were enhanced for two related reasons :
First, a larger number of samples was analysed; secondly, a more comprehensive background of petrological modelling, mainly due to O'Hara (1968, and earlier references therein), was

available for peridotites than for eclogites. It was possible, therefore, to apply the data for alkali elements discussed in the present chapter more quantitatively than could be done in the case of the eclogites considered in Chapters 2 and 3, as outlined in Section 4.2 below and Appendix 4.

The results of the study on alkalis in peridotites were presented by the writer at the Geological Society of South Africa Congress of 1968, and published by Gurney and Berg (1969) in The Geological Society of South Africa's Special Publication Number 2, the "Upper Mantle Project" (Appendix 4). Some salient aspects of this work are discussed below and should be read in conjunction with the Appendix 4.

4.2 THE RESEARCH DESIGN AND RESULTS

The relatively large number of samples (50 kimberlites and 100 peridotites) analysed by Gurney and Berg (1969) allowed the writer to use statistical techniques in the interpretation of the results to test then current models for partial melting in the mantle. In particular, O'Hara (1968) had suggested that garnet lherzolite, garnet harzburgite and harzburgite represent respectively fertile mantle, partly depleted and depleted mantle related in a partial melting event. This allowed the test described in the following paragraph.

Partial melting in the mantle is generally assumed to lead to a depletion of K from the source rocks, and hence K-poor residua, because of the incompatible character of K. Thus harzburgite residua should have lower K contents than fertile garnet lherzolite. Yet Gurney and Berg (1969) in Appendix 4 show that there is no statistical difference between the range of K contents of 36 garnet lherzolites, 20 garnet harzburgites and 29 harzburgites, which represent the model fertile mantle and residua proposed by O'Hara(1968). It could be concluded therefore, (given that O'Hara's model was correct), that the K contents of the rocks are a secondary metasomatic overprint

which post-dates the partial melting event modelled to have led to the observed garnet lherzolite - garnet harzburgite - harzburgite groupings. The writer suggested that the distribution of K in the peridotites was controlled by phlogopite (see Fig 2, Appendix 4). Therefore this phlogopite might, at least in part, post-date the partial melting event which is reflected in the mineralogy of the rocks. Inasmuch as the primary olivine, enstatite, garnet and diopside contain so little K that it is difficult to perceive these assemblages alone ever giving rise to basaltic magmas by partial melting, it was suggested that the metasomatic introduction of phlogopite may be a precursor fluxing necessary for partial melting to occur; that is to say, a recurring process through geological time. As such, the peridotites were thus perhaps "fluxed" and ready again to be partially melted. This idea, briefly outlined in Gurney and Berg (1969, p 420 - 421) was speculative. It was backed up, however, by what appears to have been the first illustration of suggested primary phlogopite in rocks from the mantle (Appendix 4, Plate 2, first shown in Pretoria at the verbal presentation of the work in 1968.)

Plate 2, referred to above, was published in the same year as the illustration of a primary mica from the mantle in a peridotite nodule from Lashaine, Tanzania, by Dawson and Powell (1969); this was remarked on in a footnote of the paper by Gurney and Berg (1969) added in the proof stage. The two papers have slightly different approaches in their fundamental petrographic premises made in concluding that primary mica had been discovered, but neither paper specifies these premises precisely. Thus, Gurney and Berg (1969) in Plate 2 illustrate a phlogopite in textural equilibrium with pyrope garnet, a mineral which implies equilibration well within the upper mantle regime on the basis of phase equilibrium studies (eg O'Hara et al (1971, and earlier references therein). To stress the point, Gurney and Berg (1969) also illustrate, as Plate 1, phlogopite in a disequilibrium texture with pyrope,

and conclude that there may be two different generations of mica in the set of samples studied.

In contrast, Dawson and Powell (1969) illustrate a phlogopite in textural equilibrium with olivine. Although olivine is not a diagnostic mineral of high-pressure paragenesis, the mineralogy of the nodule as a whole is an implicit indication of its origin in the mantle; and the independent texture of the mica which appears in no reaction relationship with another mineral, attests to Dawson and Powell's deduction that the mica is a primary constituent of the mantle assemblage. Gurney and Berg (1969, Plate 2 caption) also note that: "...the mica is not necessarily in the vicinity of the garnet". There is therefore little doubt that the mica occurrences documented by Gurney and Berg (1969) and Dawson and Powell (1969) both represent "primary phlogopite". Harte (1987) notes, with reference to Carswell (1975), that the origin of such phlogopite is difficult to assess petrographically, but that it "could indicate a metasomatic event". The present work is thus among the earlier suggestions of mantle metasomatism (Gurney and Berg, 1969, pp420 - 421), a topic which subsequently became of increasing general interest, and is now a well accepted process (see for example Menzies and Hawksworth, 1987).

Gurney and Berg (1968) may indeed have made the earliest petrographic deduction that primary mica in the mantle was present in nodules in kimberlite. However, Special Publication Number 2 of the Geological Society of South Africa, where the data finally appeared in print in 1969, seems to have had somewhat limited circulation:

Carswell (1975, Fig 1) published photomicrographs of suggested primary and secondary phlogopites which are almost identical to Plates 2 and 1 of Gurney and Berg (1969), without making any reference to this earlier work. Carswell (1975) supplies additional data in the form of microbeam analyses which

corroborate his, and implicitly Gurney and Berg's (1969) deductions.

The observation by Gurney and Berg (1969) that lherzolites have, on average, higher K contents than the other three classes of peridotite studied is also a reflection of metasomatism in the mantle. It was recorded at the time that this observation appeared to reflect an association between clinopyroxene and mica, but this aspect was not pursued as its meaning was not clear.

4.3 IMPACT AND SIGNIFICANCE OF APPENDIX 4

In summary, it could be concluded that the bulk rock geochemistry of peridotite nodules from kimberlites carry geochemical overprints of multiple events. By studying sufficient samples it was possible to recognise that some form of enrichment of alkalis in the mantle post-dated the formation of the main silicate equilibrium assemblages; that two generations of phlogopite were evident; and that one of the phlogopite assemblages could represent phlogopite that was stable in the mantle. It was clear that bulk rock analyses for alkali metals would not yield the results hoped for in the original experimental design of the program, as in the case of the eclogites discussed in the previous two chapters. The work had, however, highlighted the need to study the secondary alteration processes much more diligently. Without a firm understanding and quantification of these processes, it is unlikely that the igneous processes and pristine mantle chemistries can be fully understood.

Further possible directions of study of bulk peridotitic xenoliths from kimberlite are briefly considered later in this thesis, but attention will first be directed to problems of secondary alteration which affect the host kimberlites themselves. These aspects are considered in Chapters 5 to 9; the return to mantle assemblages is made in Chapter 10.

CHAPTER 5

Low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in fresh South African kimberlites

5.1 INTRODUCTION

A necessary component in the broad quest of understanding the history of the earth's mantle involves an understanding of the origin of kimberlite. As Boyd (1979) aptly wrote, kimberlites are the "busses" which carried as "passengers" the xenolithic nodules upon which we base much of our conception of upper mantle petrology. But the relation is actually more intimate than between "passengers" and "bus", and it is vital that we should understand it better. On the one hand, the chemistry of primitive kimberlite should reflect the constitution of the mantle where it originates. On the other hand kimberlite contains some incompatible elements like Sr whose concentrations are high in comparison to the peridotite xenoliths. For example, kimberlite may contain 700 to 1700 ppm Sr (Berg and Allsopp, 1972). Peridotite nodules generally contain <10 to 30 ppm Sr (Berg unpubl.) Such a high concentration gradient between host and xenoliths leads to a great potential for contamination. It means that 1 per cent bulk contamination of a nodule by its kimberlite host may double the concentration of Sr in the nodule. This assumes that the bulk concentrations referred to above are primary to the nodules and not already part-contaminant. The contamination in question may take place as the kimberlite picks up the mantle material that ultimately constitutes the nodule; it may take place en route to the earth's surface; or it may take place during post-emplacement hydrothermal or longer-term ground water accession. To understand the geochemical consequences of any of these possibilities we require above all a thorough knowledge of the chemistry of the kimberlite. Yet we know so little about kimberlite that Mitchell (1986) concludes his book on these rocks with the statement:

"The object of the next decade in kimberlite petrology should be to deconvolute the evidence presented to us and seek out the primitive kimberlite magma."

The work reported in this chapter was already directed towards this goal in 1972. It evolved from the previous chapters as follows:

5.2 THE RESEARCH DESIGN

5.2.1 General Background

In Appendix 3 it was suggested that leaching and re-deposition of Cs during weathering might have contributed to the build-up of high concentrations of Cs in eclogite xenoliths, the source of Cs being the host kimberlite. It was further suggested that the geochemistry of some other elements including Sr might be analogously affected. In Appendix 4, Section 5, evidence is presented to suggest that peridotite nodules with high Cs concentrations are found in kimberlites which contain relatively high concentrations of Cs. It was further suggested that abnormally high concentrations of Cs in some De Beers Mine kimberlites might be a consequence of late hydrothermal activity or downward ground water leaching. Clearly Sr in such kimberlites might also be affected, from which it followed that Sr isotopic data published on kimberlites up to 1971 might have been "corrupted" by secondary processes. Thus the present chapter merely reflects a logical extension of the work reported in Chapters 3 and 4; but it focusses on the kimberlites themselves. Furthermore, the focus is on isotope ratios rather than elemental abundances.

The results of the alkali metal and mineralogical studies undertaken for Appendices 2, 3 and 4 generally yielded information only about late-stage events. Isotopic rather than elemental measurements were undertaken for Appendix 5 in the

hope that they would yield information going further back into the history of kimberlite, for reasons expanded below.

At the time the work was undertaken there were two main hypotheses for the origin of kimberlite:

O'Hara and Yoder (1962) postulated an origin by crystal fractionation of eclogite from a picritic magma deep in the upper mantle, leaving a residual fluid of kimberlite. Dawson (1971; 1972; 1980) suggested an origin by low-degree partial melting in the mantle. These disparate hypotheses both involve crystal/liquid fractionation which can rapidly change elemental abundances in the putative kimberlite fluids. Sr isotopic **ratios** on the other hand, are not affected by such fractionation. Measurement of these ratios was therefore chosen as a tool which might bypass both the problems of late-stage alteration and the vagaries of divergent hypotheses of origin, to yield some of the secrets about the nature of the source of kimberlite in the mantle.

5.2.2 Sample selection

If the Sr isotopic ratios for kimberlites published up to 1971, (all 0.706 and above; see Appendix 5), had been affected by alteration reactions, it followed that kimberlites with lower ratios might exist but have escaped detection. The research design for Appendix 5 was formulated to seek out these low Sr isotope ratio rocks. As a working hypothesis the supposition was made that the ratios published to date had been made on **altered** materials, which are by far the most abundant in kimberlite pipes, and indeed kimberlite collections in laboratories and museums.

The intensely altered, high-Cs samples from the De Beers Mine such as KDB 17 (Appendix 5, Section 2 and Table 3b) were collected in situ and noted at the time to have water percolating through them. It was logical to measure the Sr

isotopic composition of such samples and compare the results with published data. It was equally logical to investigate kimberlites that had not been open to hydrothermal or percolating ground water; such kimberlites might have low ratios; but they might also have similar or even higher Sr isotope ratios than the altered kimberlites.

There was very limited capacity for Sr isotope measurements in the pilot study reflected in Appendix 5. Emphasis was placed on determining the ratios of unaltered kimberlites, which it was anticipated might be about 0.703 to 0.704; three out of five measurements were therefore devoted to this aspect (KDT 24, KDT 25, and KDB 13). These rocks, as well as altered materials to analyse for comparison, were carefully selected according to petrographic criteria discussed in Appendices 5 and 6 and Chapter 6. Sample KDB 17 was chosen as a manifestly altered kimberlite which was open to groundwater, partly because when it was collected in situ water was observed to be percolating through that part of the De Beers kimberlite underground. The yellow-ground, KRV 17, was selected as an even more extremely altered kimberlite than KDB 17.

5.2.3 Retrospective assessment of sample selection

The three fresh kimberlites whose Sr isotopic compositions were reported in Appendix 5 remain, in this writer's opinion, good examples of fresh kimberlites which warrant comprehensive petrological investigation. They represent what were subsequently defined as Type 1 (low Sr isotope ratio) kimberlites by Smith (1983).

Of the two altered kimberlites, KDB 17 is a somewhat extreme case. The sample is now known to carry about 15 per cent shale. The shale is as heavily altered as the kimberlite itself, however, and the whole rock is probably reasonably representative of typical Type 1 kimberlites equilibrated with

Kimberley groundwater or late hydrothermal water which might have affected these rocks.

In the wisdom of hindsight KRV 17 was a poor choice. This is because, as discussed already in Chapter 3, the Roberts Victor kimberlite is a "Type 11", which by definition has a high Sr isotopic ratio. Appendix 5, however, was published some ten years before this grouping of kimberlites had been established by Smith (1983). Fortunately even if fortuitously, the poor choice of sample KRV 17 exercised no significant effect on the outcome of the Sr isotope study.

5.4 RESULTS

The significance of Appendix 5 is that here are reported the first low Sr isotope ratios in kimberlite:

(0.7037, 0.7040 and 0.7046). It was further suggested that the higher Sr isotope ratios of 0.7068 and 0.7083 obtained respectively for the altered samples KDB 17 and KRV 17 were a consequence of alteration by ground water percolation. Although this suggestion still appears to be reasonable in the light of further study, the evidence for it in Appendix 5 is in fact rather precarious. The case of KRV 17 has been discussed above, leaving the conclusion about the effect of alteration on Sr isotopic ratios based on only one valid sample.

The broader impact of Appendix 5 is best considered together with that of Appendix 6 in Chapter 6 as these two papers really form part of one Sr isotopic investigation.

CHAPTER 6

<p style="text-align: center;"><u>Complimentary Petrographic and Strontium-Isotope Ratio Studies of South African Kimberlite</u></p>
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6.1 INTRODUCTION

The rationale for undertaking the work reported in the present Chapter is largely written into Chapter 5 and Appendix 5:

The number of samples analysed for Appendix 5 was all too small (as initially pointed out by Moorbath; see Preface).

The criteria of freshness needed to be presented in greater detail if they were to be of use to other researchers.

Moreover, the Sr isotopic composition of the water postulated to have interacted with kimberlite in alteration reactions was unknown.

The Sr isotopic compositions and where necessary K, Rb and Sr abundances of a further sixteen fresh and altered kimberlites were therefore determined. This allowed the inclusion of a greater diversity of kimberlite types, and in particular, micaceous kimberlites. The same criteria of freshness were applied as before, with the essential proviso that the writer should not have access to the Sr isotope measurements prior to making the petrographic assignments of samples as "fresh" or "altered". This proviso assured that the inescapably subjective petrographic judgements, discussed further below, would remain totally independent and unbiased by the Sr-isotope results.

The results and conclusions of Appendix 6 do not require repetition. Comment in this Chapter will concentrate on a

brief assessment of the significance of the conclusions made in Appendices 5 and 6, shortcomings of the work done, and in how far these have been resolved.

6.2 ESTABLISHMENT OF LOW SR-ISOTOPE RATIOS

That kimberlites with low (≈ 0.704) Sr isotope ratios do occur as first proposed by Berg and Allsopp (1972) and confirmed by Barret and Berg (1975) does not appear ever to have been seriously questioned; and they have since been repeatedly reported (eg. Smith, 1986).

6.3 DIFFICULTIES WITH PETROGRAPHIC CRITERIA

The petrographic criteria described in Barrett and Berg (1975), by which fresh kimberlites which may have low ratios were identified, have been criticised; particularly by Mitchell (1986) and with good reason, although with no alternative suggestions. Mitchell notes that Paul (1979) found fresh basaltic kimberlites to have high ratios and altered kimberlites low ratios; insufficient petrographic detail is available in Paul (1979) to assess possible reasons for these results. The freshness criteria remain subjective and will probably always remain so. The nub of this problem is not new; just as Carmichael et al (1974, p406) write:

".....; one man's "pigeonite" turns out to be another man's "augite";"

so one petrographer's uniform fresh serpentine is another's altered serpentine because of an almost imperceptible greenish hue. Indeed, the criteria have not always produced consistent results for the present writer: two non-micaceous samples (DiB 3 and DiB 6) were assessed as altered but yielded low ratios of 0.7043 and 0.7044 respectively. This was in contrast to the other four non-micaceous altered samples (KDB 17 (Appendix 5), BF 13, BF 21 and KDB 8 (Appendix 6)) which yielded ratios in

the range 0.7051 to 0.7083. These high ratios are ascribed to ground water interaction in Appendices 5 and 6. On the basis of the petrographic criteria, samples DiB 3 and DiB 6 would be expected also to have high ratios; two discrepant samples out of six lead to some doubt as to whether the petrographic criteria are sound or whether the groundwater interaction hypothesis is viable. Two alternative approaches which have been attempted by the writer to resolve this problem are reported in Chapters 7 and 8. It will be shown in Chapter 8 that in the case of DiB 3 the petrographic criteria failed. The sample was classified as altered on the basis of its high degree of serpentinisation, but the serpentinisation was in fact isochemical and led to no significant Sr isotopic exchange with ground water. In the case of sample DiB 6 the reason for the low Sr isotopic ratio remains unclear. The petrographic criteria do not cater particularly well for this sample because it lacks olivines and hence serpentinisation; being made of carbonate replacement material it was assumed that the original kimberlite groundmass might have been totally replaced. There is no scientific basis available at present upon which to investigate whether the carbonate in DiB 6 is a primary igneous (low Sr isotope) replacement of earlier silicate. For the purpose of the present thesis the discrepancy of DiB 6 therefore remains unresolved.

6.4 HIGH SR ISOTOPE RATIOS IN MICACEOUS KIMBERLITES

Smith (1983) writes:

"Some of the first whole-rock isotopic data for kimberlites (Berg and Allsopp, 1972; Barrett and Berg, 1975) indicated that fresh basaltic (Group I) and micaceous (Group II) varieties have initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of about 0.704 and 0.708 respectively, and the present work has verified this relationship."

This accreditation is perhaps a trifle generous. Barrett and Berg (1975) recorded that fresh micaceous kimberlites had high

Sr isotopic ratios of about 0.708, and noted that this aspect in particular warranted further study. They speculated that the high ratios might have resulted from the assimilation of radiogenic Sr from zones in the mantle locally characterised by an abundance of old mica and calcite. But it remained for Kramers (1977), Kramers et al (1981) and finally Smith (1983) to resolve, with additional Pb and Nd isotope determinations, the problem of the high Sr isotopic ratios of micaceous kimberlites. These are now generally believed to reflect a mantle source which was enriched in Rb at least 1000 my ago.

6.5 IMPACT OF APPENDICES 5 AND 6

The papers published on the basis of the work discussed in Chapters 5 and 6 have been quoted quite widely. It serves little purpose to discuss each citation separately. But it is gratifying to note as was done in the Preface, that the criteria of freshness set up by Berg and Allsopp (1972) were still found useful by Kirkley et al (1989). These authors (op cit p272) also find their stable isotope results to be consistent with the suggestion of Berg and Allsopp (1972), that hypabyssal kimberlites were more likely to have been serpentinitised by limited volume magmatic rather than larger volume meteoric waters.

Closer to the time of original publication, the report of the first low Sr isotope ratios of 0.704 for kimberlites as documented by Berg and Allsopp (1972), was highlighted in the general petrology textbook by Carmichael, Turner and Verhoogen (1974). Both positive and negative aspects of the work are discussed in this text. The positive aspect is the existence of low Sr isotope ratios. Thus Carmichael et al (1974 , p658) state in their chapter entitled : PETROLOGIC ASSESSMENT OF THE MANTLE-MAGMA SYSTEM: MAFIC MAGMAS AND MANTLE SOURCE ROCKS:

"Values of $^{87}\text{Sr}/^{86}\text{Sr}$ are variable (Berg and Allsopp, 1972): they prove to be low (0.7037 to 0.704) in fresh specimens, (sic) much higher in altered ones."

In more detailed discussion in their chapter on: CONTINENTAL MAGMAS FROM DEEP SOURCES, VOLCANIC SERIES OF EXTREME COMPOSITION: ULTRA POTASSIC SERIES, CARBONATITES, KIMBERLITES, Carmichael et al (1974, p525) note the low Sr isotope ratios reported by Berg and Allsopp (1972). Implicitly they also question the subjectivity inherent in the petrographic criteria of freshness and alteration, and hence the need to invoke ground water accession to explain the higher ratios. They write:

"The isotopic composition of strontium in kimberlites is variable. Powell (1966) gave initial whole-rock values of $^{87}\text{Sr}/^{86}\text{Sr}$ 0.705 to 0.721, and he concluded that at least some kimberlites contain strontium derived from the sialic crust. However, more recent work by Berg and Allsopp (1972) suggests that the higher ratios are restricted to altered specimens and that initial $^{87}\text{Sr}/^{86}\text{Sr}$ values for fresh kimberlites are in the range 0.7037 to 0.7046. An alternative explanation of high values, already offered to explain very high $^{87}\text{Sr}/^{86}\text{Sr}$ values in some ultra-potassic lavas, is early concentration of K (and with it Rb) in the source rock from which the kimberlite magma originated much later. **Further speculation is unwarranted until we can assess---through oxygen- and hydrogen-isotope analyses---the possible role of meteoric waters in serpentinisation of kimberlite.**" (Present writer's bold emphasis as this aspect is the subject of Chapter 7 of this thesis.).

It is fascinating to note the foresight shown in the text of Carmichael et al (1974). In effect they anticipated (in their statement on p525) both the discovery of fresh

(micaceous) kimberlites with high Sr isotopic ratios by Barrett and Berg (1975) and the presently accepted explanation of these high values as proposed by Smith (1983).

Carmichael et al (1974, p525) equally clearly saw that stable isotope measurements should, in principle, be able to elucidate the origin of the water of serpentinisation in kimberlites. This is the subject of Chapter 7.

CHAPTER 7

Stable isotope studies on fresh and altered kimberlites**7.1 INTRODUCTORY STATEMENT**

In Chapters 5 and 6, and texts such as Carmichael et al (1974, p 525) and Mitchell (1986, pp 314 - 315), the need to establish a more quantitative method than petrography for distinguishing fresh from altered kimberlites is clearly recognised. The most important agent of alteration is water. The present chapter records an attempt to "fingerprint" this water by means of stable isotope measurements, against the background set out below.

Berg and Allsopp (1972/Appendix 5) considered the following two possibilities for the source of water in fresh and altered kimberlites:

- a.) "Fresh" kimberlites were serpentinised autometasomatically, implying the influence of their own limited volume of **magmatic** water, and altered kimberlites were subsequently more intensely serpentinised by circulating **groundwater** (meteoric).
- b.) Alternatively, fresh and altered kimberlites may both have been serpentinised by meteoric waters, but to different degrees.

It was noted in Berg and Allsopp (1972), that Taylor and Forrester (1971) had successfully used stable isotope measurements to recognise ground water alteration of Tertiary volcanic rocks in Scotland. It seemed reasonable to attempt to conduct similar measurements on kimberlites, to distinguish between the alternatives for the origin of waters of serpentinisation outlined above. Ideally such measurements should be undertaken on separated co-existing minerals.

Separating minerals from the kimberlite groundmass is a daunting task, however, which has yet to be achieved; the intergrowths of minerals which would have to be separated are typically on the scale of fifteen and down to five microns, or less.⁷ The situation remains to date as summarised by Mitchell (1986, p250): "Despite the ubiquity of serpentine, few studies have been made of its compositional variations or of the polymorphs or polytypes present. This paucity of information is a consequence of the extremely small size of the serpentine crystals and their common intergrowth with other phases, rendering them intractable to routine X-ray or chemical investigation." Given these difficulties the present stable isotope study had of necessity to be conducted on bulk rocks. This reflects part of the challenge undertaken in much of this thesis, as discussed in the Introduction; that is, to establish the **limits** of what can be achieved with the analysis of **bulk-rock samples**.

In the case of the stable isotope measurements reported here the bulk rock approach failed to resolve unequivocally, any of the questions posed. The discussion in this Chapter will therefore go beyond the brief of interpreting the measurements made, and explore to what extent more meaningful results may be obtained in future by analysing pure serpentines should these become available.

7.2 THE ROLE OF WATER IN THE PETROGENESIS OF KIMBERLITE

To understand better both the potential and difficulties involved in using stable isotope measurements to elucidate the history of kimberlites, we need first to outline the role of water more comprehensively than merely as an agent of serpentinisation; viz:

⁷ A qualitative "feel" for the scale in question may be obtained by recalling that a rock powder which has passed through a "#400" ("four hundred mesh") sieve has the texture of face-powder when felt between the fingers, but carries particles of up to 37 microns.

- a.) The abundances and ratio of H_2O/CO_2 determine both the temperature and nature of melting reactions of carbonated peridotite which is widely thought to represent the source of kimberlite (eg Eggler, 1989, p491-492, and references therein). H_2O and CO_2 will similarly affect deeper sources of kimberlite such as proposed by Ringwood et al (1992), but the phase relations at these high pressures are as yet less well known.
- b.) Water under pressure dramatically lowers the melting-point of calcite as established by Wyllie and Tuttle, (1959, 1960.) Further pertinent experimental work is reviewed by Mitchell (1986, p325 ff, and references therein), who with reference to the system $CaO - MgO - H_2O - CO_2$ notes that, "The synthetic system suggests that calcite can crystallise alone down to very low temperatures ($650^\circ C$).". In more complex synthetic systems reviewed by Mitchell (1986) liquids crystallising calcite persist down to $605^\circ C$ at 1kb.⁸ Thus water may be an essential flux both in the formation of kimberlite in the mantle (a. above), and during late emplacement when magmatic carbonate is being crystallised;
- c.) The separation of volatiles including juvenile water upon decrease of pressure could contribute to the violent emplacement of many kimberlites (Clement and Reid (1989, pp641-642);
- d.) alternatively or additionally, interaction between kimberlite magma and ground water is thought to result in phreatomagmatic activity that is part of the kimberlite pipe-forming process (Lorenz 1975, 1979, 1985); and from this stage onwards,
- (e) water becomes increasingly important in alteration

⁸ On this basis the assumption will be made for the purpose of the present study that primary calcite in the kimberlite groundmass crystallises in equilibrium with water at temperatures down to about $600^\circ C$, and may re-equilibrate with water at lower temperatures. (See Section 7.6.4.4.)

reactions which may modify bulk chemistry and isotope ratios of kimberlites (Fairbairn and Robertson, 1966; Berg and Allsopp, 1972; Kresten, 1973; Barrett and Berg, 1975; Berg, 1989; and Mitchell, 1986, p319ff for review).

This greatly varied role of water must be borne in mind carefully, both when assessing earlier stable isotope work in Section 7.3, which follows, and to anticipate further pitfalls awaiting the stable isotope researcher; the latter aspect will be elaborated upon in Section 7.6, after aspects of sampling and analytical methods have been considered in Sections 7.4 and 7.5.

7.3 PREVIOUS PERTINENT STABLE ISOTOPE STUDIES

The apparent involvement of water throughout the history of kimberlite is not yet matched by a commensurate body of stable isotope measurements, particularly not hydrogen isotope determinations designed to monitor the water's source and movement.

The contribution which to date relates most closely to the present work is a preliminary study by Sheppard and Dawson (1975). In addition to measurements of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ on various megacrysts and inclusions from 13 samples of kimberlite, these authors made δD determinations on five of their bulk kimberlites, two phlogopite xenocrysts and one serpentine xenocryst. The conclusions of Sheppard and Dawson (1975) most pertinent to the present investigation are:

- (a) that there is a large input of meteoric water in the serpentinisation of the kimberlites they studied.
- (b) xenocryst micas could have equilibrated with magmatic water at high temperatures.

(c) groundmass mica could reflect equilibration with magmatic water below 500 or 600 °C; alternatively the isotopic relations of groundmass micas could reflect degassing of kimberlite and interaction with meteoric and/or metamorphic waters.

In contrast to the work of Sheppard and Dawson (1975), the bulk of published light stable isotope data for kimberlites are restricted to the carbonate phase and hence do not include hydrogen; (eg Deines and Gold, 1973; Kobelski et al, 1979; and Kirkley et al 1989). In the absence of hydrogen isotope measurements these studies are not specifically directed to studying the **source** of water involved in the history of kimberlites, inasmuch as "juvenile" magmatic water is isotopically defined by a combined δD and $\delta^{18}O$ "box" and the "meteoric water line" by a locus of δD and $\delta^{18}O$ points (see for example Sheppard and Dawson, 1975, Fig 5, adapted here as Fig 7.1). The lack of hydrogen isotope data notwithstanding, stable isotope studies on the carbonate phase of kimberlite **can** contribute to understanding aspects of the influence of water during late crystallisation, by application of the well known temperature-dependant isotopic fractionation factors of oxygen between carbonate and water. Thus Kirkley et al (1989 pp 272, 273) consider plausible, models in which magmatic water is responsible for the serpentinisation of fresh kimberlite from the Wesselton Mine, Kimberley. This is in contrast to the influence of meteoric water found to be dominant in the samples studied by Sheppard and Dawson (1975). These aspects are further explored later. For reasons outlined below, it is necessary first to compare in more detail, the samples investigated in previous studies with the samples studied in the present work.

7.4 RELATION OF SAMPLING TO STABLE ISOTOPE MEASUREMENTS

7.4.1 Statement of problem

In Chapters 5 and 6 it is postulated that magmatic water may be responsible for the serpentinisation of fresh kimberlites, and meteoric (ground) water may have serpentinised altered kimberlites (as reviewed here in Section 7.1). **Both** possibilities have been found plausible in the separate stable isotope studies reviewed in 7.3 above. A possible explanation for this is that the study which found evidence for meteoric water was based on "altered" samples and the one which finds plausible evidence for magmatic water is based on "fresh" samples. It is therefore necessary to re-examine to what extent the perceived fresh or altered character of the samples studied here can be related to the condition of samples for which data has been published in the previous work cited above.

7.4.2 Samples studied here

Eleven of the kimberlites studied here are "fresh" in the petrographic sense described in Chapters 5 and 6. Thirteen are altered (but not weathered on the Earth's surface), and two more are yellow-ground, that is, highly altered surface-weathered kimberlite. The main types of fresh and altered kimberlite analysed here have been briefly described, and some illustrated, by Berg and Allsopp (1972), Barrett and Berg (1975) and Berg (1989): (see Appendices 5, 6 and 8 respectively of this thesis). The reader is referred to the above sources for comparison with the samples discussed below.

Nine samples of present-day meteoric water were collected in the Kimberley region and analysed for δD and $\delta^{18}O$.

7.4.3 Samples studied by previous workers

7.4.3.1 Sheppard and Dawson (1975)

There are important differences between some of the kimberlites studied here compared to those examined by Sheppard and Dawson (1975). The latter authors give brief descriptions but do not distinguish between fresh and altered rocks. On the basis of their descriptions it would appear, however, that Sheppard and Dawson (1975) worked largely on what are here referred to as "altered" kimberlites (or separate constituents thereof). For example: Sample BD 1821 "Serpentine magacrysts in brown phlogopite-rich serpentine-dolomite matrix" would almost certainly be classified as altered on the basis of total serpentinisation of olivines. In contrast, Sample BD 1075 ("...aphanitic part of black massive plug...olivines fresh with very small rims of serpentine set in serpentine-calcite-magnetite matrix...") most probably represents a fresh kimberlite; but categorisation of the Sheppard and Dawson (1975) samples into fresh and altered groups, which constitutes the nub of the interest in the present work, cannot safely be made on the basis of the available sample descriptions, and indeed was not the intention of Sheppard and Dawson (1975) as noted above. The serpentine xenocryst S336 would also be classified as altered on the criteria of Berg and Allsopp (1972) and Barrett and Berg (1975) if it were shown to be a completely serpentinised olivine; Berg (1989)/Chapter 8 would add the absence of brucite as an additional criterion of alteration for S336 and BD 1821. These data are simply not available. Consequently, the Sheppard and Dawson (1975) data and interpretation can be used here for general comparative purposes, but not for comparison between fresh and altered kimberlites.

7.4.3.2 Kirkley, Smith and Gurney (1989)

The samples analysed by the above authors were selected as fresh on the basis of the petrographic diagnostics set out by Barrett and Berg (1985). As such, the data obtained by Kirkley et al (1989) should, in principle, be comparable with the data of the present work, albeit with the caveat made in Chapter 6 with reference to the statement of Carmichael et al (1974, p406).

It is not practical within the brief of this thesis for the writer to examine the thin sections of the samples analysed by Kirkley et al (1989) to make an independent assessment of their freshness according to his own (inevitably also subjective) petrographic perceptions. This will not significantly affect the interpretation of results reported here, as will become clear later.

7.4.3.3 Ukhanov and Devirts, (1983)

Insufficient detail is available to the writer to make any petrographic comparisons with the specimens analysed by Ukhanov and Devirts (1983); the δD results reported by these authors are, however, referred to later.

7.4.4 Summary of the sampling problem

Most of the samples of Sheppard and Dawson (1975) are probably altered in the sense of this thesis, while those of Kirkley et al (1989) are probably fresh. But the very subjectiveness of petrographic selection, as highlighted by Mitchell (1986, p313 - 315) with reference to Berg and Allsopp (1972) and Barrett and Berg (1975), militate against rigid comparison of results on the samples of different studies.

7.5 ANALYTICAL METHODS AND RESULTS

7.5.1 Hydrogen isotope methods

Hydrogen isotope measurements were made using standard methods in the U.S. Geological Survey laboratories at Menlo Park, California. Results are reported in Table 1.

In the extraction of water for hydrogen isotope analysis samples were held initially at about 150°C, the temperature being adjusted as required to drive off adsorbed water not held in serpentine; this was monitored on the vacuum gauge. The next heating step (to about 900°C) was made to yield the water from serpentine. In the δD determinations reported in Table 1 for fresh kimberlites, any water in brucite, which had not yet been identified when the hydrogen isotope analyses were done, will have been released together with the water of serpentinisation. For brucite-containing (fresh) kimberlites, δD values therefore refer to water carried in both serpentine and brucite.

The hydrogen isotope fractionation between serpentine and water was determined experimentally by Sakai and Tsutsumi (1978); the system for brucite and water was studied experimentally by Satake and Matsuo (1984). The latter authors note that fractionation between brucite and serpentine in natural rocks does not correspond with the experimental data referred to above, which would predict brucite of lighter δD than serpentine (Fig 7.2). There may be crystallo-chemical reasons for this discrepancy; Satake and Matsuo (1984) note that the occurrence of brucite of heavier δD (-66 per mil) than co-existing serpentine (-89 per mil), as reported by Wenner and Taylor (1974), is best explained by combining the experimentally determined D/H fractionation for brucite and water with the empirical serpentine - water D/H fractionation curve of Wenner and Taylor (1973). This approach is followed here as the most likely to pertain in kimberlites, and the

latter curve has been transferred onto fig 3 of Satake and Matsuo (1984) modified here as Fig 7.2. Examination of Fig 7.2 reveals that at approximately the temperature of serpentinisation of 340°C, previously estimated for the serpentinisation of fresh kimberlites by Berg (1989; p292/Appendix 8), the brucite and serpentine curves cross. Consequently, until measurements possibly prove otherwise, there are no grounds to assume that the serpentine and brucite in the fresh kimberlites carry water of markedly different hydrogen isotopic composition.

The fresh kimberlites carry no talc (which is incompatible with brucite) but in some cases minor chlorite may be present and also contribute water to the bulk δD analysis. The volumes are probably insufficient to affect the conclusions of the present chapter, as will be discussed later.

Altered (brucite-free) kimberlites may contain both chlorite and talc which will contribute water in addition to that from serpentine to the bulk δD data. The most heavily altered specimens also contain quite abundant clay.

Methods for δD and $\delta^{18}O$ determinations in the water samples followed standard procedures of the USGS Laboratories in Menlo Park, Calif.

7.5.1.1 Hydrogen isotope results

Hydrogen isotope results for **bulk kimberlites** are reported in Table 7.1; they are summarised and compared with published data on Figs 7.1 and 7.3.

7.5.1.2 Results for water samples

Hydrogen and oxygen isotope results for water samples are reported on Table 2 and summarised on Fig 7.5.

7.5.2 Methods for Carbonates

Oxygen and carbon isotope analyses for carbonates were made on CO₂ extracted by reaction at 25°C with phosphoric acid; the well established analytical techniques and appropriate corrections of Dr R N Clayton's laboratory at the Enrico Fermi Institute, University of Chicago, were applied.

7.5.2.1 Carbonate results

Results for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in the carbonate phase are listed in Table 7.1; the $\delta^{18}\text{O}$ data are summarised on Fig 7.4.

7.6 DISCUSSION

As the $\delta^{13}\text{C}$ data do not contribute to this Chapter's objectives of characterising fresh and altered kimberlites, they will be "disposed of" at this point, to the benefit of continuity in later discussion.

7.6.1 $\delta^{13}\text{C}$ in carbonates

There is no distinction in $\delta^{13}\text{C}$ between fresh and altered kimberlites (See Table 1).

The $\delta^{13}\text{C}$ results fall within the general ranges established by previous workers, as outlined below.

Kirkley et al (1989) report $\delta^{13}\text{C}$ values for carbonates from Wesselton with a mean value of -6.4 and standard deviation of 0.8 per mil. They find that this is within a standard deviation of the mean $\delta^{13}\text{C}$ of -5.9 with standard deviation 2.4 per mil reported by Kobelski et al (1979) for 142 samples of southern African kimberlites. From this they conclude that their data for Wesselton reflects $\delta^{13}\text{C}$ values typical of most kimberlites. The results of the present study extend less than

0.5 per mil above and below the range of $\delta^{13}\text{C}$ of the Kirkely et al (1989) Wesselton dyke kimberlite; they can therefore be taken as fairly typical.

The results recorded in Table 1 suggest $\delta^{13}\text{C}$ groupings of kimberlite bodies or types which to some extent coincide with localities. For example, the De Beers dyke kimberlites fall into the range $\delta^{13}\text{C} = -5.6$ to -6.2 and this range is extended to -4.7 to -7.0 if the altered De Beers kimberlites are included. The Du Toitspan kimberlites with $\delta^{13}\text{C} = -7.1$ to -8.4 fall just outside the De Beers range. KN 3 (fresh), KN 5 (altered) and KN 6 (altered) also fall in a restricted range of $\delta^{13}\text{C} = -5.7$ to -6.3 . XSF 2 and XSF 7, which are both from the same dyke kimberlite but with $\delta^{13}\text{C} = -4.7$ and -8.3 , do not conform with the tendency for kimberlites of similar character to have similar $\delta^{13}\text{C}$; re-analysis is indicated before drawing further conclusions from this pair of results. On balance the data indicate that specific bodies of kimberlite are frequently characterised by limited ranges of $\delta^{13}\text{C}$. This is consistent with the results of Kobelski et al (1979) and Kirkley et al (1989). These $\delta^{13}\text{C}$ distinctions seem to survive most alteration processes, presumably because relative to the carbonate, the main alteration agent, H_2O , carries relatively little C (in the form of dissolved atmospheric CO_2), and calcite does not easily exchange carbon with a fluid.

The extreme alteration due to weathering undergone by yellow-ground over-rides the foregoing suggestion. For the admittedly small number of samples which have been analysed, the yellow-ground samples as a type appear to have characteristically heavy carbon: $\delta^{13}\text{C} = -4.6$ and -4.8 for KRV 17 and KRV 18 respectively, within about 1 per mil of the value of $\delta^{13}\text{C} = -5.9$ reported by Sheppard and Dawson (1975) for their yellow ground sample S437. The values for KRV 17 and KRV 18, both from Roberts Victor, bear no obvious relation to the only other Roberts Victor sample analysed here (KRV 14; $\delta^{13}\text{C} = -7.3$).

Because yellow-ground is a heavily leached residue consisting predominately of clay and calcite, it is possible that its $\delta^{13}\text{C}$ reflects equilibration with atmospheric CO_2 dissolved in meteoric waters. That is to say, $\delta^{13}\text{C}$ of yellow-ground may be unrelated to the isotopic composition of its fresh precursor; however, insufficient data are here available to **prove** this speculation. It has, of course, little bearing on the main thrust of this Chapter.

7.6.2 Hydrogen isotopes

7.6.2.1 Comparison with previously published data

The range of $\delta\text{D} = -78$ to -110 found here for 23 fresh and altered (but unweathered) kimberlites (Table 1), slightly expands the range of $\delta\text{D} = -89$ to -102 observed by Sheppard and Dawson (1975, table 2) for four bulk unweathered kimberlites and a serpentine megacryst (See Fig 7.3) The two yellow ground (heavily weathered) samples KRV 17 and KRV 18 from Roberts Victor, with $\delta\text{D} = -74$ and -82 are comparable with the value of $\delta\text{D} = -72$ reported by Sheppard and Dawson (1975) for a sample of yellow ground, S437, from Benfontein.

Since the samples studied by Sheppard and Dawson (1975) cannot be assigned to the fresh and altered categories of the samples studied here (Section 7.4.3.1), the above comparison serves only to show that the samples studied here are not drastically different, in terms of δD , from the five South African samples analysed previously.

δD values from -137 to -147 which have been reported for Yakutian kimberlites (Ukhanov and Devirts, 1983) are significantly lighter than any observed in the present study; (See 7.6.2.2 and 7.6.4 for further discussion).

7.6.2.2 Do bulk δD values distinguish fresh from altered kimberlites?

δD values for the fresh kimberlites fall into two distinct groups (Table 1; Fig 7.3): First, -81 to -86 for De Beers (hypabyssal, "basaltic"); and second, -96 to -101 for Du Toitspan (massive, magmatic, "basaltic"); the two single fresh micaceous kimberlites from Newlands and Southern Fissures (-104) barely expand the Du Toitspan range. All these values in turn fall within the range of $\delta D = -74$ to -110 found for altered kimberlites (Table 1; Fig. 7.3). Thus, the fresh De Beers dyke range of $\delta D = -80$ to -86 is shared by the slightly altered kimberlites KBen 1 and KBen 3 (-81), **but also** the grossly altered yellow-ground KRV 18 (-82), while KDB 8 (altered, $\delta D = -78$) is barely heavier. Similarly, for example, the fresh Du Toitspan range of $\delta D = -96$ to -101 is shared or close to the altered KBult 36 (-96) and KDB 18 (-94, very heavily altered). Given this panoply of overlapping results for fresh, totally weathered, and altered but unweathered kimberlites, it is clear that bulk δD measurements will never discriminate fresh from altered kimberlites from the type area of Kimberley.

The failure of the bulk δD measurements to act as a fresh/altered discriminant may simply be a consequence of the relative closeness of δD of magmatic and local meteoric waters of serpentinisation. Present-day Kimberley ground water was found to have $\delta D = -9$ to -36 (Table 7.2), which abuts the magmatic water box (Fig 7.1). There is no compelling evidence to suggest that meteoric water at the time of intrusion of the kimberlites (125 ma and 90 ma) was grossly different. This is in contrast to the situation in Siberia; here $\delta D = -137$ to -147 in serpentine (Ukhanov and Devirts, 1983) indicates equilibration with water in the approximate range $\delta D = -100$ to -120 at serpentinisation temperatures of 150⁰C to 350⁰C respectively (See Fig 7.2). This is substantially outside the magmatic water box and clearly reflects the isotopically light meteoric water of high latitudes. In such environments bulk

δD measurements may be sufficient to distinguish magmatic from meteoric waters of serpentinisation.

In summary, the δD measurements reported here for bulk kimberlites from the Kimberley district of South Africa fail to achieve the prime objective of this chapter viz.: to establish a means of distinguishing fresh from altered kimberlites by recognising different mechanisms or waters of serpentinisation between the two groups. It does not follow that different styles or waters of serpentinisation were not involved; the complex history of kimberlites may merely have disguised them for reasons considered later. As a background it is necessary first to consider what constraints more detailed interpretation of the δD data can put on the history of individual kimberlites.

7.6.2.3 General interpretation of δD in kimberlites

As a first step in unravelling the equivocal overlap between the hydrogen isotopic ratios of fresh and altered bulk kimberlites (Table 7.1; Fig 7.3), we need to define two extreme forms of serpentinisation with juvenile magmatic water: The one "end-member" is when all the water present in a magma is uniformly used up to form serpentine, so that the bulk serpentine has the same δD as the water; this will hereafter be referred to as closed system auto-metasomatism (after Berg and Allsopp, 1972). At the other end of the spectrum we have serpentine equilibrated with an infinite volume of water; in this case the serpentine will have δD prescribed by the temperature-dependant partitioning between serpentine and water (Fig 7.2). Between these extremes we have a range of possibilities where serpentine is equilibrated with (heavier) water of limited volume which ultimately escapes from the system.

Considered in isolation, the result of $\delta D = -81$ for the fresh brucite-containing KDB 13 might just be consistent with

this rock having been auto-metasomatically serpentinised by all the juvenile water it carried. This water would be at the extreme light limit of the extended "magmatic water box" illustrated by Sheppard and Dawson (1975, fig 5, here modified as Fig 7.1). The still lighter values of $\delta D = -83$ and -86 for the closely related kimberlites KDB 12 and KDB 10 respectively, lead to some doubt whether the closed system juvenile magmatic-water serpentinisation model is viable. However, limited open-system serpentinisation by juvenile water could theoretically yield the lighter serpentines in KDB 10 and KDB 12 compared to KDB 13, if migration of (heavier) water through a partially consolidated kimberlite magma is invoked as follows:

The water in equilibrium with serpentine is always heavier than the serpentine itself according to Wenner and Taylor (1974, fig 7), (see Fig 7.2). It is plausible, therefore, that the De Beers dyke kimberlite KDB 10 was serpentinised by juvenile water originally of about $\delta D = -80$ (by analogy with KDB 13 on the supposition that this sample reflects closed system serpentinisation). If this water equilibrated with the serpentine in KDB 10 ($\delta D = -86$) and part of it escaped instead of being incorporated in serpentine, the heavier water (as required by mass balance and the equilibration imposed by the partitioning illustrated on Fig 7.2) would leave behind a lighter serpentine. This represents an intermediate model between the two "end member" extremes outlined in the opening paragraph to the present Section.

Being distinctly lighter than the light limit of the magmatic water box ($\delta D = -80$, Fig 7.1), the values of $\delta D = -96$ to -101 for the water released by the fresh Du Toitspan (KDT) kimberlites preclude any possibility of the fresh Du Toitspan kimberlites having been autometasomatised by magmatic water in a closed system. However, given a large volume of magmatic water equilibrated with serpentine about 25 δD units lighter than the water at some 340°C (see Fig 7.2), the KDT kimberlites

could, like KDB 10 and KDB 12, have been serpentinised by magmatic water, provided that a sufficient (and for the KDT rocks larger) volume of it escaped from the system as noted above. Yet Sheppard and Dawson (1975) have shown that serpentines such as S 336 ($\delta D = -89$, within 7 δD units of the "heaviest" KDT kimberlites), were serpentinised by **meteoric water**. Following the reasoning of Sheppard and Dawson (1975), meteoric water need merely have been some 10 to 15 δD units lighter than present-day meteoric water in Kimberley (Table 2), to have serpentinised the Du Toitspan samples. To illustrate this an approximate average δD for Du Toitspan is labelled on Fig 7.1 as "KDT 0.5"; this denotes a hypothetical $\delta^{18}O = 0.5$ in KDT serpentines.

The critical measurement which determines that S336 (and the hypothetical "KDT 0.5") were serpentinised by meteoric and not magmatic water, is $\delta^{18}O$ of the serpentine. Thus a result like "KDT 7.0" on a separated serpentine (Fig 7.1) would suggest serpentinisation by magmatic water, in contrast to "KDT 0.5" and S336. In practice the situation is more complex. To clarify this potential complexity it is profitable now to digress to an overview of $\delta^{18}O$ in the carbonate phase, because this may have an important influence on the oxygen isotopic composition of serpentinising waters in some kimberlites.

7.6.3 $\delta^{18}O$ in the carbonate phase

7.6.3.1 Does $\delta^{18}O$ of the carbonate phase distinguish fresh from altered kimberlites?

$\delta^{18}O$ of the carbonate phase is the best, though not a practical, discriminant between the fresh and altered kimberlites studied here (Fig 7.4). This is probably in part because extreme alteration involves extensive low temperature interaction with large volumes of water, a process which favours large water-carbonate fractionation factors (see O'Neil et al 1969, fig 1). Thus the yellow ground samples KRV 17 and KRV 18 are the most extensively altered kimberlites of all the

samples studied here, and at $\delta^{18}\text{O} = 21.7$ have the heaviest $\delta^{18}\text{O}$ value recorded in the carbonate phase. This matches the value of $\delta^{18}\text{O} = 26.5$ for the single sample of yellow ground from Benfontein reported by Sheppard and Dawson (1975).

Samples KDB 17 and KDB 18 are extremely permeable to water; this was observed when they were collected in the De Beers Mine. They are very heavily altered (no unserpentinised olivine and extensive development of clays) and have the next heaviest oxygen in the carbonate phase, at $\delta^{18}\text{O} = 17.7$ and 18.5 .

There is close overlap of fresh and altered kimberlites in the range $\delta^{18}\text{O} = 12 - 14$, while in the range $\delta^{18}\text{O} = 6$ to 12 , there are 5 fresh kimberlites and only one, (KDB 8) classified as altered. The result for KDB 8 of course cautions against attempting to set up a $\delta^{18}\text{O}$ (carbonate) boundary between fresh and altered kimberlites; the overlap between $\delta^{18}\text{O} = 12$ and 14 also indicates that $\delta^{18}\text{O}$ in carbonate will not supply a viable criterion with which to tell fresh from altered kimberlites.

7.6.3.2 General interpretation of $\delta^{18}\text{O}$ in carbonates

It was suggested above that **extreme** alteration involved large quantities of relatively cold water and was reflected by $\delta^{18}\text{O}$ of the carbonate in the general range of 17 to 25 per mil. An explanation is still required for the variation in oxygen isotopic composition of carbonates in the range $\delta^{18}\text{O} = 7$ to 14 . Sheppard and Dawson (1975) suggested that meteoric/hydrothermal waters were responsible. Kirkley et al (1989) and the present writer concur that this is plausible in the rocks studied by Sheppard and Dawson (1975).

Kirkley et al (1989, p272) point out, however, that in the case of their Wesselton kimberlites, there is no petrographic or geochemical evidence for extensive interaction with meteoric water. They point further to the fact that the Wesselton dyke kimberlite studied was originally intruded 2300 metres below

the surface, into granitic gneisses and schists thought not to have been as conducive to meteoric water penetration as the sediments and metasediments constituting the country rock at shallower levels. In the face of this negative evidence for meteoric/hydrothermal water accession, Kirkley et al (1989) investigated two models which invoke magmatic rather than meteoric water to account for the range of $\delta^{18}\text{O} = 7$ to 15 in Wesselton carbonates.

The first model is based on water/carbonate oxygen isotopic fractionation factors. By application of equations given by Sheppard et al (1969) and Taylor (1978), Kirkley et al (1989, p272) conclude that interaction with **magmatic** water could account for the general range of $\delta^{18}\text{O}$ in Wesselton, for example with the following parameters:

Magmatic water	$\delta^{18}\text{O} = 8$ per mil
Initial carbonate component	$\delta^{18}\text{O} = 7$ per mil
Final carbonate	$\delta^{18}\text{O} = 12$ per mil
Final water	$\delta^{18}\text{O} = -1$ per mil

at a ratio of 30 wt% of oxygen in the water and 70 wt% in the carbonate.

A second model is considered on the basis of partitioning of oxygen isotopes in mass balance to account for the observed and reported $\delta^{18}\text{O}$ values for all minerals and whole rock values. Kirkley et al (1998) consider that both models may contribute to the observed range of data.

The results and modelling of Kirkley et al (1989) lend credence to the suggestion of Berg and Allsopp (1972) that "fresh" kimberlites were serpentinised by magmatic water. In point of fact this represents little progress in the terms of reference of the present chapter, because the choice of meteoric or magmatic water model for a particular kimberlite still depends on initial petrographic assesment!

The data for carbonates can now be integrated with the continuing discussion of the δD vs $\delta^{18}\text{O}$ relation, which is explored in Section 7.6.4 below.

7.6.4 Combined interpretation of δD and $\delta^{18}O$

7.6.4.1 Basic interpretation

On the face of Fig 7.1, as discussed at the end of Section 7.6.2.3, it would seem possible to distinguish between meteoric and magmatic waters of serpentinisation if it were possible to separate the serpentines from the fresh Du Toitspan and De Beers kimberlites and determine both δD and $\delta^{18}O$ on them. The difficulties inherent in separating minerals from kimberlites (Section 7.1) militate against this solution, although special separation methods may be developed and laser techniques referred to later may circumvent part of this problem.

Sheppard and Dawson (1975, Table 2; Figs 1 and 5) circumvented the difficulty of mineral separation in two ways so as to obtain data for the δD vs $\delta^{18}O$ correlation: On the one hand they analysed a monomineralic serpentine xenocryst (S336) for both δD and $\delta^{18}O$. This is an innovative way of getting preliminary data for at least some serpentines from kimberlite, but is inapplicable to the fresh kimberlites of the present study because they contain no such large serpentine xenocrysts. On the other hand, in the case of **bulk** kimberlites, Sheppard and Dawson (1975) carried out analysis for δD as was done here on bulk powders, and then made the closest possible approximation to obtain a matching $\delta^{18}O$. This was done by determining $\delta^{18}O$ on the residue of whole rock minus carbonate ("WR-C") which remained after the carbonate had been reacted with phosphoric acid to yield CO_2 for the determination of $\delta^{13}C$ and $\delta^{18}O$ in the carbonate phase. The resulting data are plotted on the $\delta^{18}O$ vs δD diagram by Sheppard and Dawson (1975, fig 1; See Fig 7.1). The latter approach is also inapplicable to fresh kimberlites of the present work. This is because the contribution of oxygen extracted from the "WR-C" **non-hydrous** components (olivine, monicellite, apatite and opaques) would dominate volumetrically over the oxygen of the serpentines (which are believed to have yielded the dominant δD value). In

other words, to plot bulk δD against WR-C $\delta^{18}O$ in the case of fresh kimberlites, would relate hydrogen isotopes from the hydrous minerals (dominantly serpentine) against a combination of oxygen from serpentine, brucite and unaltered **olivine** as well as unhydrated groundmass minerals such as monticellite and opaques. In most fresh kimberlites, olivine, which is not equilibrated with the hydrous minerals, would be dominant, so that a δD vs $\delta^{18}O$ plot would be a meaningless relation of unrelated isotopes. Sheppard and Dawson (1975) have interpreted single minerals in terms of their fig 1 relation of δD vs $\delta^{18}O$, but also note: "...All other samples are polymineralic and thus their ^{18}O values should not be interpreted too specifically at this stage...".

Superficially, then, it would appear that to obtain a more meaningful interpretation **requires** that both δD and $\delta^{18}O$ be measured **for serpentines** and related to one another as was done by Sheppard and Dawson (1975, fig 1). Thus, values of about $\delta^{18}O = 0.5$ to 2 for serpentine from fresh kimberlite ($\delta D = -80$ to -100) would indicate equilibration with water of meteoric ancestry (See Fig 7.1), as in the case of sample S336 of Sheppard and Dawson (1975). In contrast, $\delta^{18}O = 5$ to 8 would indicate equilibration with juvenile magmatic water, the volumes implied depending in part on temperatures of serpentinisation assumed; (see Fig 7.1, "KDT 7.0"). In practice this approach may turn out to be over-simplified, as now becomes clear with reference to and extension of the earlier discussion for carbonates (Section 7.6.3).

7.6.4.2 Possible modification of $\delta^{18}O$ of magmatic water before serpentinisation

We must now consider what the effect of variations in $\delta^{18}O$ of carbonates is on co-existing magmatic water which subsequently serpentinises olivines? The answer is in part already given, with reference to the modelling undertaken by Kirkley et al (1989) discussed in the previous section:

magmatic might have $\delta^{18}\text{O} = -1$. The broader picture follows below.

Serpentinisation follows the crystallisation of calcite in kimberlites:

Kirkley et al (1989, p273) consider the paragenetic crystallisation sequence in Wesselton kimberlite which is analogous to the fresh kimberlites studied here, to be olivine/phlogopite, opaques, calcite, serpentine; (Mitchell, 1986, p346) similarly notes, "Petrographic studies have shown that the sequence spinel (magnetite), calcite, calcite plus serpentine, serpentine is observed during the final stages of groundmass crystallisation". It follows from the calculations of Kirkley et al (1989), that even if serpentinisation is by juvenile magmatic water in a closed or predominantly closed system, the oxygen isotopic composition of this water is likely to have become lighter in response to the preferential partitioning of ^{18}O into calcite, before serpentinisation commences. Consequently, instead of the "normal fingerprint" of magmatic water, kimberlitic serpentine carrying magmatic water is likely to carry a "modified fingerprint" of magmatic water, with $\delta^{18}\text{O}$ that could match meteoric water.

Is there any more **direct** evidence for serpentinisation by magmatic water in the light of stable isotope data currently at hand? The answer to this question lies at heavy rather than the light end of the spectrum of $\delta^{18}\text{O}$ values obtained for the carbonate phase of kimberlites.

7.6.4.4 An alternative approach to estimating the original $\delta^{18}\text{O}$ of serpentinising waters in fresh kimberlites

Let us assume in the light of the foregoing discussion, that $\delta^{18}\text{O}$ of juvenile magmatic serpentinising waters will be affected by re-equilibration with calcite before serpentinisation commences. To ascertain the original $\delta^{18}\text{O}$ of the water before its inter-action with calcite, it is logical

to seek out a mineral earlier in the paragenetic crystallisation sequence; that is to say, a mineral which was equilibrated with the water before the precipitation and/or re-equilibration of calcite so drastically changed the water's $\delta^{18}\text{O}$. Given a knowledge of the partitioning of oxygen isotopes between the "earlier" mineral and water, the oxygen isotopic composition of the water before the "calcite effect" might thus be deduced. There is little choice of such minerals. Ideally a hydrous mineral is needed, both to give unequivocal evidence for the presence of water, and to indicate its isotopic composition.

The only hydrous mineral that might fullfill these requirements is phlogopite; it occurs in two generations. The first generation, "Type A" of Sheppard and Dawson (1975), is xenocrystic and irrelevant to the problem. The second generation, "Type B" groundmass mica, does indeed have δD and $\delta^{18}\text{O}$ values consistent with magmatic water if crystallisation occurred at about 500 to 600°C (Sheppard and Dawson (1975); but groundmass micas are present in significant quantities only in phlogopite kimberlites, and likely to be at least as difficult to separate as serpentine in many of these.

Opaques precede calcite, but they are also difficult to separate and varied in composition; furthermore, they are susceptible to late-stage re-equilibration and overgrowth (Haggerty, 1973, 1975). And being non-hydrous, the presence of water in equilibrium with opaques is simply an assumption. Olivine, in turn, is simply too far removed in the crystallisation sequence.

The remaining choice boils down to discovering the earliest calcites to crystallise, or those equilibrated with water at the highest temperatures. Being non-hydrous, the equilibration of calcite with water is also something of an assumption, but it has a better basis than in the case of opaques: the range in $\delta^{18}\text{O}$ of the calcite in kimberlite is attributed to exchange with

water by Sheppard and Dawson (1975), Kirkley et al (1989) and the present writer; the question is: what water?

In Section 7.2 evidence was reviewed from which it was concluded that calcite could be considered to have crystallised in the kimberlite groundmass at about 600°C. The fractionation factor for oxygen between calcite and water at this temperature is close to zero (O'Neil et al, 1969).

Thus the lowest values of $\delta^{18}\text{O}$ for carbonates in fresh kimberlites, should be about the same as the water in the kimberlite magma at the **onset** of calcite crystallisation. The lowest values recorded are:

Wesselton kimberlite,
Kobelski et al (1979, Fig 4) $\delta^{18}\text{O} = 6.6$ (approx)

Wesselton hyperbyssal kimberlite,
Kirkley et al (1989, Table 15.1) $\delta^{18}\text{O} = 7.9$

De Beers reputed dyke kimberlite
This work, Table 7.1, KDB 12) $\delta^{18}\text{O} = 6.7$

These values all fall in the magmatic water range. They lend yet further credence to the suggestion that magmatic water was present at the onset of calcite crystallisation; that with falling temperature partitioning of ^{18}O into calcite reduced $\delta^{18}\text{O}$ of the water; and that relatively minor serpentinisation (typical of fresh kimberlites) then involved water with a δD value at the light end of the "magmatic water box", but a modified $\delta^{18}\text{O}$ mimicing that of meteoric water.

The evidence supplied by the minimum $\delta^{18}\text{O}$ in carbonate is **independant** of petrography. Two of the three lowest values listed above turn out to be from kimberlites assessed petrographically as fresh (Kirkley et al, 1989; this work (KDB 12)). Data are not available to categorise as fresh or altered, the third light carbonate sample, analysed by Kobelski et al (1979).

On the negative side, it should be noted that these are three samples out of approximately 200 analysed, so that their statistical significance may be questioned. It should further be noted that calcite being non-hydrous, the supposition that water of later serpentinisation was earlier equilibrated with it is somewhat circumstantial. Nevertheless, the evidence is consistent with the presence of magmatic water in certain fresh kimberlites. How can we further test this hypothesis?

7.6.4.4 Possible future approaches

Two directions of further research follow from the preceding discussion. First, magmatic water would be far more easily identified if it did not share a range of δD adjacent to that of the local meteoric water, as appears to be the case in the Kimberley region of South Africa. Ukhanov and Devirts (1983), referred to earlier, report values of $\delta D = -137$ to -147 for serpentines from Siberian kimberlites. Any serpentines containing magmatic water should readily be recognised in this environment. Similarly, the recently discovered kimberlites in the high latitudes of Canada offer the prospect of easier discrimination between magmatic and meteoric water of serpentinisation on the basis of δD alone, once mining or deep drilling reveals hyperbyssal kimberlites emplaced at levels reasonably safe from ground water accession. Second, in the case of the kimberlites from South Africa studied here, it is essential to either separate serpentines or obtain both δD and $\delta^{18}O$ analyses of them by ion probe or laser release methods. An inverse relation between heavy calcite and light water of serpentinisation would yield at least circumstantial evidence supporting fractionation of oxygen isotopes between calcite and magmatic water before serpentinisation after the model investigated by Kirkley et al (1989).

7.7 CONCLUSIONS

Carmichael, Turner and Verhoogen (1974, p525), with reference to Berg and Allsopp's (1972) discussion of fresh and altered kimberlites with respect to Sr isotopes, suggested that hydrogen and oxygen isotope measurements would help to clarify the role of meteoric water in the serpentinisation of kimberlites.

In principle, this is a solid approach. However, compared to basic lavas, for example (eg Taylor, 1968), kimberlites are less amenable to investigation by the measurement of light stable isotope ratios on bulk-rocks. This is explained by the complexity of the role of water in the kimberlite system, as outlined in the introduction to this chapter. In particular, the interaction of magmatic water, if present, with calcite during groundmass crystallisation, is likely to corrupt the magmatic water signature in later-formed serpentines.

The approach of Berg (1989) of monitoring the nature of the serpentinisation reaction, by determining the presence or absence of brucite, appears to offer a better means of placing at least relative limits on the quantities of water which have interacted with a kimberlite. Unfortunately this mineralogical approach does not solve the problem of determining the **source** of the water, but it represents a step in the right direction which is discussed further in the following chapter.

CHAPTER 8

The Significance of Brucite in South African Kimberlites.**8.1 INTRODUCTORY STATEMENT**

As reported in Chapter 7, stable isotope measurements failed to supply a means of discriminating between fresh and altered kimberlites, and the present chapter reflects a mineralogical approach to solving the same problem.

8.2 THE SEARCH FOR A MINERALOGICAL DISCRIMINANT**8.2.1 Background information**

Kresten (1973) gives an excellent short summary of the sequence of reactions which characterise the progressive alteration of kimberlite by the action of water. Kresten (1973) suggests that the alteration reactions can be divided into three broad stages, namely,

- a.) serpentine,
- b.) vermiculite, and
- c.) saponite.

Kresten notes that the progression of stages in part **requires** the loss of $\text{Mg}(\text{OH})_2$ in solution to stabilise the later-stage minerals of lower $\text{MgO} : \text{SiO}_2$. A physical obstruction to the passage of such solutions will inhibit alteration and a local build-up of $\text{Mg}(\text{OH})_2$ may lead to retrogressive reactions. There is also an increase in degree of hydration with progressive alteration. The alteration stages of Kresten (1973) are adapted by Dawson (1980, fig 38), on which an apparent discrepancy arises from the re-naming of the first stage of alteration as "talc/serpentine". Talc is discrepant because it has a lower $\text{MgO} : \text{SiO}_2$ ratio (6 : 8) than the accompanying type mineral, serpentine (12 : 8), and of the following stage's chlorite (12 : 8, like serpentine).

Because of enstatite's low MgO : SiO₂ (8 : 8), when it hydrates to serpentine (12 : 8), some talc (6 : 8) is simultaneously produced, the pair balancing to maintain the orthopyroxene's 8 : 8 MgO : SiO₂ ratio in a closed system. Increasing loss of Mg(OH)₂ in solution leads to more talc and less serpentine being formed. In contrast during the serpentinisation and subsequent alteration sequence of olivine, the MgO : SiO₂ equivalent of talc (Mg₆Si₈O₂₀(OH)₄) is reached only in the vermiculite ((Mg,Ca)_{0.7}(Mg,Fe³⁺,Al)₆(Al,Si)₈O₂₀(OH)₄.8H₂O), that is to say, the **second** stage. In terms of only MgO and SiO₂, talc is also the "simplified" equivalent of the final saponite ((¹/₂Ca,Na)_{0.66}Mg₆Al_{0.66}Si_{7.34}O₂₀(OH)₄) stage of Kresten (1973). Including "Talc" as part of the first alteration stage therefore obscures the progressive loss of Mg(OH)₂, the importance of which is emphasised by Kresten (1973). The term "serpentine" without reference to talc is therefore preferred here for the first alteration stage, the loss or retention of brucite being the cardinal point of this Chapter and its Appendix.

8.2.2 The research design

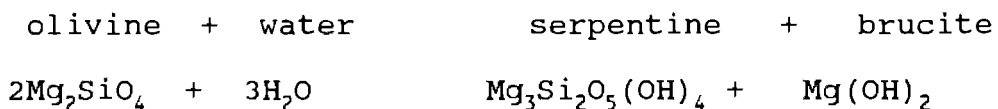
The study of Kresten discussed above, combined with the petrographic observations of Berg and Allsopp (1972) and Barrett and Berg (1975), suggested that detailed investigation of the serpentinisation of olivine might yield a mineralogical discriminant of freshness in kimberlite. Difficulties due to the early production of talc by exceptionally abundant orthopyroxene, or other high silica phases⁹ would have to be borne in mind. In general, however, orthopyroxene is relatively rare in kimberlite. It appears to be in a reaction relationship with kimberlite magma at crustal pressures, judging from rare corroded remnants which can be observed embayed in olivine. Olivine, in turn, is a stable late-stage

⁹ Later consideration also suggested that under high CO₂ activity, olivine may desilicate to talc and Mg carbonate; see Appendix 8, p294 for discussion; and Skinner and Clement (1979, Fig 2) for illustration of steatitised olivine.

liquidus phase; this can be deduced from the presence of euhedral groundmass olivines. The omission of any consideration of orthopyroxene and its alteration to talc will therefore not significantly bias the investigation of the reactions considered here.

Clearly, the progressive alteration documented by Kresten (1973) refers to a process of open system alteration. This is what was postulated to have occurred in the "altered" kimberlites of Berg and Allsopp (1972) and Barrett and Berg (1975). In contra-distinction, the fresh kimberlites were considered by Berg and Allsopp (1972) to have been serpentinised by "...water contained in the original kimberlite rather than introduced subsequent to its consolidation." In Barrett and Berg (1975) this was stated as "...a rock in which alteration is believed to have been predominantly isochemical (autometasomatic)".

Isochemical serpentinisation implies reaction with the magma's self-contained water, or the **addition**, but **not circulation**, of water. The pertinent reaction is:



The implication of isochemical serpentinisation is that the brucite will remain in the rock, instead of being flushed out as deduced by Kresten (1973) for the Lesotho kimberlites he studied. A search for brucite was therefore undertaken with a view to detecting rocks which had been serpentinised isochemically, thereby contributing an additional and less subjective test for freshness of kimberlites than thin section petrography.

8.2.3 Work undertaken

Brucite was determined in 81 fresh and altered kimberlites; it was found to be present in the majority of fresh specimens and generally absent in the altered ones.

In accordance with the principle of avoiding repetition, as set out in the Introduction of this thesis, the reader is now referred to Appendix 8, where the work introduced above is comprehensively recorded and discussed. Section 8.3 will then follow in context.

8.3 SCOPE AND IMPACT OF APPENDIX 8

The scope of Appendix 8 can be assessed on general and specific levels. The presence of brucite in bulk "basaltic" kimberlites has proven generally consistent with earlier petrographic assessments of freshness. To a large extent this may be taken as confirming the effectiveness of the petrographic assessments; but this should by no means be taken to conclude that the reservations which have been voiced in the literature about the subjectivity inherent in petrographic assessments should be dismissed. They are valid and must be continually borne in mind, and additional tests of freshness applied, as illustrated in the example below.

On the more specific level of individual sample assessment, the additional test of thermal analysis was found to be a superior means of deducing the type of serpentinisation undergone by a particular kimberlite (DiB 3), in an instance where the petrographic criteria of Barrett and Berg (1975) were thereby proved to have been totally inadequate (see Appendix 8, Section 16.4.3 (d)). This re-emphasises the problem of subjectivity inherent in petrographic assessment of freshness which was noted by Berg and Allsopp (1972) from the outset, and commented upon in the literature as reviewed earlier. The

experience of DiB3 documents a practical remedy for the problem.

The determination of brucite as a measure of freshness has been shown to have questionable utility in the case of micaceous kimberlites. It may be a consequence of the decomposition of mica in the groundmass raising the activity of silica upon alteration leading to the production of more serpentine instead of brucite. But this is not readily quantifiable, as discussed in Appendix 8, Section 16.4.3, c, (ii). The presence of 0.43 wt% brucite in JagK9, which is highly micaceous, also shows that the the formation of brucite in micaceous kimberlites is not inevitably inhibited by the presence of phlogopite; brucite containing micaceous kimberlites may therefore profitably be sought when building up future sample collections.

The impact of Appendix 8c remains to be seen in the light of future kimberlite research. The pertinent questions have been posed by Mitchell (1986, p399):

"Are kimberlite studies in the next decade to meander, as they have done in the past, without a common direction; flounder in the abyss of increasing specialisation; or progress by means of comprehensive co-operative studies of all facets of kimberlite petrology?.....The majority of investigations have been concerned with one facet of kimberlites in isolation from others.....The object is to delineate the evolution of kimberlite magmas from their birth in the upper mantle to their final resting place in the upper crust...."

If the longer term co-operative research projects needed to consolidate our knowledge materialise, the late stage events in the kimberlites' "resting place in the upper crust" need to be clearly understood as explained repeatedly in this thesis, to select samples which will reveal the earlier history of the

rocks as unambiguously as possible. Thermal analysis for brucite should become part of such co-operative endeavours, to help overcome the subjective element in thin section petrography.

The alteration reactions undergone by kimberlite are also interesting in their own right, and further studies may reveal further mineralogical discriminants which can overcome the limitations experienced here in the case of micaceous kimberlites. It was argued in Appendix 8 that samples of kimberlite containing serpentine not supported by brucite were suspect, **except** in cases such as phlogopite kimberlite where such brucite might not be formed. To resolve these cases it might be profitable to investigate **negative** mineralogical indicators; that is to say, check whether vermiculite, for example, might characterise altered micaceous kimberlites by indicating open system flushing of K from phlogopite and $Mg(OH)_2$ from serpentine, but be absent in fresh micaceous kimberlites which were altered predominantly isochemically. This would require a systematic investigation of alteration minerals in fresh and altered kimberlite, to follow up the preliminary study of Kresten (1973) and the present work; it would be on a far larger scale than the present study, but could in part be carried out on the same specimens.

The present chapter concentrated on the incipient stage of alteration of kimberlite. To assess aspects of the breadth of alteration reactions not yet investigated, the following chapter records a preliminary study into the opposite end of the alteration spectrum: grossly contaminated and extremely altered kimberlites.

CHAPTER 9

Aegerine and the distribution of sodium in kimberlites**9.1 INTRODUCTION**

The geochemistry of sodium in kimberlites has received relatively little attention. Dawson (1980, p 53) notes that kimberlites have very high K/Na ratios, and similarly, Mitchell (1986) writes, "Their Na₂O/K₂O ratios are very low (<0.5), illustrating their potassic nature." Kimberlite may contain up to 5 wt% K₂O (Dawson, 1980, p 51), and up to about 2 wt% Na₂O (Dawson, 1980; Berg, 1982/Appendix 8a).

More is known about the geochemistry of potassium in kimberlites than of sodium. Given the association of K and Rb in kimberlites (eg Gurney and Berg, 1969/Appendix 4), combined with the Rb/Sr systematics implicit in the isotope data presented for micaceous kimberlites by Smith (1983), the K₂O in kimberlite is, in general, considered to be a primary constituent inherited from the kimberlite source in the mantle.

In contrast, high concentrations of Na₂O are never observed in fresh kimberlites. Although sodium concentrations may be as high as 2 wt% Na₂O, these levels are found in kimberlites that are heavily altered and manifestly contaminated by country rock (Berg, 1982/Appendices 8a and 9a; Clement, 1982; Clement et al, 1984; Mitchell, 1986 p 277). This suggests that further understanding of late-stage crystallisation, contamination and alteration reactions may be gained by studying the geochemistry of sodium in kimberlite in more detail than has been attempted hitherto. Previous studies concerned with sodium in kimberlites (referred to later), have tended to concentrate on mineralogy; the present chapter attempts for the first time to quantitatively relate mineralogy to the bulk rock chemistry of kimberlite.

When investigating how bulk-rock chemistry relates to late- and post-emplacement processes affecting kimberlite, it is useful to include studies of rocks that have been exceptionally heavily altered and contaminated. The resultant extreme chemical effects observed in such rocks can alert us to less obvious chemical aberrations in samples that appear superficially to be uncontaminated and fresh, but which suffer from unrecognised alteration or the "occult" contamination discussed by Dawson (1980 p 55) with reference to Fesq et al. (1975). Accordingly, as part of the study of the geochemistry of Na₂O in 69 bulk kimberlites reported in this chapter, five of the most contaminated, altered and sodic samples were selected for study under the electron microprobe. After a preliminary survey had established their general mineral chemistry, detailed work was concentrated on three of them (See Table 9.1, Appendix 9c).

The microbeam strategy was to determine which minerals hosted Na; it was hoped that available mineral stability data would then contribute to the understanding of late-stage contamination and alteration reactions. This approach led to the discovery that one of the host minerals of sodium in kimberlites is aegerine (Berg, 1990/Appendix 9b). The only aegerine previously on record in association with kimberlite is an inclusion in a diamond (Meyer and McCallum 1986).

Sphene was found closely associated with the newly-discovered aegerine, in what appears to be a new paragenesis for sphene in kimberlite.

9.2 SAMPLE DESCRIPTIONS AND ANALYTICAL METHODS

9.2.1 Samples analysed

The 69 samples whose bulk major element analyses are used or referred to here represent a cross-section of fresh and altered kimberlites, both from the type area of Kimberley,

South Africa, and adjoining regions as far afield as Jagersfontein. Data on all or some these samples have previously been presented for the alkali metals K, Rb and Cs (Gurney and Berg, 1969/Appendix 4); petrography and Sr isotopes (Berg and Allsopp, 1972/Appendix 5; Barrett and Berg, 1975/Appendix 6); contamination and alteration, (Berg, 1982a/Appendix 8a; 1982b/Appendix 9a); and the presence of brucite and serpentinisation reactions (Berg, 1986, 1989/Appendices 8b, c). Stable isotope data were presented in Chapter 7. The descriptions given in the works quoted above generally suffice for the purpose of the present chapter, because we are concerned largely with inter-element relations of groups of rocks, rather than individual specimens. Additional descriptions are necessary for the individual rocks studied under the electron microprobe, as outlined below.

The five high-Na samples studied are clay-mineralised lithic tuffisitic kimberlites or kimberlite breccias (following the terminology of Clement and Skinner, 1985). Hand specimens are characterised by a dull, sometimes porous aspect and the presence of both black and white, generally angular, inclusions taken to represent argillite. The evidence for the presence of clay is broad X-Ray Diffraction (XRD) lines at about 14 Angstroms, obtained in preliminary study of the bulk rock powders. Detailed clay-mineral analysis was not undertaken. The presence of clay is also reflected in high values of H_2O^- . (See analysis E, Appendix 8a). H_2O^- probably represents at least a semi-quantitative measure of the volume of clay in a rock. Typical inclusions which yielded aegerine and pectolite analyses (Table 9.1, Appendix 9c) are illustrated on Plate 9.1, Appendix 9d.

9.2.2 Analytical techniques

The analyses referred to in this chapter were carried out in Cape Town, Edinburgh and Port Elizabeth. Methods used are

well-established standard techniques and in the interests of continuity are summarised in Appendix 9e.

9.3 RESULTS

9.3.1 Major Element Geochemistry

9.3.1.1 Background and presentation

Major element bulk-rock analyses of the 69 kimberlites have yielded a complex series of inter-element relations which reflect, (in the reverse sequence of their chronological occurrence), groundwater/hydrothermal alteration, contamination by country-rock, assimilation/reaction with mantle rocks, as well as crystal fractionation differentiation (Berg, in prep).

Bivariate relations consistent with the assimilation of country rock shale involve the elements MgO, SiO₂, Al₂O₃, K₂O, Cr₂O₃, NiO, and Fe₂O₃ (tot) (Berg, in prep). For example, the relation of Al₂O₃ vs SiO₂ (Fig 9.1, Appendix 9f) is consistent with a shale mixing line. This interpretation is based on the observations that:

- a.) The concentration of Al₂O₃ in the **fresh** kimberlites (eg Analyses A and B, Appendix 8a; see Fig 9.1) is never greater than about 2 wt% Al₂O₃¹⁰;
- b.) Data points for rocks containing about 3 to 7 wt% Al₂O₃ trend towards the "shale" point of 67 wt% SiO₂ and 16 wt% Al₂O₃;
- c.) The interpretation is consistent with the other inter element relations listed above;
- d.) The high-Al₂O₃ samples carry argillite inclusions visible in hand specimen.

¹⁰ In this interpretation allowance must be made for the Al₂O₃ in phlogopite which may be present in a rock; it is easily done by assessing the K₂O vs Al₂O₃ relation, but this aspect is not pursued here because it contributes little to the scope of the present Chapter, which is focussed on sodium.

The inter element relations referred to above are complicated by varying degrees of hydration and varying calcite contents of the kimberlite specimens. Consequently, correlations and regression lines for individual inter element relations based on the raw analytical data are not tightly constrained; but the consistent trends for many inter element relations lend credence to the shale assimilation hypothesis. Recalculation to water-free and both water- and calcite-free analyses, leads to tighter correlations in the inter-element relations, but also disguises information. Examination of this aspect and all the inter-element relations of kimberlite is beyond the scope of the present Chapter, but Fig 9.1 serves as an example, which is particularly pertinent here because both SiO_2 and Al_2O_3 show correlations with Na_2O , as shown in Section 9.3.1.2 below.

9.3.1.2 Inter-element relations involving Na_2O

Kimberlites containing high concentrations of Na_2O also tend to have high concentrations of SiO_2 , Al_2O_3 and H_2O^+ (See analyses D and E in Appendix 8a for example, and Figs. 9.2, 9.3 and 9.4 respectively).

In contrast to the trends referred to in Section 9.3.1.1 which are consistent with the assimilation of shale (eg Fig 9.1), inter-element relations involving Na_2O display some apparent inconsistencies with the shale-assimilation model. For example, the Na_2O vs Al_2O_3 relation (Fig 9.3) does display an apparent positive correlation for concentrations of greater than about 2 wt% Al_2O_3 , but the data points deviate from any plausible kimberlite - shale mixing line. This is because extrapolation to 16% Al_2O_3 , which is typical of Dwyka and Ecca shales (Danchin 1970), would imply a shale end member carrying about 7 wt% Na_2O . There are no such Karoo shales. On the assumption that the shale-assimilation model is correct because most inter element relations other than those involving Na_2O are consistent with it, the implication of Fig 9.3 is that there

was an additional source which provided Na_2O over and above that introduced into the kimberlites by the simple addition of their shale xenoliths.¹¹

Fig 9.3 does not indicate the source of the excess sodium or its location in the kimberlite. However, the microprobe analyses (Table 9.1), discussed in more detail in Section 9.3.2), have revealed two Na-bearing phases which occur in kimberlite: pectolite and aegerine. It is instructive to anticipate these analyses at this stage, to investigate in how far aegerine and pectolite may control the bulk rock geochemistry of Na in the high-Na/high- SiO_2 kimberlites. To do this the bulk-rock chemical concentrations of elements must be related which ideally occur only in the Na-rich phases; the choice is limited to Na_2O , SiO_2 , Fe_2O_3 , and CaO , these being the constituents of the two minerals in question, (apart from H_2O^+ in pectolite).

Relations involving CaO will not serve our purpose. This is because in most, if not all kimberlites, more Ca occurs in calcite than in pectolite. Similarly iron occurs in so many other minerals besides aegerine in kimberlite, that inter element relations involving iron cannot be used to test possible mineralogical control by aegerine of bulk Na_2O .

SiO_2 also occurs in a wide variety of minerals in kimberlite, such as olivine and serpentine. However, the only minerals apart from pectolite and aegerine in which SiO_2 is present in concentrations as high as 50 - 52 wt% SiO_2 are: enstatite (approx 57 wt% SiO_2), and diopside (approx 54 wt% SiO_2 and generally less than 1% Na_2O). Diopside is abundant in the groundmass of some kimberlites (Skinner and Clement (1979), in particular tuffisitic kimberlite breccias, which have been

¹¹ The alternative interpretation of Fig 9.3, that the samples have lost Al_2O_3 relative to Na_2O gained from the assimilation of shale is considered unlikely; this is because in its correlation with other elements Al_2O_3 generally has an apparent regression relationship consistent with the assimilation of shale (Berg, in prep; eg Fig 9.1); only the relation of Al_2O_3 with Na_2O (Fig 9.3) is aberrant.

classified here as altered. But the sodium concentration in these diopsides is generally not higher than about 1 wt% Na₂O (Mitchell 1986). Enstatite is relatively rare in kimberlite. These minerals will therefore affect the SiO₂ vs Na₂O relation little compared to pectolite or aegerine, if the latter minerals are relatively abundant. Thus the SiO₂ vs Na₂O relation is the only one available to test for a pectolite (Ca₂NaHSi₃O₉) or aegerine (NaFe³⁺Si₂O₆) control line. For this we refer to Fig 9.2.

The relation of Na₂O to SiO₂ (Fig 9.2) reveals a trend which, as in the case of Fig 9.3, is inconsistent with a shale contamination control line. Instead, Fig 9.2 is consistent with mineralogical control of Na₂O in the bulk-rocks by either or both of pectolite or aegerine, but cannot be used to discriminate between these two possibilities. This superficially simple picture is complicated by the relation Na₂O vs H₂O⁻ (Fig 9.4).

High concentrations of H₂O⁻ often reflect large amounts of clay, particularly smectite or vermiculite. The close correlation between H₂O⁻ and Na₂O (Fig 9.4) considered in isolation, therefore suggests that Na₂O may be located in a clay; however, no evidence could be found for such a clay in the microprobe study reported in the following Section.

In summary, the major element relations indicate that:

- 1.) Kimberlites that carry relatively abundant shale inclusions also carry relatively high concentrations of Na₂O;
- 2.) The high concentrations of Na₂O exceed the amount of sodium introduced by the shale;
- 3.) The high bulk concentrations of Na₂O are mineralogically controlled by pectolite and/or aegerine and aegerine-augite;
- 4.) There is an apparent relation between high bulk Na₂O and bulk volume of clay (as reflected by H₂O⁻). Clay does not

appear to be the **host** of the Na_2O . It may therefore be postulated that clay forms as a proportionate part of the same reaction which gives rise to the pectolite and /or aegerine (See Section 9.4.2).

Further insight first requires more detailed examination of the microbeam results which follows below.

9.3.2 Microprobe Analysis

9.3.2.1 General scope

On the basis of the association of Na_2O with Al_2O_3 and SiO_2 (Figs. 9.3 and 9.2 respectively), high concentrations of which are thought to reflect assimilated shale, the search for sodic minerals was concentrated within and around areas of inclusions thought to represent country-rock argillite xenoliths; this included heavily altered xenoliths whose identity as meta-shale may be open to debate. The Na_2O -rich minerals identified within inclusions using this approach are aegerine, aegerine-augite and pectolite (Table 9.1). Searches for sodic minerals in the groundmass away from argillite inclusions revealed pectolite such as illustrated by Scott-Smith et al (1983, fig 1), but no other sodic mineral.

9.3.2.2 Pyroxene location

Aegerine and aegerine-augite (collectively referred to hereafter as sodic pyroxene) were found generally within semi-opaque black inclusions, taken to be xenoliths of argillite (Plate 9.1 A). They were also found in one mottled grain, but were restricted to black areas; the clear areas were found to carry pectolite. Due to the combination of their opacity, fine grain size and the presence other phases, the sodic pyroxenes are optically unresolved in transmitted light. They tend to occur towards the outside borders of the xenoliths (see

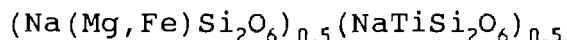
locations on Plate 9.1 A). Immediately outside and girdling the borders of some black xenoliths, diopside was found.

In reflected light the sodic pyroxenes are often observed as laths of about 4 by 10 microns, and more rarely up to 8 by 20 microns; these laths are sometimes clustered over areas of about 100 microns.

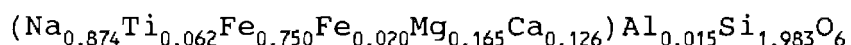
Some sodic pyroxenes showed no reflected light expression at all, and were only found by scanning the sample across the static, centred, electron beam, searching for maximum volume with a loudspeaker connected to the spectrometer set at the sodium wavelength.

9.3.2.3 Pyroxene chemistry

A selection of the analyses taken to reflect aegerine and aegerine-augite on the basis of their chemistry and pyroxene stoichiometry is presented in Table 9.1. An aegerine analysis from Deer et al. (1966) is shown for comparison (Analysis 1). Agreement between Analysis 1 and Analysis 2 is close except for the lower Fe_2O_3 in Analysis 2, which is compensated by higher TiO_2 . There is an excess of Na over Fe^{3+} in Analysis 2, even if all Al is combined with Na to make jadeite. This Na may be balanced by including the component neptunite,



following Ferguson (1977). Morimoto et al (1988) suggest a simpler calculation-scheme for the purposes of classification. Analysis 5 may be approximated by the formula:



But it suffices for the present Chapter to simply use the cation proportion ("cats") of Na as an approximation of percentage-aegerine. This gives an acceptable approximation because Al is generally so low that very little Na has to be calculated as jadeite. On this basis, Analyses 2, 3, 4 and 5 (Table 9.1) represent aegerine. Analysis 6 reflects aegerine-

augite, because Na (0.778 cats) is less than the 80 % limit suggested by Morimoto et al (1978) for aegerine.

As noted above, the pyroxenes under discussion have significant concentrations of TiO_2 . Analysis 4, as listed in Table 9.1, falls just short of the 0.1 cations of Ti per formula unit to be called "titanian aegerine" (see Morimoto et al (1988)). But it will be given this appellation here by rounding up the last decimal. It should be noted that CaO in Analysis 4 is equal to only 0.3 wt%. The relatively high concentration of TiO_2 can therefore not be a consequence of a mixed analysis involving neighbouring sphene. Some analyses were discarded due to such interference.

The range of sodic pyroxene located in KWes 25 begins at essentially pure aegerine (Table 9.1, Analyses 2 to 4), and runs to aegerine-augite similar to that found in KWes 24.

No "pure" aegerine was found in black argillite inclusions in KWes 24. Analysis 7 falls close to the border between aegerine and aegerine-augite: of 0.830 cats Na, only 0.009 have to be combined with Al as jadeite.¹² Analyses 8 and 9 are aegerine augites, the latter containing only about 60 % of the aegerine component.

Inclusions of argillite in KBult 27, which on the basis of the results reported above would have been expected to contain sodic pyroxene, yielded only diopsides (Analyses 10 - 11). They are nevertheless related to the pyroxenes of KWes 24 and KWes 25 by their:

- a.) being found in xenoliths taken to represent shale, and
- b) having the same very fine-grained submicroscopic texture.

¹² Analyses 8ZAF and 8BA represent the same analysis calculated by the ZAF and Bence-Albee procedures respectively. They serve to illustrate that high totals associated with the ZAF reduction procedure for iron-rich minerals such as aegerine, do not effect the calculated stoichiometry when compared with results obtained using the Bence-Albee procedure.

Mitchell (1986, p 185) notes with respect to clinopyroxenes of 0.1 to 1.5mm in hyperbyssal kimberlites, "...the phenocrystal and groundmass pyroxenes are essentially pure diopside with very little solid solution towards other end-member pyroxenes...". With respect to diatrema facies kimberlite Mitchell (1986, p 186) notes, "...diatrema facies kimberlites commonly contain pelletal lapilli and xenoliths which have been replaced by cryptocrystalline aggregates of diopside and phlogopite and that similar pyroxenes occur as irregular segregations. Analyses of this very fine material are not available." The analyses presented here (Table 9.1, 2 - 9), of pyroxenes from this very fine, cryptocrystalline, xenolith-replacement material, are the first available. They have a far wider range of chemistry than reported hitherto in the groundmass of kimberlites. The question of why xenoliths of similar appearance should carry pyroxenes of such variable character is best addressed in conjunction with information on the co-existing minerals which follows.

9.3.2.4 Pectolite location

Pectolite was identified primarily on the basis of microprobe analyses. The criteria for identification were similar chemistries to the pectolites described by Scott-Smith et al (1983) and hence stoichiometries consistent with pectolite, combined in some cases with the occurrence of pectolite chemistries in radiating acicular crystals similar to those illustrated by Scott-Smith et al (1983).

Pectolite was found most frequently in altered xenoliths taken to be partly digested shale, as reported also by Scott-Smith et al.(1983). Such pectolite was found accompanying Na rich pyroxene in KWes 24 and KWes 25 and accompanying diopside in KBult 27. The 1 by 2 cm white xenolith in KWes 24 (Plate 9.1 B) contains abundant pectolite, but no pyroxene was detected in it in a traverse of 108 regularly-spaced analyses across the the short axis of the

grain. The pertinent analyses are listed in Table 9.2 and their chemical variation is illustrated on Fig 9.5.

Black xenoliths within 1 cm of the white grain illustrated on Plate 9.1 B contain pectolite **together** with aegerine-augite. Whether the presence or absence of pyroxene in a xenolith which contains pectolite is controlled by the original mineralogy of the xenolith, or the nature of its reaction with the host kimberlite, is not clear at this stage; it is clearly an important question for a comprehensive hypothesis which attempts to explain the origin of both minerals.

9.3.2.5 Pectolite chemistry

The chemistry of pectolites observed in the present work (Table 9.1, Analyses 12 - 15), covers the same general range as the pectolites analysed by Scott-Smith et al. (1983), except for higher concentrations of MnO reported here. Between 1.45 and 2.69% MnO was found in the pectolites in the white xenolith in KWes 24 (Table 9.1). The substitution of Mn for Ca in pectolite is well known (Deer et al. 1966), but is reported here for the first time in kimberlites.

9.3.2.6 Sphene location

The sphene for which analyses are given in Table 9.3 generally occurs as scattered grains within argillite xenoliths; it is sometimes adjacent to Na rich pyroxene. (See Appendix 9e for details of resultant analytical difficulties). One black grain on whose borders sodic pyroxene was found, and which is of similar semi-opaque appearance to the grain illustrated in Plate 9.1 A, turned out to be made up of about 50% sphene.

Previous reports of sphene in kimberlite are of alteration products of, or intergrowths with:

- a.) perovskite,
 - b.) ilmenite, and,
 - c.) titano-magnetite/ilmenite
- (Dawson, 1980, p 82 para 3; Frick, 1973; Haggerty, 1975, fig 1e).

The sphene reported here in partly digested country-rock inclusions therefore reflects a new paragenesis of sphene in kimberlite.

9.3.2.7 Sphene chemistry

There is nothing unusual about the chemistry of the sphene analyses (Table 9.1, Analyses 16 - 19); see also Deer et al (1966, pp 17 - 19).

9.4 DISCUSSION

9.4.1 Comparison with other occurrences of aegerine

Aegerine occurs typically in late-stage magmatic environments which are often peralkaline (Deer et al 1966). Depletion of magmatic aluminium by crystallisation of feldspars may be a prerequisite to the formation of aegerine in a magmatic environment (Bailey and Schairer 1966, ref by Flower 1974).

The above general case emphasizes the unusual nature of the sodic pyroxenes described here, in xenoliths taken to represent argillite in kimberlite. If the xenoliths are correctly interpreted to represent argillaceous country-rock, they must at least initially have been **rich** in aluminium; and the kimberlite host is of course not known to crystallize feldspar. The only comparable occurrence is the aegerine¹³ reported by Milton and Eugster (1959) in the Green River Formation of

¹³ The name "aegerine" is here given preference to "acmite" as applied to Milton and Eugster (1959), following the recommendation of Morimoto et al (1988).

Wyoming. Milton and Eugster (1959) describe the pertinent environment as a carbonate-rich lacustrine sequence in which late stage saline muds in ever smaller basins gave rise to a series of sodium minerals including authigenic aegerine and shortite. Well-crystallised aegerine is reported to occur sometimes within shortite and both minerals are considered to have "unquestionably formed at or near room temperature."

The Green River paragenesis has four (partly superficial) aspects in common with kimberlites:

- a.) The presence of carbonate;
- b.) Subordinate shale (analogy to shale xenoliths?);
- c.) Tuff beds which contain sodic silicates (analogy to tuffisitic kimberlite breccia?); and
- d.) The presence of shortite (reported in the Upper Canada Mine kimberlite dykes by Watkinson and Chow (1973)).

Kimberlites in general do not share the sodic character of the pertinent parts of the Green River formation. But local enrichment of Na_2O by the assimilation of shale or metasomatism has been suggested to explain the presence in kimberlites of pectolite (Scott-Smith et al. 1983). The bulk rock data (Section 9.3.1.2) of the present work supply further evidence for the introduction of Na_2O into some specific kimberlites, **after** their emplacement and incorporation of shale xenoliths. The sodic character of the beds of the Green River formation in which aegerine occurs appears to be a local effect of a different kind; it has been attributed to syn-depositional dessication to yield saline mud-flats which are in turn overlain by normal, non-sodic beds (Milton and Eugster (1959)).

Because it is restricted to the xenoliths, the aegerine reported here could in principle, together with its host shale, predate the kimberlite. However, neither aegerine nor saline muds have been reported from the Dwyka or Ecca shales. Until such evidence is forthcoming, it is more logical to seek a

common origin for both aegerine and pectolite, which co-exist in the xenoliths.

9.4.2 The occurrence and formation of pectolite

The occurrence of pectolite in South African kimberlite has already been documented by Scott-Smith et al (1983), to whose paper the reader is referred for background information. Previous reports of pectolite in kimberlite (Akella et al, 1979; Agee et al, 1982) are in papers not specifically directed to the study of this mineral. The present work has contributed a slightly wider range of chemical analyses, (see 9.3.2.5), and a replacement profile illustrated on Fig 9.5 and discussed below:

The main observation to be made on Fig 9.5 are that along the line of the single traverse made:

- a.) Points where all the five elements plotted on Fig 9.5 are absent represent calcite; (in the interest of clarity, CaO is not plotted on Fig 9.5, however.)
- b.) Replacement of the white grain by pectolite is in places sufficiently complete that five consecutive analyses of essentially pure pectolite were obtained. These areas are reflected mainly by the right hand side (RHS) of the graphs on Fig 9.5, where $\text{SiO}_2 = 52 \text{ wt\%}$ together with $\text{Na}_2\text{O} = 9 \text{ wt\%}$.
- c.) In the areas consisting predominantly of pectolite (see the last 50 analyses, RHS of Fig 9.5; about 52 wt% SiO_2 and 7 to 9 wt% Na_2O), there appear to be slightly greater amounts of Al, Fe and Mg as the proportion of pectolite decreases; these elements represent some minor phase intermixed with the pectolite. In areas consisting of about 30 to 60 % pectolite (See LHS of graph; 2 - 5 wt% Na_2O , but SiO_2 high due to other silicates) the concentration of Al_2O_3 is between 2 and 8 wt%. This relatively high- Al_2O_3 region of the white inclusion may reflect clay belonging to the

(assumed) original argillite. What then happened to the Al_2O_3 in that part of the inclusion taken to be completely replaced by pectolite?

The following working hypothesis is suggested, although any interpretation based on a single traverse must clearly be tentative:

The solutions which reacted with the xenolith were rich in Ca (saturated with the primary calcite of the kimberlite) and Na. The silica of the argillite, which reacted with the solutions to form pectolite, originally was held partly in clays; the Al_2O_3 in these clays was displaced from the xenolith when the local combination of SiO_2 , CaO and Na_2O activities led to exclusive pectolite saturation. The Al_2O_3 thus displaced in solution re-formed a clay where the local chemical potentials no longer favoured exclusive pectolite precipitation. The remarkable correlation between Na_2O and H_2O (Section 9.3.1.2; Fig 9.4) would thus be explained; it suggests that the two-stage displacement and re-formation of clay during the precipitation of pectolite, as postulated above, was at least semi-quantitative.

9.4.3 The formation of aegerine

The presence of Fe^{3+} instead of Ca constitutes the essential chemical difference between pectolite and aegerine, apart from pectolite's minor water. The formation of aegerine rather than pectolite may therefore be controlled both by the local availability and/or oxidation state of iron.

Potential sources of iron are either the kimberlite or the shale. If the kimberlite is the source, the observation of decreased opaque contents in heavily altered compared to fresh kimberlites (Barret and Berg, 1975/ Appendix 6, Fig 5) may be pertinent: it suggests that much of the alteration of kimberlites takes place under conditions where iron becomes

mobile, presumably in the ferrous state. Such iron mobilised from opaques, or freed from dissolving olivine, may be introduced into the region of altering shale which supplies silica in order that aegerine may form. The iron, accompanied by Na, must then be oxidised locally to form aegerine. If the restriction of aegerine and aegerine-augite to argillite xenoliths is confirmed, it seems that the oxidising geochemical barrier is formed by a constituent within the xenoliths themselves, assuming the above model.

An alternative model (I.C. Rust, Pers. Comm. 1992) is that the iron is already localised in particular shale horizons in the form of pyrite, and that aegerine forms in those shales during the course of oxidation reactions. Analyses of shale wall rock from Kimberley to test this model are not at hand, but an indication of possible compositions may be derived from Danchin (1970), who reports the following total iron concentrations expressed as Fe_2O_3 on a dry basis in some Karoo shales:

	Mean	Range
Southern Ecca Facies	5.79	2 - 8 (approx)
Central Ecca Facies	6.60	1 - 11 (approx)

These values are consistent with the presence of pyrite, but also other forms of iron, in Karoo shales possibly equivalent to the wall rock at Kimberley. To form aegerine, the iron from shale would then have to combine with Si in the shale, and Na in solution, evidence for the presence of which was given in Section 9.3.1.2, para 2. Since

- a.) typical groundmass diopside was found immediately adjacent to black xenoliths carrying aegerine, and
- b.) some black xenoliths carry diopside instead of aegerine,

the assignment of both the source of iron and oxidising geochemical barrier to specific aegerine-containing xenoliths is attractive, but not proven.

9.4.4 The occurrence and formation of sphene

Sphene has been reported as an alteration product of perovskite, ilmenite and titanomagnetite in the groundmass or inclusions of kimberlite (Section 9.3.2.6). In discussion of the petrogenesis of kimberlite and specifically the silica activity of the groundmass liquids, Mitchell (1986, p376; fig 9.2) writes, "As sphene is not found in kimberlites, and perovskite is a ubiquitous groundmass phase, one can employ a silica buffer involving these two minerals to define the maximum activity of silica in the groundmass liquid...". To form the sphene reported in this Chapter, the proposed maximum buffer was clearly reached (if not exceeded) locally, combined with the general high activity of Ti in "late stage Ti-rich liquids" (Haggerty, 1975).

9.5 SUMMARY AND PERSPECTIVE

A preliminary microbeam study designed to investigate the mineralogical control responsible for the association of Na₂O with SiO₂, Al₂O₃ and H₂O in bulk kimberlites, revealed the presence of sub-microscopic aegerine and aegerine-augite within semi-digested country rock inclusions. This (Berg, 1990/ Appendix 9b) is the first report of such pyroxene from a kimberlite, except for a single report of aegerine as an inclusion in a diamond by Meyer and McCallum (1986). A new paragenesis of sphene in kimberlite, associated with the aegerine, was found in the process. The micro-petrographic texture of this association remains to be mapped, but the writer's impression is that equilibrium between the two minerals is plausible.

Aegerine is stable under a wide range of magmatic conditions (eg Bailey, 1969). However, as Bailey (1969, p 12) notes, it also has a propensity to form metasomatically, which is clearly the case here. The conditions of this metasomatic

environment can be quantified to the extent that the activity of SiO_2 must have reached or exceeded the perovskite - sphene buffer discussed in Section 9.4.4, if equilibrium between sphene and aegerine pertained. If the general patterns of equilibria found by Bailey (1969) for aegerine compositions close to the water-saturated magmatic solidus carry over to metasomatic conditions, it may be speculated that the oxygen fugacity was at some value below which arfvedsonite would form. Perhaps arfvedsonite or riebeckite remain to be found in xenoliths of the type studied here.

The most radical and significant discovery of a new occurrence of a silicate mineral in long-studied kimberlites was, in this writer's opinion, that of monticellite as a major groundmass phase (Clement et al, 1975). Previous tentative reports of optical identifications of monticellite (See Mitchell 1986, and refs therein) never observed the abundance of the mineral in the groundmass. In part, no doubt, this was because much of the monticellite is smaller than the thickness of the normal petrographic thin section. Clement et al (1975) followed a careful optical investigation with microbeam analyses confirming monticellite. Given how long this important and abundant mineral eluded us, it is perhaps not surprising that further minerals, such as the aegerine discussed here, remained undiscovered. To date the aegerine has been "seen" only by microbeam methods. Aegerine does not have the informative significance of montecellite in kimberlite, because (together with sphene) it reflects variable, localised and probably often transient equilibria. Its significance lies rather in reminding us that there **is** information still lurking in unlikely places in kimberlite, but that it has to be elicited by microbeam exploration. This same microbeam approach yielded data of more fundamental significance in peridotite nodules. For this contribution we must turn to the final Chapter of this thesis.

CHAPTER 10

<p>Brucite/calcite intergrowths in peridotite nodules from kimberlite pipes; evidence for carbonate in the mantle</p>
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10.1 INTRODUCTION

The apparent absence of primary carbonate minerals in samples of the mantle recovered from kimberlite pipes was for long an enigma (eg Wyllie 1980), in the face of clear experimental evidence that carbonates are in fact stable in the mantle (eg Wyllie, 1969; Egglar, 1978; Kushiro et al, 1975).

To explain this paradox between the expectations based on experimental petrology and observations made on the rocks themselves, Egglar (1975) suggested that mantle carbonates are consumed by decarbonation reactions with co-existing silicates while their host nodules are transported to the surface. Boyd and Gurney (1982), on the other hand, suggested that mantle carbonates were not observed because extremely rapid decarbonation during emplacement led to explosive decrepitation of both carbonates and their host rocks.

I suggested, in contrast, that there **is** in fact evidence for carbonate in peridotite nodules from kimberlite, but that this evidence has previously been overlooked, both because of its submicroscopic scale and the effect of alteration reactions (Berg, 1986a, b;/ Appendices 10a, 8b). The evidence lies in the occurrence of finely intergrown brucite and calcite in some peridotite nodules from kimberlites (See Fig 1, Appendix 10). The present chapter documents these intergrowths in more detail, and investigates possible implications with respect to the presence of carbonate in the upper mantle.

10.2 MATERIALS STUDIED

10.2.1 Source of samples

Twelve peridotite nodules were selected for study from kimberlites of the type area of Kimberley, South Africa, and surrounding areas as far as Jagersfontein. They form part of a collection of 100 nodules analysed for major elements by Berg (in prep). This collection is thought to be reasonably representative of the main mineralogical groupings encountered in Kimberley. However, nodules with deformed textures and advanced metasomatic alteration may be under-represented in the sample collection compared to the actual population carried by the kimberlites, due to a subjective bias towards "fresh" samples during collection (see Epilogue reference to Chapters 3 and 4).

10.2.2 Selection criteria

Ten samples were selected initially, for two purposes:

First, it was planned to check whether there is a correlation between such brucite as the rocks might contain as by-products of serpentinisation, and the petrographic character of their serpentine (cf Hostettler et al, 1966). This required the selection of samples containing as wide a petrographic range of serpentines and textures as possible. Eight samples were taken to cover a range from clear green serpentines to a clear colourless variety that has an overall "black" aspect due to opaque borders and stringers within the serpentine veins. Secondly, two samples were selected to include abundant "black lenticles"¹⁴. The foregoing ten samples were studied by thermal analysis, and the two containing black lenticles also

¹⁴ "Black" refers to the appearance in hand specimen. "Lenticle" is used here partly on the basis of the description of "lenticles of... glass" by Boyd and Nixon (1978); see Section 10.6. Epytimologically "lenticle" alludes to a double-convex shape. The black grains on Plate 10.1 D and 10.2 C fulfill this specification. The term lenticle is extended to all grains of similar petrographic aspect in this Chapter, whether they are deformed lenticles or originally grew in non-lenticular forms.

by microbeam methods. A further two samples (KDB 3 and KDB 4) were added later and their black lenticles studied by petrographic or microbeam methods only. Except for the illustration of Plate 10.2 C results on the latter two samples are not discussed in this Chapter because they add little to the information yielded by samples KBult 22 and KBult 23.

10.2.3 Petrography

10.2.3.1 Scope of descriptions

Descriptions of the samples which were studied primarily for their serpentines are recorded briefly in Appendix 10e because they became of secondary interest immediately the virtual absence of brucite in them was ascertained (See Section 10.3.1). The samples carrying the black lenticles are described below because they are the main subject of the investigation reported in this Chapter.

The **silicate** mineralogy of the type of xenolith discussed here is well known and documented in the literature (See for example Boyd and Nixon, 1978). For the purpose of this Chapter it is therefore only necessary to describe in detail the black lenticles on which the present study is focussed. Silicates are discussed to the extent that they affect these black lenticles and the presence of brucite elsewhere in the rocks.

10.2.3.2 Sample KBult 22

This sample is a wehrlite with a porphyroclastic texture. It carries the highest amount of brucite (5.22 wt%) recorded to date in a peridotite xenolith from kimberlite (Table 10.1, Appendix 10d).

Olivine constitutes approximately 85% of the section studied. About 50% of the **olivine** occurs in grains of up to 12mm with undulose extinction, the rest being sheared; grain-

sizes in the sheared areas range from about 0.02 to 0.1mm. Alteration of the **olivine** consists mainly of green **serpentine**. It cuts across the larger **olivines** in veins of 25 to 150 microns wide. (Microbeam analyses indicate the presence of minor **brucite**, not visible optically, in this serpentine; see Table 10.3, Analysis 7, in Appendix 10d). **Serpentine** is more abundant in the finer-grained granulated areas than in the large strained **olivine** grains.

Orthopyroxene (opx) was not observed in the section studied; hence the designation of wehrlite. The absence of **opx** is particularly relevant because it may be the critical factor controlling the presence of dolomitic carbonate rather than magnesite at high pressure (See Sections 10.4 and 10.5).

Clinopyroxene (cpx) occurs in grains of about 1 mm either surrounded by **olivine**, or occasionally adjacent to (or intergrown with?) **phlogopite** (Plate 10.1 A). In sheared areas **cpx** also occurs within a few microns (Plate 10.1 B) of the black lenticles which are described later. Alteration of **cpx** is particularly pronounced in some zones which appear to have allowed the passage of fluids (Plate 10.1 C).

The **black lenticles** appear in hand specimen as 2-5 mm black grains which are sometimes referred to colloquially as "graphite" or "carbon"¹⁵. In thin section they display a variety of forms ranging from simple spheroids and lenticles to more complex forms with convoluted borders (Plates 10.1 D, 10.2 A, B and C). The origin of the forms is not known but the irregular shapes may result from ductile shearing during deformation of the host silicate rock. This is thought to put constraints on the history of the lenticles (see 10.4.5.3.).

The **black lenticles** in KBult 22 are generally isolated in areas of granulated olivine. However, they occasionally show a

¹⁵ Graphite grains are sometimes known to occur in peridotite xenoliths, as described most recently by Pearson et al (1990). The black lenticles discussed here may be mistaken for such graphite in hand specimen.

close association with phlogopite (eg Plate 10.2 D). This latter association, when combined with the possible phlogopite-cpx association illustrated on Plate 10.1 A, suggests that the possibility of there existing an association of phlogopite, cpx and black lenticles, as a metasomatic assemblage, should be entertained. It is possible, however, that the black lenticle/phlogopite proximity illustrated in Plate 10.2D is all or in part mechanically induced during deformation/shearing.

Optical properties of the black lenticles are very variable, even within grains. Both semi-opaque to opaque brown/black, as well as transparent colourless areas, may either be found in the same grain, or to characterise whole grains. It is not clear what causes the variations in grain coloration and opacity. The presence of glass might be a factor by general analogy with brown glasses in mafic rocks (See also Boyd and Nixon, 1978) and reference thereto in Section 10.5).

Intergrowths of brucite and calcite can be ascertained on a 20 micron scale in both the brown semi-opaque and clear areas described above. The intergrowth textures can be observed fairly readily under the petrographic microscope in colourless areas of thin sections at medium to high magnification. Oil immersion optics were used for such observations. However, because the intergrowth textures are finer than the 30 micron thickness of the normal petrographic thin section, electron back-scatter images were later used to make detailed observations (eg Appendix 10a, Fig 1).

Calcite in the calcite/brucite intergrowths can usually be identified by its optical properties with reasonable certainty. In contrast, the identification of **brucite** under the optical microscope is precarious, given its propensity to be replaced by serpentine, with which it has many optical properties in common. Where **brucite** is referred to in these petrographic

descriptions, its identification is therefore based on a combination of the optics described here, with X-Ray diffraction, microbeam, and thermal analytical techniques which are detailed in the following sections.

Brucite/calcite intergrowths are largely replaced by **serpentine**; when optically clear such serpentines exhibit fine-grained "serporphite" optics in transmitted light. In general, to ascertain the presence of reasonably pure serpentine, however, it was found necessary to carry out electron microbeam analyses, because optical serpentine frequently carries minor brucite, as is detailed in Section 10.3.3.

Whereas the brucite/calcite **intergrowths** are on a 20 micron scale, the calcite phase of these intergrowths has been observed to be optically continuous on a 500 micron scale and larger (Plate 10.3).

10.2.3.3 Sample KBult 23

Sample KBult 23 is a granular garnet lherzolite, the silicates of which require no detailed description here.

Black lenticles are relatively rare, about one per thin section. They are lenticular in the strict sense, possibly due to the absence of visible deformation of the rock as a whole. The black lenticles consist dominantly of serpentine, and only rare 50-micron elipsoidal "islands" of calcite/brucite-serpentine intergrowth were ascertained by microbeam methods. Whether these islands are remnants of a once larger area of calcite/brucite intergrowth, or reflect a low volume of calcite component in an original carbonate grain is discussed later.

10.3 ANALYTICAL METHODS AND RESULTS

10.3.1 Thermal Analysis

Bulk peridotite powders were studied by differential thermogravimetry (DTG); 20 mg samples were used and further analytical details are given in Appendix 8c (Section 16.2.2b) in Volume 2. Results of quantitative thermal analysis of brucite in 10 peridotites are recorded in Appendix 10c, Table 10.1

The highest concentrations of brucite in bulk rocks coincided with the presence of the greatest number of black lenticles. These black lenticles were therefore examined by X-ray diffraction (XRD) as outlined below.

10.3.2 X-ray diffraction

Samples of about 5 mg chips of black lenticles were mechanically removed from hand specimens by means of an engraving tool and examined by standard XRD techniques for small samples. Details of the apparatus and methods used, as well as d-spacings obtained and their interpretation, are presented as Appendix 10d, Table 10.2.

For the purpose of the following discussion the pertinent results are:

- a.) Some black nodules consist of brucite and calcite only;
- b.) In addition to brucite and calcite, black nodules may contain phlogopite, serpentine and graphite.

10.3.3 Microbeam analysis

Microbeam methods were applied to determine the spacial disposition of the minerals known from the XRD results to be present in the black lenticles. Details of the analytical

procedure, typical analyses and their interpretation to identify phases are given in Appendix 10d, Table 10.3.

The mutual dispositions of calcite and brucite were recorded for selected areas by means of electron backscatter photographs (eg Appendix 10a, Fig 1).

10.4 DISCUSSION OF RESULTS

10.4.1 Layout of Discussion

The present section (10.4) concentrates mainly on summarising the mineral chemistry and elucidating the textures of the black lenticles. This requires an integration of all the thermal, XRD and microbeam analytical and textural data. The observations made lead to the conclusion that the brucite/calcite intergrowths are the youngest remaining primary texture of the black lenticles, and that the serpentine and probably graphite reflect secondary alteration. From this follows the hypothesis that the black lenticles represent metamorphosed dolomitic carbonate from the mantle. This hypothesis is examined further in Section 10.5.

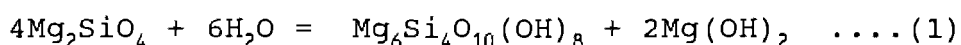
The low brucite contents of most of the rocks studied (Appendix 10d, Table 10.1) are very relevant to the **preservation** of the brucite/calcite intergrowths, but not to the interpretation of their origin. The low brucite contents will therefore be treated first and separately in this discussion under Section 10.4.2.

The presence of graphite deduced from the XRD data will similarly be "disposed of" early in the discussion under Section 10.4.3, because this, too, appears irrelevant to the origin of the black lenticles.

10.4.2 Thermal analysis

The amounts of brucite in most of the peridotites studied by DTG are substantially lower than would be found if the rocks had been serpentinitised isochemically (Appendix 10d, Table 10.1). The basis for this interpretation is explained below:

The isochemical reaction for the serpentinitisation of forsterite (Fo):



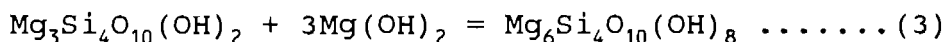
produces 17.39 wt% of brucite and 82.61 wt% of serpentine; these combined carry 16.1 wt% of water, giving 1.08 wt% brucite for every 1 wt% H_2O^+ . This (17.39) is the theoretical maximum amount of brucite that can be expected in an isochemically serpentinitised Mg-rich dunite.¹⁶ The amount of brucite that will be present in partially but isochemically serpentinitised dunites can be calculated for individual cases on the basis of the H_2O^+ analysis.

The theoretical maximum amount of brucite based on equation (1) will never be achieved in a typical peridotite nodule from a kimberlite because of the presence of enstatite. Enstatite on its own would produce serpentine and talc according to the reaction:

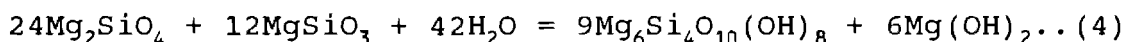


¹⁶The olivines from peridotite xenoliths from kimberlite are about Fo_{90} . The effect of the iron in these olivines on the serpentinitisation reaction depends on the oxygen fugacity. At high oxygen fugacities iron, as Fe^{3+} , goes into magnetite, and consequently serpentine and brucite are relatively magnesian. At lower oxygen fugacities, where iron is Fe^{2+} , iron-rich serpentines and ferro-brucites form (see Appendix 8 for examples from kimberlites). The serpentines from peridotites (analyses appear on Table 10.2, Appendix 10) contain on average about 2.5 wt% FeO (total iron expressed as FeO), and the brucites about 6 wt% FeO. In both cases this represents about half the amounts of FeO relative to MgO as compared to the Mg/Fe relation in Fo_{90} . The proportions of phases calculated here using the pure magnesian equations will therefore be accurate to about 5 - 10% of those likely to occur in the natural rocks; this is an adequate approximation for the following discussion.

In practice the talc would not be realised during isochemical serpentinisation of a peridotite in which olivine is the dominant phase, because talc is not stable in the presence of brucite with which it would react to make more serpentine thus:

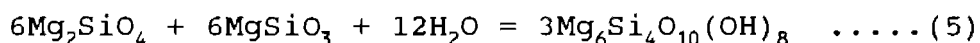


The complete reaction can be written as follows for the case of a model harzburgite xenolith in kimberlite with 2 moles of olivine to 1 mole of orthopyroxene:



For the right-hand side combined $\text{H}_2\text{O}^+ = 14.16 \text{ wt}\%$, and
brucite = 6.55 wt%.

The reaction for equal molar proportions of olivine and enstatite leads to serpentine plus zero brucite thus:



with $\text{H}_2\text{O} = 12.99 \text{ wt}\%$ for the serpentine.

The calculation of the amount of brucite that would be produced by the isochemical serpentinisation of individual rocks is complex; first it requires accurate estimates of olivine to orthopyroxene (opx) proportions; then it must be assumed that olivine and opx are serpentinised to the same degree, which petrographic observations suggest is not the case. For the present purpose of assessing whether serpentinisation of the rocks was isochemical or open-system, the assumption is made that Equation 4 will give an acceptable approximation. This is considered reasonable because opx generally does not exceed about one third of the volume in typical harzburgites of the type studied, and garnet and cpx combined are generally below 10% in the garnet lherzolites. Thus Table 10.1 was calculated on the basis that the amount of

brucite to be expected if isochemical serpentinisation pertained can be approximated by " H_2O^+ "/14.16 times 6.55. " H_2O^+ " was taken to be approximated by the available loss of ignition data (LOI) at 950°C (Berg, unpublished). This latter approximation may be in error for two reasons: (a.) it is reduced below the value of true H_2O^+ because of the oxidation of iron, and (b.) it will be increased because the loss of CO_2 from calcite will be calculated as water. The results of these calculations are given in Table 10.1, together with the actual percentages of brucite measured.

Comparison of the calculations with the results measured leads to two clear conclusions:

First, most samples carry significantly less brucite than would be produced by isochemical serpentinisation. This implies that the rocks were serpentinised as open systems and have lost brucite in solution during the serpentinisation process. As a result their bulk compositions will have lower MgO/SiO_2 ratios than the original fresh unserpentinised rocks they represent in the mantle. The effect of this loss could be significant in the interpretation of bulk major analyses of xenoliths, but this aspect is outside the scope of the present Chapter.

The apparent loss of brucite to brucite-under-saturated serpentinising fluids implies the passage of solutions which will with equal facility dissolve brucite which is already present in the rocks prior to the serpentinisation. This is thought to explain the poor preservation potential of the calcite/brucite intergrowths which are the main subject of this Chapter, and hence in part why they were overlooked for so many decades.

The second significant observation to be made on Table 10.1 is that only KBult 22 contains enough brucite to suggest that the rock might have been more or less isochemically

serpentinised. However, microbeam analyses combined with petrographic study indicate that the brucite is concentrated in calcite/brucite intergrowths, and not significantly associated with the serpentinisation of silicates (see Sections 10.2.3.2 and 10.4.4).

Ideally a quantitative DTG study should have been made on the same powder which yielded the first XRD pattern of calcite and brucite, to determine their relative volumes. Unfortunately the thermal apparatus was rendered inoperable by a laboratory explosion before this could be done.

10.4.3 X-Ray diffraction

10.4.3.1 Minerals whose origin must be explained

As recorded in 10.3.2 and Appendix 10d, Table 10.2, XRD of black lenticles revealed two assemblages whose histories must be explained:

- 1.) brucite and calcite, and
- 2.) brucite, calcite, serpentine and graphite.

These minerals are discussed in more detail below:

10.4.3.2 Graphite

Graphite is considered together with serpentine to probably reflect a secondary replacement of brucite and calcite. It may appear irrational to discuss replacement minerals before it has been shown that brucite and calcite really represent the primary assemblage. But the elucidation of the history of the brucite/calcite intergrowths will require recourse to microbeam data combined with XRD, whereas graphite was detected by XRD

only; graphite is therefore discussed here, to the benefit of continuity of later discussion.

Graphite has been observed in kimberlite by Pasteris (1981), who considers as possible sources:

- (a) carbon in solid solution in olivines,
- (b) carbon in CO₂-rich fluid inclusions in olivines, and
- (c) carbon precipitated from the carbonate-rich kimberlite environment during serpentinisation under reducing conditions.

Pasteris (1981) favours alternative (c) above; she notes in support of reducing conditions the paucity of magnetite in serpentinised olivines where the graphite is found. The iron from serpentinised olivine appears to have remained in the ferrous (reduced) state, giving rise to iron-rich serpentines. Examples of analyses of such serpentines are given by Mitchell (1986, Table 6.32, including reference to Pasteris, 1980, PhD thesis); and by Berg (1989/Appendix 8c, Table 16.4. Anal. 10). Whatever the source of the carbon, the prime evidence presented by Pasteris (1981) which links graphite with serpentine is a close petrographic association: graphite flakes are aligned with the zoning of zoned serpentines. Pasteris (1981) further reports having observed graphite in a peridotite xenolith, but presents no further details.

Pasteris (1988) describes additional occurrences of graphite, co-existing with carbonate within fluid inclusions in olivines from the Kao kimberlite from Lesotho; this kimberlite is also reported to contain graphite within areas of serpentinisation of olivines (op.cit.). As in the case of the graphite associated with serpentine, Pasteris (1988) shows that the graphite associated with calcite in fluid inclusions probably formed at less than 2 kb.

Against the above background and the limited data at present available, there is no unequivocal evidence with which to characterise the graphite identified by XRD in KBult 22 (Table 10.2, Appendix 10d) as secondary or primary. A primary origin remains plausible in the light of:

- a.) the documentation of primary graphite in peridotite nodules (Pearson et al 1990),
- b.) the observations of Pasteris (1988) on the possible stability of graphite at high temperatures and pressures, and,
- c.) the evidence for the operation of buffers in the mantle such as EMOG (enstatite, magnesite, olivine, graphite) and GEDOD (graphite, enstatite diopside, olivine, dolomite) at which graphite could co-exist with carbonate in the mantle (see for example Blundy et al (1991) and references therein).

Since graphite in the black lenticles is indicated by XRD only, its petrographic association is largely unknown. Three powders were examined. Two of them were found to contain brucite and calcite only (eg Table 10.2a). In the third powder graphite **and** serpentine were found in addition (see Appendix 10d, Table 10.2b). This association the only detected graphite with serpentine, combined with Pasteris's (1981) observations on graphite associated with serpentine in kimberlite, suggests a secondary origin for the graphite in the black lenticles, associated with their pervasive, sometimes total, serpentinisation. It is emphasised that Pasteris (1981) considers serpentinisation in **kimberlites**, but it is not unreasonable to apply her deductions to nodules such as KBult 22, on the supposition that 30 cm sized nodules cannot escape the conditions of serpentinisation of their host-kimberlites.

The origin of the graphite in KBult 22 might be elucidated by polished section study as described by Pasteris (1981), but Raman spectroscopy might yield more definitive results.

Pearson et al (1990) note that primary graphite in peridotites is characterised by two single Raman lines at 2700 cm^{-1} and 1581 cm^{-1} . In contrast, the graphite thought by Pasteris (1981) and Pasteris (1988) to probably be a low temperature secondary mineral has an additional Raman peak at 1350 cm^{-1} , which reflects structural disorder.

Should primary graphite be proven to be part of the postulated precursor carbonate of the brucite/calcite intergrowths, it would not change the main conclusion made here. It would merely constrain the conditions of origin of the original carbonate more tightly to a graphite-containing buffer.

10.4.4 Microbeam Analysis

10.4.4.1 General observations

Typical brucite, calcite and serpentine analyses are assembled on Table 10.3 of Appendix 10d, together with detailed interpretations.

Brucite and calcite were located in areas such as those illustrated on Fig 1, Appendix 10a.

Brucite was observed under the electron microbeam in three textural associations, namely:

- a.) In brucite/calcite intergrowths making up black lenticles of up to 4 mm in cross section (eg. Analyses 1, 2 and 8, KBult 22, Table 10.3, Appendix 10d).
- b.) Brucite as relatively minor patches of about 15 microns within serpentine which constitutes the bulk of a black

lenticle, and is interpreted as a replacement of brucite/calcite intergrowth. Compositions do not differ significantly from those reported under (a.) above.

- c.) Brucite in serpentine which replaces the **olivine** of the peridotite host; such brucite is very fine and is inferred from mixed analyses (eg. Analysis 7, Table 10.3, Appendix 10d).

The texture of assemblage (a) is thought to be critical to the interpretation of the history of the black lenticles, as discussed below.

10.4.5. Microbeam Petrographic Textures

10.4.5.1 The critical role of textural interpretation

The identification by XRD of coexisting brucite and calcite in black lenticles was undertaken before the microbeam analyses. The combination of these two minerals immediately suggested that the black lenticles could represent metamorphosed dolomite (Harker 1974, p77). This interpretation is based primarily on the co-existence of brucite and calcite, a well known association for which no other origin than the thermal metamorphism of dolomite is known. The XRD results **on their own** do not exclude alternative modes of formation, however; and such alternatives must be considered to assure a sound interpretation. For example, might the black nodules not represent concentrations of brucite formed during the course of serpentinisation, together with calcite unrelated to the serpentinisation? This question is reasonable because post kimberlite-emplacment serpentinising solutions may be saturated with the calcite of the kimberlite host through which they have to pass before they affect the xenoliths; and veins of transported brucite in association with serpentinising systems are known (see for example Luce 1971; Barnes et al 1972). An origin of brucite formed during serpentinisation, occurring together with unrelated calcite, would, however,

probably lead to recognisable textures such as cross-cutting relationships or random intergrowths with little optical continuity in the calcites. There is no evidence for cross-cutting in the textures introduced in Section 10.2.3.2; nor does the parallel optical continuity of some of the calcites (10.2.3.2 and Plate 10.3) suggest deposition from circulating solutions. Yet the textures of the brucite/calcite intergrowths do not remotely resemble those of thermally metamorphosed dolomites either.

It will be argued below that the brucite/calcite intergrowths considered here most probably do reflect metamorphosed dolomitic carbonate, from the mantle; but that their textures differ from those of presently documented calcite/brucite assemblages such as predazzite marbles, because they followed different metamorphic paths and thus kinetics. In common metamorphosed dolomite, decarbonation takes place up-temperature, and slowly. In contrast, the decarbonisation reaction in the rocks studied here took place down-pressure, and rapidly. The evidence lies in the combination of the morphology of the intergrowths and the topology of the black lenticles in which they occur.

10.4.5.2 Morphology of the intergrowths

The brucite/calcite intergrowth textures, exemplified by Fig 1, Appendix 10a, resemble both in pattern and scale the type of intergrowth illustrated by de Wit (1980, fig 9), and discussed by him with reference to the text by Nicholson and Davies (1971).

The textures are best referred to as eutectoid. These are textures formed during solid state reactions; the textures are morphologically very similar to textures which can form by eutectic crystallisation from melts. The solid state analogue of eutectic crystallisation is "eutectoidal decomposition which involves the formation of two new phases from a parent matrix"

(de Wit, op. cit.). This is thought to apply here to a first stage decarbonation of dolomite to yield calcite and periclase¹⁷, with the additional factor of the loss of a gas phase. Eutectoidal textures of the type described and referred to here are characteristic of rapid growth in the solid state. This is consistent with the solid state decarbonation of a dolomitic carbonate in the down-pressure regime of a relatively hot nodule en route from the mantle to the surface.

The timing of metamorphism can sometimes be constrained relative to deformation by petrographic studies (Spry, 1969; Vernon 1979). Such chronological evidence as may be applicable to the rocks studied here is evaluated below:

10.4.5.3 Topology of the lenticles in relation to textures of host-rocks

Two fundamentally different textures in peridotite nodules from kimberlite were recognised as granular and sheared by Boyd (1973). For the purpose of the present study these distinctions are adequate; they are now referred to as coarse and porphyroclastic respectively, following Harte (1977), who discusses in more detail the nature and nomenclature of these textures.

Originally Boyd (1973) suggested that sheared nodules reflected movement at the base of lithospheric plates. The more generally accepted interpretation at present is that the sheared nodules reflect the movement of a diapir in the mantle, from which kimberlites formed and took samples, in the form of nodules, with them to the surface, (Green and Guegan, 1983).

In a transmission electron microscope study of the microstructure in olivines in a porphyroclastic peridotite

¹⁷ See also Footnote 19 of Section 10.5.2.6

nodule from the Thaba Putsoa kimberlite, Lesotho, Green and Guegan (1983) conclude that deformation and recrystallisation continued at a high strain rate until nodules were finally entrained by the host kimberlite for their trip to the surface. They further conclude that the nodule "reached the surface after not more than a few days (probably much less) in the magma....Moreover, the lack of low temperature (110) slip bands and the presence of annealing recrystallisation indicate that no significant deformation occurred during the trip to the surface" (p 84).

What can this deformation chronology contribute here?

Sample KBult 23 is coarse, granular, and offers little topological information on the chronology of how the black lenticles were formed or evolved.

KBult 22 is sheared and the black lenticles appear to be deformed by the shearing (Plate 10.1 B). Being thus affected by a pre-entrainment deformation, this would imply that the black lenticles were present in the mantle before the nodule commenced its journey to the surface. (The condition of the lenticles, whether solid or partially molten during shearing, is not necessarily revealed by their exterior form. The dihedral angles (28 degrees) of carbonate melts in rocks of mantle composition, determined by Hunter and McKenzie (1989), nevertheless indicate that the lenticles were not completely molten.)

The brucite/calcite intergrowth texture within the black lenticles is not deformed by the shearing event (Fig 1, Appendix 10a). Given the above discussion, it therefore follows that the eutectoid intergrowth post-dates the beginning of the journey to the surface.

In summary, the chronology implied by the topology of the lenticles and their interior textural relations constrains the

formation (or introduction) of the black lenticles to prior to entrainment, and the development of the brucite/calcite eutectoidal intergrowths, subsequent thereto; as will be shown they probably developed during ascent.

What constraints can be attached to this ascent to the surface on the basis of previously published work?

10.5 GENERAL DISCUSSION

10.5.1 Preliminary discussion of the ascent path

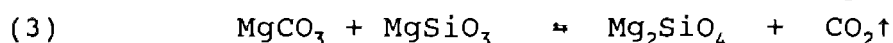
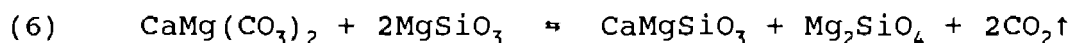
10.5.1.1 Ascent and emplacement velocities

There is little consensus on the **rate** of ascent of kimberlites. High velocities, of up to Mach 1 at the final exit stage, have been modelled (eg McGetchen and Ullrich, 1973; Anderson, 1979); but Egglar (1989) argues that kimberlites need not have higher emplacement velocities than other alkaline rocks. Egglar (1979) reviews evidence for velocities of the order of 1.5 to 30 km/hr. Thus we have no independent evidence with which to constrain the ascent rates over the specific depth intervals pertinent to the present study. These ascent rates are important, because combined with atomic diffusion rates, they determine whether there is enough time for nodules to re-equilibrate to lower P,T assemblages as they travel upwards. The intervals of particular interest here are:

- a.) in the 20 - 40 kb regions where carbonate, given enough time, would decarbonate by reaction with silicates (see 10.5.1.2), and
- b.) in the pressure range below about 12 kb where carbonates decarbonate independently of silicates (10.5.1.3).

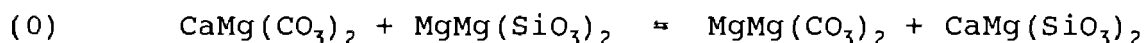
10.5.1.2 Silicate-carbonate reactions during ascent

In the 20 - 40 kb pressure range, depending on temperature and composition, decarbonation by reactions 3 and 6 reviewed by Wyllie et al (1983) may occur as a nodule travels to the surface.¹⁸ These reactions are:



These are the reactions postulated by Eggler (1975) to be responsible for the paucity of carbonate in the peridotite xenoliths. (On Fig 10, Appendix 10c, reaction 6 is the transition between LH + CO₂ and Do LHZ).

An additional reaction of interest concerns whether dolomite or magnesite are stable in a given mantle assemblage; this is Reaction 0:



(See the transition from Do LHZ to Mag LHZ, Fig 10.)

Silicate-carbonate decarbonation reactions are considered in more detail in Section 10.5.2.4, and implications of Reaction 0 are explored in Section 10.5.2.6.

10.5.1.3 Decarbonation independent of silicates

The decarbonation curve for dolomite determined by Goldsmith (1980) is shown on Fig 10. The ascent path becomes critical for this reaction between about 13 and 5 kb, depending on the temperature.

¹⁸ This Chapter follows the numbers designated for carbonation reactions by Wyllie et al (1983), including the "degenerate" Reaction 0.

The wide range of ascent paths that have been modelled for kimberlites is illustrated on Fig 10. The path followed by kimberlites in practice depends on the combination of rate of ascent and rate of heat loss. The adiabatic heat loss can be calculated (eg, Anderson, 1979); the ascent rate is poorly constrained, however, even if only the relatively low rates advocated by Eggler (1989) are entertained (10.5.1.1.); and there are too many variables ever to calculate the rate of heat loss by conduction.

The information about ascent paths pertinent to decarbonation reactions must therefore be sought in the rocks themselves. The only available such ascent path was deduced by Green and Guegan (1983) on the basis of solid-state exsolution phenomena in olivine, observed by transmission electron microscopy in a peridotite nodule from Thaba Putsoa. This ascent path will be related to the brucite/calcite intergrowths in nodules from Kimberley in Section 10.5.2.6.

10.5.2 Evidence for carbonate in the mantle

10.5.2.1 Scope of discussion

Evidence and counter-evidence for carbonate in the mantle, based on rocks or simulated rocks in experiments, is of five kinds:

- a.) it is not there because conditions are too reducing; (see 10.5.2.2)
- b.) it must be there on the basis of experiments; (see 10.5.2.3)
- c.) we rarely see it because it reacts with silicates before reaching the surface; (see 10.5.2.4)
- d.) we rarely see it because it decarbonates explosively during emplacement; (see 10.5.2.5) or,
- e.) it is metamorphosed en route to the surface to fine grained assemblages that have such a poor preservation potential that they have been largely lost, due to dissolution

replacement in post-emplacement water circulation, or simply overlooked to date (see 10.5.2.6).

These suggestions are discussed under the next five headings, with emphasis on areas where the present study may contribute.

10.5.2.2 The oxidation state of the mantle

The possibility has been investigated that the oxidation state of the mantle is so low that carbon is in the form of CH_4 rather than carbonate (see Arculus and Delano, 1987 and Boetcher, 1984). This field of study remains active (see for example Blundy et al, 1991). The present work suggests that rather than just CH_4 , carbonate may indeed be present, but contributes nothing further on the oxidation state of the mantle. This subject is therefore not pursued here.

10.5.2.3 Experimentally determined carbonation reactions

Experimental evidence that carbonate can form in the mantle above about 20 kb is well established, assuming appropriate oxygen fugacities (see Wyllie, 1969; Egglar, 1978 for early experiments, and the subsequent review by Wyllie et al, 1983). The foregoing work concerns the stability of carbonate in the mantle to pressures of around 50 to 60 kb. More recent experimental studies have established the stability of carbonate in the lower mantle to pressures of about 500 kb (Biellmann et al, 1993). The results of the present work are consistent with the general experimental predictions that carbonate occurs in the mantle; possible inconsistencies between experimental predictions and the type of observed (meta)-carbonate (dolomite or magnesite?) are discussed in Section 10.5.2.6

10.5.2.4 Silicate-carbonate decarbonation reactions

The argument that carbonates react with silicates en route to the surface and are therefore not observed in samples of the mantle has been referred to previously (Section 10.5.1.2.), with reference to Egglar (1975). It seems plausible that such reactions, being very rapid, might produce reaction coronas. No such petrographic evidence has been reported, but it should be searched for.

Whereas Egglar (1975) suggested that the above-mentioned reactions consumed carbonates at between 60 to 120 km below the surface before emplacement, an alternative body of opinion suggests that the carbonates survived to decarbonate independently at much shallower levels (Boyd and Gurney, 1982; Wyllie et al 1983; Berg, 1986). Canil (1990) sought to resolve the two approaches experimentally, as discussed below:

Canil (op. cit.) designed his experiments to "...simulate the entrainment of a carbonate-bearing xenolith in a host magma at a depth of about 75 km...". To achieve this he used starting materials of enstatite and calcite ground to less than 10 microns. At experimental decompression rates equivalent to between 45 and 90 km/hr all carbonate was reacted out, with the evolution of CO₂.

On this basis Canil (op. cit.) concludes that "...the results of this study indicate that carbonate-silicate breakdown reactions.....can be considered mechanisms that prevent the preservation of carbonate in mantle xenoliths."; and, ".....the results reported here clearly demonstrate that carbonates can decompose to produce fluid within minutes by reaction with their coexisting pyroxenes during decompression...."; and further that, "With such kinetic limits on their stability, it would be virtually impossible for carbonates in mantle xenoliths to survive entrainment in their typical host magmas".

Canil (op. cit.) thus doubts the likelihood of carbonate ever surviving to be observed (metamorphosed) as suggested by Berg (1986) or to decrepitate explosively as suggested by Boyd and Gurney (1982).

Canil (op. cit.) is quoted uncritically by Blundy et. al. (1991) to the effect that, "...it has recently been shown experimentally that carbonates in mantle assemblages rapidly decompose on decompression. Thus the apparent lack of carbonate in mantle samples...may entirely be an artefact of the volcanic processes which brought them to the surface". It may indeed, but not necessarily for the reasons implied above.

The grainsize in mantle xenoliths is 2 to 3 orders of magnitude larger than in the mixes used by Canil (op. cit.) to investigate the kinetics of silicate-carbonate reactions. Furthermore, a carbonate grain in a rock may not necessarily be in contact with a pyroxene with which it would react given time for perfect equilibrium. The relevance of Canil's (op. cit.) 10 micron experiments to reaction rates in real rocks in the mantle therefore remains open to debate.

There is little other evidence available on reaction rates. Green and Guegan (1983) have documented exsolution precipitation of spinels and fluid inclusions from olivines in the peridotite from Thaba Putsoa referred to previously. The spinel could only form after the host nodule had passed the garnet/spinel transition at about 75 km depth en route to the surface. Thus we do have evidence that there was time for within-grain exsolution-precipitation, but this yields no information on the feasibility of between-grain decarbonation reactions postulated by Eggler (1975) and Canil (1990) to have occurred at about the same time.

The only contribution of the present work to the silicate-carbonate decarbonation problem is to suggest that either emplacement rates were too rapid for these reactions to occur,

or if they occurred they did not necessarily do so in all kimberlite intrusion events or use up all the available carbonate. The evidence lies in the existence of the brucite/calcite intergrowths discussed again in Section 10.5.2.6.

10.5.2.5 Explosive decarbonation

That rapid decarbonation may have led to decrepitation of both carbonate and host nodules is backed by evidence reviewed below; sources are Boyd and Gurney (1982) and Gurney (pers comm 1991 and submitted for publication).

Diamondiferous kimberlites carry discreet subcalcic garnets; the Ca content of these garnets is significantly lower than 4 wt% CaO which is the minimum that could exist in a garnet in equilibrium with diopside; these garnets could therefore only have been equilibrated in diopside-absent assemblages, which were probably harzburgites.

Evidence that such harzburgites might have contained carbonates includes the following:

- a.) The discreet subcalcic garnets carry unusually high concentrations of Sr, suggesting equilibration with a carbonate that included a calcic component which made it a potential Sr reservoir;
- b.) the low-Ca garnets are light REE enriched, also consistent with equilibration with a carbonate;
- c.) the low-Ca character of the discreet subcalcic garnets is consistent with equilibration with a carbonate into which Ca partitions strongly;
- d.) Finally, the presence of very low-Ca garnets only as discrete minerals, but not in harzburgite nodules, is consistent with the carbonate which such nodules are thought to have contained for reasons outlined above, having decrepitated explosively during emplacement.

It will be of interest to measure the Sr concentration in the calcite of the brucite/calcite intergrowths described by Berg (1986)/(Appendix 10a). This data may help test the postulated model for Sr enrichment of low-Ca discrete garnets, when appropriate partitioning data becomes available. Brenan and Watson (1991) report partitioning for some elements between carbonate melt, clinopyroxene and olivine; data for garnet will be a useful addition to corroborate aspects of the evidence summarised under (a) to (d) above. The co-existing silicate and carbonate minerals in the rocks studied here should in the meantime be studied further in the light of the partitioning data published by Brenan and Watson (1991).

On the available evidence reviewed above, there is no reason to dispute that decrepitation of nodules may occur by explosive decarbonation. However, this need not happen universally and the hypothesis should be tempered with the evidence for extreme delicacy of the products of decarbonation proposed in the present work.

10.5.2.6 Non-explosive decarbonation independent of silicates

Wyllie (1979) wrote in connection with a diagram illustrating dolomite in the mantle: "...I would feel happier about this diagram if there were more occurrences of dolomite in peridotite nodules than the single example reported by McGetchin and Besancon (1973)". Further direct evidence has accrued but slowly.

Herwig and Smith (1981) report the presence of dolomite in a chrome diopside crystal from the Bellsbank kimberlite. These authors suggest that both the dolomite and its host diopside crystallised from a partial melt in the mantle at a depth of less than about 100 km. As such it represents evidence for a carbonated melt, like kimberlite, in the mantle, and is not a sample of carbonate within a postulated source mantle peridotite or mineral constituent thereof; it was therefore not

referred to by Berg (1986). J.V. Smith (pers. comm. 1987) considered this a significant omission. In the strict, if pedantic, sense, the Herwig and Smith (1981) report of dolomite in chrome diopside crystals is an occurrence of carbonate **from** the mantle and this was mentioned in a short Corrigendum (Berg, 1987) together with reference to Hunter and Smith (1981); these authors (op. cit.) reported inclusions of dolomite in crystal fragments of pyrope from diatremes of the Navajo Province, similar to those described by McGetchin and Besancon (1973), in a paper unfortunately overlooked by Berg (1986a). Smith (1987) further investigated the pyropes from the Colorado plateau, and finds most of the evidence to point to an origin for their carbonate inclusions related to the parental mantle melts of the ultramafic host rocks.

Berg (1986 a,b) reported the first suggested protoliths of carbonate in olivine bearing mantle assemblages. He concluded that the brucite/calcite intergrowths discussed here represented decompression-metamorphosed dolomite from the mantle, and it is pertinent to now discuss some pros and cons of this model.

How and when did the brucite/calcite assemblage form? Do they really represent carbonate from the mantle? If so, why is it dolomite and not magnesite? Explosive decrepitation of nodules is a plausible mechanism, as discussed above; if it occurred for harzburgites carrying high-Cr/low-Ca garnets, how did the nodules carrying black lenticles taken to represent meta-carbonate survive? These questions are addressed below.

It is suggested (Berg, 1986a) that the black lenticles described here had dolomite precursors by analogy with the general reaction (sic) $\text{Ca}(\text{CO}_3)_2 = \text{CaCO}_3 + \text{MgO} + \text{CO}_2$ used by Harker (1974, p.77) to illustrate the formation of pectatite and predazzite marbles, the production of periclase

being followed by its hydration to brucite¹⁹. In the rocks studied here the simple reaction depicted above will be complicated solid solution effects (Graf and Goldsmith, 1955; Goldsmith, 1959), and the probable non-stoichiometry of the starting material implied by the narrowing of the dolomite-magnesite solvus with increasing temperature at high pressures (Irving and Wyllie, 1975). The term "dolomite" is therefore used here in the broad sense to indicate what was probably a dolomite-magnesite solid solution precursor of the brucite/calcite intergrowths. Further elucidation of this aspect requires determination of brucite/calcite ratios; these will be difficult to obtain because of the poor preservation potential of the intergrowths. Progress may be made by means of thermal analysis (10.4.2) and/or texture analysis of back-scatter images of intergrowths.

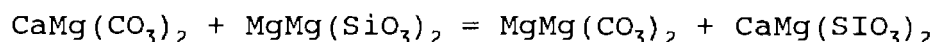
Instead of being formed as a result of increasing temperature as is the case in most metamorphic reactions, the brucite/calcite intergrowths described here are thought to have formed in response to decompression upon kimberlite emplacement. This is reflected in their eutectoidal textures as discussed in Section 10.4.5.

In the preliminary discussion of the ascent paths followed by kimberlite (10.5.1.3), it was concluded that the best source of information lay in the rocks themselves. To date only the study of Green and Guegan (1983) has yielded an ascent path deduced from solid-state exsolution phenomena. This ascent path has been transferred onto Fig 10, labelled "GG 83". I could not have drawn a better hypothetical ascent curve on Fig 10 with which to account for the calcite/brucite intergrowths in black lenticles, except perhaps in the lowest-temperature region where the GG 83 ascent curve deviates from the dolomite

¹⁹ The hydration of periclase by **addition** of water involves a significant increase in volume. Such an increase might be expected to destroy the delicate intergrowth texture illustrated on Fig 1 of Appendix 10a. It is not clear whether the preservation of the texture is due to partial dissolution of brucite, analogously to constant volume serpentinisation, or whether brucite was formed directly in the dolomite decarbonation reaction due to a high partial pressure of water.

decomposition curve of Goldsmith (1980). The GG 83 curve best accounts for the calcite/brucite intergrowths because it runs close to the equilibrium between the postulated precursor dolomite, and the calcite, magnesite and carbon dioxide decomposition products. Hovering, as it does, on the equilibrium, this ascent path is least likely to lead to the reaction being spontaneously explosive. In contrast, the two extreme possible ascent paths illustrated by Egglar (1989) ("EG89?" on Fig 10), well illustrate ascent paths likely to lead to explosive decrepitation. This is because these paths pass over the equilibrium almost at right angles and proceed as far as 10 kb into the metastable brucite/calcite region. The result is a high driving force for the reaction to proceed, which may become explosive as pressure is rapidly reduced below equilibrium. Evidence reviewed here and in the previous Section suggests that both explosive and equilibrium paths may be followed; it is not unreasonable, therefore, to postulate at this stage that kimberlites do not all follow the same ascent rates of emplacement.

We now continue to higher pressures through the questions posed early in this Section. The problem of how carbonate survives into the region between silicate-carbonate decarbonation reactions and decarbonation of the carbonate independantly on or down-pressure of the Goldsmith (1980) dolomite stability curve has already been addressed in Section 10.5.1.2. We can therefore proceed to consider why dolomite instead of magnesite is found in some nodules from kimberlites; this question relates to the degenerate exchange reaction (0):



The P,T position of reaction (0) has been reported over a considerable range; five curves are reviewed by Wyllie et al (1983, Fig 8), which differ from one another by as much as 15 kb at 900 °C.

When the work discussed here was first orally presented at the Fourth International Kimberlite Conference in 1986 in Perth, I suggested that the highest pressure estimate for reaction (0), reported by Egger, Kushiro and Holloway (1976) (labelled "EKH" by Wyllie et al 1983, fig 8) might prove most consistent with the evidence of brucite/calcite intergrowths in the rocks from the mantle; this is because the high pressure curve is closest to the Boyd and Nixon (1978) geotherm of the lithosphere. Egger (Pers. Comm. 1986), however, doubted the validity of the EKH curve, and rather concurred with Wyllie et al (1983) who prefer the result of Brey et al (1983).²⁰ According to this curve all carbonated lherzolites and harzburgites from kimberlites such as Premier Mine (and by analogy, Kimberley) should carry magnesite rather than dolomite. The problem of this apparent discrepancy may be resolved, at least in part, as follows:

First, the experimental determination of the curve for reaction (0) proved to be rather difficult. Of the five determinations reviewed by Wyllie et al (1983) these authors' preference for the curve of Brey et al (1983) must be accepted. However, bearing in mind the disparate estimates that were made over a dozen years or so, as reviewed by Wyllie et al (1983), it may be prudent to allow for at least minor refinements in the position of reaction (0). The effect of iron on the equilibrium is not clear. The equilibria of interest have not yet been determined for the iron carbonates, which involve formidable considerable experimental difficulties (Wyllie Pers comm 1986).²¹

Second, with reference to the dolomite here inferred to have existed in the mantle in KBult 22, reaction (0) predicts

²⁰ That is not to say that Egger thereby rejected the evidence reported here; he writes in the proceedings of IKC4 with reference to Appendix 10 (Berg 1986), "Although dolomite and magnesite are rarely observed peridotite minerals, Berg (1986) has found possible protoliths of dolomite in brucite-bearing peridotites."

²¹ Note added in proof: A paper co-authored by D Wood, has since resolved this problem, but came in too late for inclusion here.

magnesite rather than dolomite in lherzolites. KBult 22 is a wehrlite. Reaction (0) can therefore not proceed for lack of enstatite. The presence of a dolomitic solid solution in this particular carbonated peridotite on the geotherm defined by the Boyd and Nixon (1978) geobarometer is therefore hardly remarkable. It is constrained by the bulk chemistry of that local environment. The rock is carbonated to a high degree, presumably by metasomatism, which may have reacted out all available enstatite.

Reaction (0) does pose a problem to the hypothesis that the intergrowth studied in the garnet lherzolite KBult 23 reflect remnants of decompression-metamorphosed dolomite. As discussed previously, dolomite in the pertinent P,T environment of the Boyd and Nixon (1978) geotherm for Kimberley would react, according to Reaction 0, with enstatite to form magnesite. It seems premature, however, to dismiss the evidence in this sample out of hand on the basis of reaction (0). More black lenticles need to be studied before firmer conclusions can be made in this area. In particular, we need garnet lherzolites carrying better preserved calcite/brucite intergrowth, to be certain that the "islands" of calcite/brucite intergrowth observed in KBult 23 are correctly interpreted to represent remnants of a larger uniform intergrowth pattern which has for the most part been replaced by serpentine. The alternative interpretation is that the islands represent the limited amount of calcic component of a calcic **magnesite**; that the bulk of the black lenticle consisted of brucite; and that this was more readily serpentinised than the brucite where it was intergrown with calcite. There is no evidence to sustain this interpretation at present.

It is perhaps pertinent at this stage to note that there is evidence that dolomite can exist within the diamond stability field. Hill (1989) reports the first inclusion of dolomite in diamond. The formation of this dolomite, like that of KBult 22, appears to be controlled by special conditions which

isolated or otherwise precluded it from the possibility of reaction (0); in this case the diamond appears to have formed in an eclogitic environment, and armoured its dolomite inclusion from further reactions. Fig 9 of Wyllie et al (1983), partly reproduced above as Fig 10, also **illustrates** the dolomite lherzolite field just penetrating the diamond stability zone near near the carbonated solidus at about 1400°C, but at about 10 kb lower pressure than the Lesotho geotherm.

Given that magnesite is the most likely carbonate to exist in the mantle sampled by kimberlite, what then are the chances of detecting it and what evidence should be looked for? If not decrepitated explosively, magnesite will decarbonate to periclase and CO₂, or directly form brucite and CO₂, on the magnesite decomposition curve. This curve is of similar form to the dolomite decomposition curve illustrated on Fig 10 but lies at a slightly higher pressure; it has been omitted from Fig 10 for clarity.

The preservation potential of brucite in serpentinitising xenoliths is poor even when it is intimately intergrown with calcite. On its own in a peridotite nodule being serpentinitised non-isochemically, brucite may be lost even more rapidly. The only evidence of magnesite may then be the characteristic **outer forms** of black lenticles, now made up entirely of replacement serpentine. The diagnostic form in question will only be found in sheared nodules where the difference in rheological properties between silicates and carbonates appears to give rise to the smeared and boudinaged (?) forms partially illustrated in Plates 10.1 B and 10.2 C.

10.6 CONCLUSIONS

Experimental petrology reviewed or referred to earlier in this chapter has left little doubt that the carbon found in

carbonate-rich igneous rocks such as carbonatites and kimberlites is stored at their source in the mantle also as a carbonate. A wide spectrum of possible reasons why this carbonate could not readily be detected in accessible samples of the mantle such as nodules in kimberlite has been argued by earth scientists (10.5.2.). Most of the reasons suggested remain plausible, but supply little **positive** evidence that there **is** carbonate in the mantle. Until 1986 reported samples of carbonate from the mantle were limited to minute inclusions in single crystals of garnet (two reports from the same general locality), and in a chrome diopside crystal thought by the authors making the report to represent a precipitate from a **magma** in the mantle. The present Chapter and its associated Appendix 10 in Vol 2 record the first evidence for carbonate **in an olivine-bearing mantle assemblage**, and hence more direct evidence than was available previously that carbonate is indeed present in the mantle. It is shown that in this paragenesis the evidence to be sought lies in the decompression-metamorphosed products of the original carbonate protoliths, that is to say, fine-grained brucite/calcite intergrowths for dolomite, and simply brucite alone for magnesite; the latter has yet to be observed. The brucite/calcite assemblages are difficult to observe both because of their sub-microscopic textures and because they are very fragile in the late or post-emplacement environment of their host peridotite xenoliths. These xenoliths are generally serpentinitised as open systems, as shown by the low bulk-contents of brucite determined in most of the xenoliths studied (10.4.2.); brucite that originated from metamorphosed carbonate is therefore rapidly leached out and replaced by serpentine; in the case of brucite/calcite intergrowths the filigree of calcite is also ultimately dissolved out. The stable end product for practical purposes is serpentine, but in very heavily altered host-kimberlite further degradation to clays can be expected.

The key to discovering metacarbonate as reported by Berg (1986) may have been the fortuitous combination of two factors:

The first is the apparent existence of dolomite under P, T conditions where, according to experimental data, magnesite is probably prevalent; this might be a consequence of the absence of enstatite in KBult 22 (10.5.2.6). The resultant brucite/calcite meta-dolomite assemblage is easy to interpret. In contrast, meta-magnesite in the form of brucite alone is far less definitive as a meta-carbonate; if found on its own a lenticle of brucite could equally logically have been interpreted as a product of serpentinisation. Secondly, KBult 22 appears not to have been serpentinised as a totally open system, thus allowing the partial preservation of the intergrowth textures. Once documented in so obvious a form as in KBult 22, less well-preserved remnants of the textures may more readily be identified in other rocks.

The abundance of carbonate protoliths in the mantle is not yet clear; this is partly because it is not clear whether the brucite/calcite assemblages and/or their alteration products, or possibly altered meta-magnesites, have been described previously. It seems possible that they may be represented among the grains described by Boyd and Nixon (1978) as follows:

"Wavy 2-4 mm lenticles of dull brown, near isotropic, devitrified glass (?) were noted in about one-third of the nodule studied. These lenticles have the appearance of kelyphite but commonly are not associated with garnet. X-ray study showed that they are mainly chrysotile."

As noted previously (10.2.1.) and discussed in the Epilogue, both sheared and heavily metasomatised nodules are probably under-represented in the collection from which the rocks studied here were drawn. The observation of lenticles of glass (?) in about a third of the nodules studied by Boyd and Nixon (1978) would therefore form the best available estimate of the proportion of nodules which carried meta-carbonate if discussion with these authors and further study

confirms identity of the lenticles they observed with the meta-carbonates studied here.

This thesis set out to "...establish some of the limits of what can be achieved with bulk-rock analyses of kimberlites and their xenoliths..." (Ch 1). In this final Chapter we have considered the bulk-rock analysis of brucite in peridotite xenoliths, and evaluated the results to the extent further referred to in the Introduction (Ch 1): viz "..... Although the emphasis is on the understanding of secondary reactions, some fundamental data such asthe significance of brucite in kimberlite, and with respect to carbonate in the mantle, were revealed as part of the process." The results reported here and in Appendix 10 suggest that it may be fruitful to undertake further study devoted specifically to investigating possible meta-carbonates in mantle xenoliths. The relevance of the subject is re-emphasised by the work of Canil (1990), but its extension is beyond the frame of reference of this thesis.

SUMMARY AND EPILOGUE

Scope

When this thesis was begun in 1963 geologists wanted to know what the mantle is made of. Sufficient progress has been made in this direction since, that now we also want to know how the mantle works. We wish to understand the processes of partial melting which ultimately give rise to volcanic rocks at the Earth's surface (including kimberlites); and we wish to understand the convection dynamics in the mantle which drive plate tectonic movements (and, in turn, partial melting). This evolution of emphasis in research objectives reflects an inter-related progress in both geochemistry and geophysics, of which some aspects pertinent to the present thesis are traced below:

The interdependence between geochemistry and geophysics

When the thesis was begun the mantle was considered to be fairly static. The widespread study of samples such as those examined here has yielded a detailed picture of both the crystallo-chemical constitution of the upper mantle and some of the chemical processes which take place in it. (viz. Nixon, 1987). However, it was the concept of plate tectonics and sea-floor spreading rather than the enhanced knowledge of the chemistry of the earth's interior which improved our current understanding of the physical dynamics of the mantle. The evidence of sea-floor spreading has in turn been supplemented and partly overtaken by detailed seismic tomography, which is used to delineate three-dimensional temperature domains on a scale of thousands of kilometres in the mantle (eg. Su and Dziewonski, 1991). Relatively hot volumes are interpreted as the upward-moving zones of convection in the mantle; relatively cold (dense) volumes are interpreted as zones of downward, return currents of convection. The latter coincide with subduction of oceanic lithospheric slabs, some of which reside permanently in the transition zone between the upper and lower

mantle, and some of which are recycled into the lower mantle (Peltier and Solheim, 1992; Tackley et al 1993). Seismic tomography is revolutionising our understanding of mantle dynamics, and it seems to refine, rather than contradict, sea-floor spreading-subduction concepts (Haggerty 1994).

Originally, plate tectonics theory was based on geophysical data, and almost independent of petrological/geochemical models for the mantle and the genesis of magmas. It now appears that at the rate of convection required to account for observed lithospheric plate movements, convection is the dominant mechanism of heat transfer from the mantle to the Earth's surface (eg Hess 1989, p101; Haggerty, 1994 and many references therein). This continuously dissipated heat is not only that inherited from the time of the Earth's formation, as thought by Lord Kelvin, but is continually, if diminishingly, being supplemented by heat from radioactive decay, predominantly of ^{235}U and ^{40}K . A knowledge of the mantle's geochemistry of U, Th and K is therefore one of the many essential geochemical parameters in the construction of internally consistent geophysical models for the dynamics of the mantle. Some aspects of interpreting the geochemistry of K are considered in the first three chapters of this thesis:

It was concluded that the mica in eclogites was secondary and related to their host kimberlites (Ch. 3); that there were two generations of phlogopite in peridotite nodules, one primary and one secondary; that the primary phlogopite reflected mantle metasomatism, and that such metasomatism might recur repeatedly to "fertilise" the mantle prior to partial melting. No attempt was made to account for the source of the metasomatic K (Ch. 4).

Haggerty (1994, p66) writes 25 years later that there is no obvious source of K for upper mantle metasomatism. In the wisdom of hindsight I think that the source is perfectly obvious:

O'Hara and Yoder (1967, p115) conclude in summary that:

"Fractional crystallisation at high pressure of the liquid produced by partial melting of garnet lherzolite is believed to give rise to biminerally eclogite accumulates and a series of silica-poor alkaline residual liquids which have the geochemical characteristics of the groundmass of kimberlite, or of potassic mafic lavas. The association of nodules of garnet peridotite (a possible source rock and mantle material) with nodules of eclogite (a possible accumulate) in kimberlite (a possible residual fluid of high-pressure fractionation) is regarded as significant."

This model for the formation of kimberlite is not generally accepted (see Ch 7 and Haggerty 1994 p63). But the principle of locking Na in the omphacite of eclogite and enriching K in the residual fluid needs little modification to account for K metasomatism in the mantle. It is merely necessary to apply the principle to the solid state metamorphism of oceanic crust to eclogite during subduction. The K from the sea-floor pile which cannot be accommodated in the new garnet and omphacite may reside in a variety of locations: It may form a primary mica in the eclogite, contrary to the assertion of Berg (1968) (see Ch 3); or it may migrate in complex solution into the surrounding peridotite and form dispersed "primary metasomatic" phlogopite of the kind illustrated in Appendix 4; or it may form more concentrated pods of phlogopite.

A more striking but less direct example of the interdependence between geochemical and geophysical investigations of the mantle becomes clear with the realisation that at least some eclogites in kimberlite almost certainly represent subducted oceanic crust. Part of the evidence for this is geochemical; it lies largely in the equivalence of the bulk chemistries of many eclogites and basalt, combined with the oxygen isotopic composition of kimberlitic eclogites which matches oceanic mafic rocks that have interacted with sea-

water. In addition, the carbon isotopic composition of the diamonds contained in some eclogites extends far beyond the range of approximately $\delta^{13}\text{C} = -1$ to -9 established for the mantle carbon reservoir; eclogitic diamonds have a large range of approximately $\delta^{13}\text{C} = 0$ to -30 (see Gurney 1990 and references therein). The lighter values are in the range of crustal carbon, and this constitutes further, perhaps even more compelling evidence for a crustal origin of the host eclogites. (On the other hand, Haggerty (1994) points out that $\delta^{13}\text{C}$ values down to -20 occur also in meteorites).

From the point of view of mantle dynamics the significant factor is the age of these eclogite samples: in some cases greater than 2000 my. The combined data yields graphic evidence for the operation of mantle recycling (via subduction) at least as far back as the Mid-Proterozoic. Given these ages, the formation of eclogite as considered in previous paragraphs could account for ancient zones of "enriched mantle" of the kind reflected in the Sr and Nd-isotopic relations of the micaceous Type 2 kimberlites. In answer to Haggerty (1994) I would suggest, therefore, that K metasomatism in the mantle is the hall-mark of subduction and conversion of oceanic crust to eclogite. The source of K (and with it Rb and other incompatibles) is the material rejected by the primary eclogite garnet and omphacite.

As the above discussion illustrates, this thesis has a scientific mission combined with a flavour of the history of the scientific discipline addressed. At the onset of the work reported here, questions were being asked about kimberlites and the mantle which 30 years later during the assembly of the thesis are largely assumed. Some of these questions were answered in the published work of this thesis, reproduced as Appendices in Volume 2. This PhD thesis has had the benefit of 30 years of hindsight; what then is its contribution?

Chapters 2 to 4

Early on, during the 1960's, the contribution was by way of a cautionary check on the methodology of data-interpretation of bulk-rock chemical analyses and hence true mantle compositions. Disequilibrium secondary alteration was observed in eclogites in the incomplete alteration of pyroxene to analcite (Chapter 3); it was further seen in the coronas of phlogopite formed around garnets in both eclogites and peridotites (Chapter 3, and early work on Chapter 4). The processes responsible for these alterations were taken to be short-term events related to kimberlite emplacement or post-emplacement damage, and irrelevant to the composition of the mantle. Some of the complexities of the history of nodules in kimberlite were thus highlighted, and it became clear why bulk-rock analyses carried so much potentially misleading information. This part of the work thus stressed the difficulties attached to interpreting bulk-rock analyses of K, whose importance to the earth's heat-budget was referred to above (Berg, 1968, Appendix 3; Gurney and Berg, 1969, Appendix 4). When published, the paper by Berg (1968) was the first systematic study of its kind on eclogites. It appears to have alerted some other workers to these problems (eg Ringwood, 1975, as noted in Ch 3; and Dawson, 1980 p 166). The general problem is now so well recognised that Caparoscia and Smyth (1990), for example, write "It has been widely recognised that there are late stage metasomatism and metamorphic overprints on these samples. Secondary phases.....are ubiquitous.....and have been documented in eclogite xenoliths found worldwide (Dawson, 1980)." This is gratifying; it also characterises the nature of Appendix 3: a stepping stone in methodology, referred to in texts such as Dawson (1980), rather than a data-base.

Occasional passing reference to Appendix 4, for example by Hills and Haggerty (1989, p414), still acknowledges aspects of that paper, in this case 21 years after publication.

While the initial caution outlined above appears to have made a useful contribution at the time, that same caution became almost an obsession in the continuation of the present work.

It was soon conceived, as a general rule, that phlogopite was secondary, and for a long time this misconception "blinded" me to the possibility that primary phlogopite might also be present in the nodules. This ignorance lasted for about five years. Then, when preparing for the 1968 Upper Mantle Conference in Pretoria, it became irrefutably clear from petrographic re-evaluation, that the mica in Sample AA4 was not of the typical disequilibrium reaction corona-type found around the vast majority of garnets in the nodules (Appendix 3, Plate 1), but must have equilibrated with garnet at high temperature and pressure (Appendix 3, Plate 2). Since garnet is stable only at depths greater than 40 to 50 km in lherzolites (O'Hara et al 1971), the mica in equilibrium with the garnet could therefore be a stable phase in the mantle, but not at any crustal pressures. I thus reported the first primary phlogopite in a mantle nodule at the Upper Mantle Conference in Pretoria in 1968. It was progress of a kind, but on two important fronts it had little impact.

On the one hand, the lack of impact was external. Boetcher et al (1975) refer to Gurney and Berg (1969) in the context that the proposed primary mica indicated a partly hydrous gas phase in the partial melting environment in which kimberlites form. On the other hand, the South African Upper Mantle publication was not widely read, so that Carswell (1975) re-discovered primary and secondary micas, as outlined in Chapter 4, p38.

More importantly, the lack of impact was "internal". First, I must have admitted the presence of primary mica to myself with reluctance, because the possible presence of other primary minerals carrying alkali and water was not pursued as a

logical consequence of the discovery of primary phlogopite. In particular, the possible presence of amphibole in the rocks was not aggressively investigated, despite the suggestion by visiting scientists to UCT from Japan that it should be there. In this way the important subject of high pressure/temperature metasomatism in the mantle was largely bypassed. This in itself was not a serious problem because there were so many areas of interest to investigate, and one person could not deal with them all. Metasomatism was later elucidated with considerable success by numerous other scientists, and I subsequently "re-entered" this field on the subject of carbonate in the mantle as reported in Chapter/Appendix 10.

The problem lay rather in the narrow view of science that I followed during the remorseless caution with respect to secondary alteration. It became a single-mindedness of purpose.

A significant effect of this initial narrowness in approach was that the collection of peridotite nodules probably became biased. Thirty of the hundred peridotites available for study were inherited from the Williams Collection. A further sixty-five were collected by the writer in Kimberley and five more donated by Dr L.G. Murray of De Beers. Those sixty-five were collected before it was recognised that some mica in nodules might be primary. Thus, nodules exhibiting abundant mica in hand-specimen were almost certainly (unconsciously) discriminated against. Fortunately, examples of "intensely altered nodules" were taken to be analysed "for comparative purposes",²² but almost certainly not in numerical proportion to their abundance in the total Kimberley population. These

²² For this precautionary philosophy in sample collection I would like to acknowledge the late Prof L H Ahrens, who always encouraged his students to broaden any data-base for "comparative purposes". The practice of analysing samples without a more specific model to test or problem to solve has been described as "slop-bucket geochemistry" by a greatly valued colleague working in a more systematic discipline in our science; he criticized what he saw as accumulating data to "see what falls out". In the exploratory Upper Mantle context of the time, however, the practice of collecting "comparative" material and data can almost be looked upon as a necessary step in defining the problems to be investigated.

"altered" nodules in part represent the metasomatised suite, where the most obvious evidence for carbonate in the mantle is to be found. The lesson here is simple: ideally, in a broad preliminary study of the kind undertaken, samples should be classified already during the collection stage, all types collected, and their proportions in the parent population estimated. Alternatively, collection should be totally random, with a view to obtaining a sample fully representative of the parent population. Bearing in mind the number of mines in Kimberley, and the fact that the whole problem of their mineralogy and geochemistry could not be solved by one PhD student, the bias in collection is perhaps excusable as a means of keeping the project to a manageable size; but the danger of entertaining preconceived ideas already when sampling are plain. A slightly narrower or more systematic application of the bias against altered nodules without the precaution of collecting some of them to elucidate the nature of the "alteration", might have led to samples containing evidence for carbonate in the mantle being excluded altogether. I would then not have been able to write Chapter 10.

Chapters 5 and 6

By reporting the first low Sr isotope ratios in kimberlites, the Edinburgh phase of the thesis produced a more lasting, original and fundamental contribution to the geochemistry of kimberlite and hence also the mantle. It came about simply by the more positive approach of analysing primarily fresh material, together with typical altered kimberlite for comparison. The comparison was here designed to test the supposition, based on the petrographic study of seventy kimberlites, that published Sr-isotope data reflected secondary alteration, for which a keen sense had been developed in the studies reported in Chapters 2 to 4.

Some 30 references to Appendices 5 and 6 have been located, including that in the standard text on Igneous Petrology by

Carmichael, Turner and Verhoogen (1976) discussed in Chapter 6. Fifteen years later another text on Igneous Petrogenesis refers back to the same low Sr-isotope ratios: Hess (1989, p250) notes the potential problem of disturbance of Sr-isotope ratios in kimberlite by continental fluids and rocks. He observes, however, that lower ratios have been reported, with reference to Fiermans et al (1984) and Barrett and Berg (1975). Similarly, Richardson (1990) writes with reference to the Kimberley and Finsch kimberlites, "...These kimberlites are respectively representative of the two classic types of kimberlite (basaltic or Group 1, and micaceous or Group 11), recognised on the basis of petrographic chemical and isotopic characteristics (Barret and Berg, 1975; Smith, 1983). Thus Appendices 5 and 6 seem to have contributed a useful facet to kimberlite studies which has stood the test of a decade and a half, and helped lay the foundation for the "state of the art" work on combined Sr and Nd isotope measurements by Smith (1983), and many subsequent papers (eg Bizzi et al 1992).

Chapter 7

A form of scientific "blindness" recurred while the stable isotope measurements reported in Chapter 7 were being undertaken. At that same time I also determined $\delta^{18}\text{O}$ on some minerals separated from eclogites from the Roberts Victor Mine. The object was, in the first instance, to check whether the great range of $\delta^{18}\text{O} = 2 - 8$ in Roberts Victor eclogites, previously reported by Garlick et al (1971), might be an artifact of alteration of the kind discussed in Chapter 3. My (unpublished) results showed that it was not; a surprisingly large range of $\delta^{18}\text{O}$ really existed in the cleanest eclogite mineral separates.

The $\delta^{18}\text{O}$ in eclogites interested me because of its significance to the model of kimberlite formation proposed by O'Hara and Yoder (1967). As noted previously, it is proposed in the O'Hara and Yoder model that eclogite (high Na; low K)

precipitates out of a deep-seated picritic liquid in the mantle, leaving a small volume of kimberlitic residual fluid, (with balancing low Na, high K). If eclogites in kimberlite represent such precipitates, their range in $\delta^{18}\text{O}$ should then be balanced by a complimentary range of $\delta^{18}\text{O}$ in kimberlites. I found no matching range in $\delta^{18}\text{O}$ in kimberlites (unpublished data on $\delta^{18}\text{O}$ in olivines from fresh kimberlites) and had to conclude therefore that the O'Hara and Yoder model failed the oxygen isotope test. Since the oxygen isotope data for eclogites were already available in Garlick et al (1971), it was pointless publishing my data on oxygen isotopes in eclogites which simply duplicated what was already in the literature. I had contributed nothing new; I was puzzled, but made no progress.

On the coffee table in Chicago, where I did the stable isotope measurements, lay a journal containing an article that depicted the subduction of oceanic crust deep into the mantle. At an appropriate depth, the basaltic constituents on the sea-floor were shown to change to eclogite by high-pressure phase-transformation. The exact reference was not recorded at the time, but there were a number of possible sources, such as Ringwood (1972, Fig 3), and (probably) Ringwood (1969). The latter illustration is now reproduced and most easily referred to in Ringwood (1975, p305, fig 8-6). The illustrations in Ringwood (1975) are all developments of a concept first proposed as early as Ringwood and Green (1966), and evolved to its present status of subduction to form garnetite in the 670 km discontinuity layer just prior to Ringwood's death (Ringwood et al, 1992). I had referred in Berg and Allsopp (1972) (Appendix 5) to the work of Taylor and Forrester (1971) in which it was shown that interaction with hot waters could lower, not increase, the $\delta^{18}\text{O}$ of basaltic rocks. Work in the Chicago stable isotope laboratory had in turn drawn attention to oceanic basalts and their altered equivalents with a large range of $\delta^{18}\text{O} = 5.5$ to 17.5 (Muehlenbachs and Clayton, 1972a). In any case, implicit in any diagram illustrating the meteoric water line (eg Sheppard et al, 1971) it can be seen that

interaction with cold water leads to alteration products of rocks in which ^{18}O is concentrated. Furthermore, Muehlenbachs and Clayton (1972b) had reported $\delta^{18}\text{O} = 2.8 - 6.8$ in 14 submarine greenstones. So by the early 1970's there was a background of isotopic information from which a range of $\delta^{18}\text{O}$ for subducted ocean-floor basalts, as illustrated by Ringwood (1972), covering the range of $\delta^{18}\text{O} = 2$ to 8 discovered for eclogites by Garlick et al (1971), could readily be deduced. In addition, Prof Charles Frank (Frank 1969) had already suggested that the nitrogen in diamonds had a biological origin from proteins collected on the ocean floor prior to recycling into the mantle.

Despite the availability of all this information, I never even considered that Green and Ringwood's speculations on the subduction of ocean-floor basalts to form eclogite were compatible with the stable isotope data for eclogites from kimberlites, which I had just confirmed. It took another decade, until Jagoutz et al (1984) suggested that the range in $\delta^{18}\text{O}$ observed in Roberts Victor eclogites had its origin on the sea-floor. The long time-lapse until this interpretation was put forward is intriguing.

Herwart Helmstaedt of Queens University, long championed eclogite in kimberlites of the Colorado Plateau as subducted oceanic crust (Helmstaedt and Doig, 1973, 1975; Helmstaedt and Schulze, 1979). But not even Helmstaedt made use of the published oxygen isotopic data which suggested so strongly that his subduction hypothesis for the Colorado eclogites might apply to eclogites from the Roberts Victor kimberlite as well. There is no obvious reason for this omission, particularly as sea water interaction is discussed in Helmstaedt's papers. Perhaps it merely reflects the specialised nature of our science. Helmstaedt is specialised in tectonics and mineralogy, the combination of which he applied very successfully to deduce an ocean-floor history for eclogite from some kimberlites; but at the time he may not have been familiar

with stable isotope systematics, or indeed have preferred not to speculate on the origin of Roberts Victor eclogites when working on the eclogites from Colorado.

Why I never saw the connection between sea-floor alteration and the variation of oxygen isotopic compositions of kimberlitic eclogites on which I was working is easy to explain: I set out to test two hypotheses; first, were the oxygen ratios an artifact of post-kimberlite emplacement alteration, and second, if not, could the eclogite fractionation model for the origin of kimberlite still be sustained? The answers to both questions were negative; and progress ceased, simply because no further questions were asked. Had the isotopic implications of Ringwood's eclogite subduction model, first published five years before the range in oxygen isotopic composition of Roberts Victor eclogites was revealed by Garlick et al (1971), been reasoned through from spreading ridge to subduction into the mantle, by me or anybody else, "the penny might have dropped" in 1973 instead of 1984. Why did it take so long?

A number of different factors may have inhibited the interpretation of the range of $\delta^{18}\text{O}$ in eclogite as sea-floor alteration. The main sea-floor alteration arguments were only first discussed in 1971 (Hart, 1973 a,b; Muehlenbachs and Clayton, 1972a). Moreover, the first active hydrothermal hot vents were only discovered on the East Pacific Rise in 1978 (summarised by Press and Siever, 1986, p285). The relatively great distance of Kimberley from any known subduction zone may also have been a contributory factor, particularly until Kramers (1979) first showed that the eclogites from Roberts Victor were of the order of 2000 million years old, making present-day subduction zones irrelevant to the problem. Thus when Sharp (1974) suggested a subduction zone connection with the formation of kimberlite, Newton and Gurney (1975) drew attention to the difficulties with respect to the shallow angle of subduction required with respect to the **Cretaceous**

continental configuration. But Helmstaedt and Doig (1972, 1975) had already suggested the possibility of very shallow-angle subduction in the case of the Colorado. Helmstaedt and Gurney (1982) re-assessed the possible role of subduction in assessing aspects of the origin of kimberlite, and Gurney (1990) now accepts as viable, the model of Jagoutz et al (1984) concerning the sea-floor alteration of basaltic materials prior to subduction, as an explanation of the wide range in δ^{80} of Roberts Victor eclogites. Perhaps the time taken merely reflects a difficulty in the integration of results from the many analytical techniques now at the disposal of earth scientists; then it points to the increasing need to encourage the "multi-disciplinary approach".

In the wisdom of hindsight, special credit is due to Prof Charles Frank of Bristol University who first suggested that subducted materials are to be found in kimberlitic inclusions, (viz. nitrogen in diamonds). But this message was evidently not widely picked up and reference to Frank (1969) is strangely missing from the papers advocating eclogites to be subducted oceanic material, until it is referred to by Kirkley et al (1991) in a review on carbon isotopes in diamonds. The currently widely accepted interpretation of the oxygen isotopic composition of the eclogites from kimberlites must be credited to Jagoutz et al (1984) who suggested a sea-floor origin with reference primarily to the data already available since 1971. Numerous further publications have supported this viewpoint. However, the presence of subducted oceanic crust in the mantle does not **preclude** the presence of eclogites formed by other igneous processes (Haggerty, 1994).

It is also noteworthy that dissenting voices of kimberlitic eclogites as subducted oceanic crust are still to be heard (eg Smyth et al, 1991). Experience shows that they should be listened to carefully; particularly so since an entirely new issue has been introduced since the publication by Smyth (1987) of evidence for the presence of water in nominally anhydrous

mantle minerals (Bell and Rossman, 1992; Thompson, 1992). Given such water, the analcime found in eclogites as reported by Berg (1968) might indeed have formed in the mantle upon decompression of nominally anhydrous omphacite as suggested by Smyth et al (1991), rather than in the weathering environment as suggested by Berg (1968). It might then have become enriched in Cs later during weathering (see Ch 4).

The slow communication and comprehension process reviewed above seems to be neither new or exceptional. Anderson (1988) says it all with much greater brevity in the very first sentence of his book: "The maturing of the earth sciences has led to a fragmentation into sub-disciplines which speak imperfectly to one another." So do the scientists within these sub-diciplines it would seem.

Chapter 7

The comparative study of stable isotopes in fresh and altered kimberlites (Ch 7) was a logical extension at the time of the work reported in Chapters 5 and 6 on the radiogenic isotopes (Sr), as pointed out by Carmichael et al (1974). However, although the approach of analysing bulk kimberlites for stable isotopes was disappointing, it made two minor contributions:

The most obvious contribution is the simple establishment that that kimberlites are too complex to yield useful data from bulk analyses in the manner applied to basalts by Taylor (1968). Work on oxygen and hydrogen isotopes in the silicate phases of kimberlites must concentrate on obtaining data for specific minerals by applying techniques not available when the work reported in Ch 7 was done.

The second contribution of Chapter 7 was indirect: the need to circumvent the intractability of kimberlites to bulk- rock stable isotope study, led to the first discovery of brucite in

South African kimberlites, (Appendix 8). This should be exploited in future when setting up new collections of kimberlite for detailed study aimed at that yet elusive quest upon which the book on kimberlite by Mitchell (1986) ends: "...to deconvolute the evidence presented to us and seek out the primitive kimberlite magma."

Chapter 8

Chapter 8 in turn led indirectly to the discovery of possible protoliths of carbonate from the mantle, inasmuch as facilities were established for the analysis of brucite, which is a metamorphic product of such carbonate. This is a field wide open to development.

Chapter 9

Whilst Chapter 8 reported the first brucite in **South African** kimberlites, Chapter 9 reports the first acmite in **any** kimberlite. It is a mineralogical by-way whose significance has yet to be assessed. No extension of this work will help us to understand how the mantle works, but extension of Chapter 10, which deals with carbonate in the mantle, might well do so.

Chapter 10

Evidence for carbonate in the mantle was elusive for many years in which it became increasingly clear from the experimental work reviewed in Ch 10 that carbonate **must** be there, given the right oxygen fugacity. It appeared almost inevitable that carbonate in mantle xenoliths will en route to the surface decarbonate; but contrary to earlier suggestions reviewed in Ch 10, the evidence has not all been decrepitated or resorbed in carbonate-silicate reactions. Part, or all, of the solid residue of the decarbonation will be periclase, which will inevitably hydrate to brucite, unless brucite is formed directly as the decarbonation residue. Brucite is one of the

most fragile minerals in the post-emplacement open-system environment which prevails in most parts of a kimberlite pipe. But it has been found, as documented in Ch 10, in samples of nodules from kimberlite not even collected specifically for this purpose. There is bound to be more in samples not yet examined. Samples found in fresh impermeable kimberlites would be especially suitable for study. The impermeable host rocks of such nodules will supply the best preservation potential for brucite which may reflect mantle carbonate. But a special collection of this kind is unlikely ever to yield sufficient samples to supply an estimate of the proportion of nodules and hence their volume and location in the mantle which actually carries carbonate. It will be necessary, therefore, to continue to attempt to identify possible traces of carbonate reaction residues in run of the mill specimens as undertaken in Ch 10. The problems involved here lie in the field developed in the course of this thesis: to see through the noise which obscures the real evidence of the composition of our rocks. It is difficult and represents a special challenge; it is akin to fishing like a connoisseur for the large trout under the far bank instead of the easy but smaller one nearby.* The likelihood of success is not entirely predictable, but the reward may be big.

* Paraphrasing Charles Ritz

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