4 / A

A Geochemical and Stable Isotope Study of some Rocks from the Bandelierkop Formation, Southern Marginal Zone of the Limpopo Belt, South Africa

by

Torsten Walter Vennemann

Volume 1

Text

A Thesis Submitted in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

Department of Geochemistry

University of Cape Town

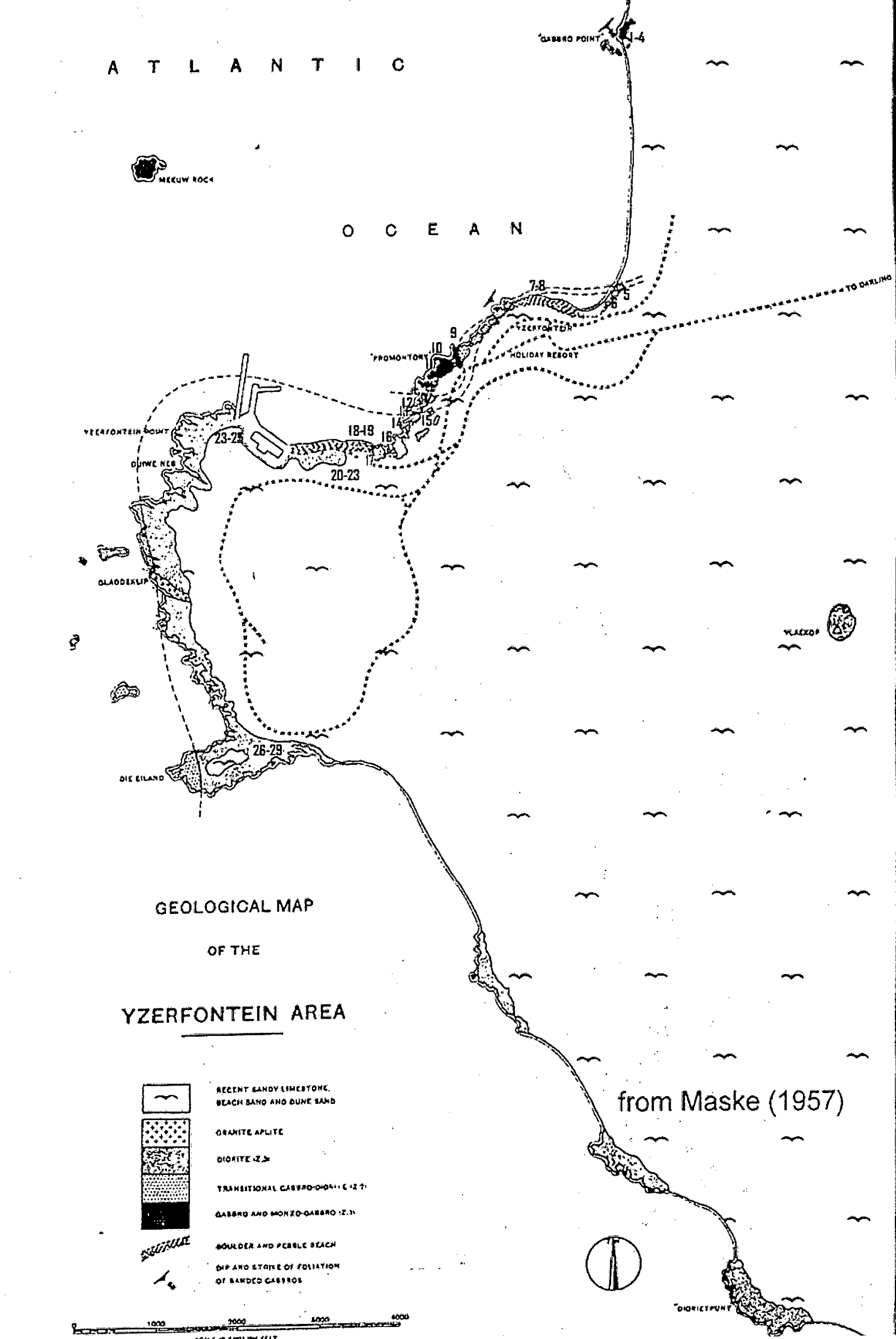
August, 1989

The University of Cape Town has been given the right to reproduce this thesis in whole or in part. Copyright is held by the author.

The copyright of this thesis vests in the author. No quotation from it or information derived from it is to be published without full acknowledgement of the source. The thesis is to be used for private study or non-commercial research purposes only.

Published by the University of Cape Town (UCT) in terms of the non-exclusive license granted to UCT by the author.

University of Cape Town


ATLANTIC
OCEAN
MEEUW ROCK
GABBRO POINT
1-4
7-8
5
6
TO DARLING
YZERFONTEIN
9
10
PROMONTORY
HOLIDAY RESORT
12
14
15
18-19
16
17
23-25
YZERFONTEIN POINT
DUIWE NEB
20-23
GLADDEKLIP
VLAKKOP
26-29
DIE EILAND
GEOLOGICAL MAP
OF THE
YZERFONTEIN AREA
RECENT SANDY LIMESTONE, BEACH SAND AND DUNE SAND
GRANITE APLITE
DIORITE
TRANSITIONAL GABBRO-DIORITE
GABBRO AND MONZO-GABBRO
BOULDER AND PEBBLE BEACH
DIP AND STRIKE OF FOLIATION OF BANDED GABBROS
DIORITE PUNT
from Maske (1957)

CONTENTS

ABSTRACT

The Bandelierkop Formation of the Southern Marginal Zone (SMZ) of the Limpopo Belt consists of metamorphosed ultramafic, mafic and sedimentary rocks. Metamorphic conditions indicated by the petrography of these different rock groups are consistent with upper amphibolite to granulite facies. The ultramafic and mafic rocks are geochemically akin to peridotitic-pyroxenitic intrusive rocks and high-Mg basalts respectively. Metamorphism of these two rock groups in the SMZ was an essentially closed system process, except for the highly volatile phases such as H_2O and CO_2. The metasediments appear to represent a sequence of high (Mg+Fe)-greywackes and/or deep-water shales with minor amounts of iron formation material. The unusually mafic character of the metasediments can be ascribed to a high ultramafic + mafic source component to the original sediment. Some modification of the major and trace element compositions of the pelitic rocks has been caused by the removal of partial melts and the metamorphism of the pelitic rocks is not therefore considered to have occurred under closed system conditions. Variable extraction of partial melts is implied by the chemical variations shown by the pelitic rocks and is also suggested by the presence of large pegmatitic felsic bodies which are commonly found close to the pelitic rocks.

Detailed petrographic study of the Bandelierkop Formation rocks suggests an increase in metamorphic grade, and/or a decrease in water activity, from south to north within the Southern Marginal Zone. Peak metamorphic conditions of

730°C ± 65°C at pressures of 6.1 ± 1.5 kbars may be deduced from a careful application of several cation thermometers and barometers on selected mineral analyses. A rigorous application of garnet-biotite thermometry to the pelitic rocks indicates that the transition from orthoamphibole gneisses in the south to orthopyroxene-bearing rocks in the north of the SMZ terrane, is a function of changing biotite composition and/or decreasing water activities rather than an increase in metamorphic temperatures.

In contrast to the major and trace element data, the stable isotope data for the ultramafic and mafic rocks in the SMZ indicate open system behaviour for some of these rocks, but closed system behaviour for the pelites. Extraction of 50 to 70% partial melts from the pelitic rocks, should not, however, have affected the $\delta^{18}O$ value of the restite. Petrological and stable isotope data in the SMZ rocks are consistent with retrogression in all these rocks and open system behaviour for oxygen in some ultramafic and mafic rocks, being caused by the crystallization and accompanying fluid release of melts produced during prograde metamorphism of the pelitic rocks.

Small scale (~5 to 30m's) heterogeneity is implied by both oxygen and carbon stable isotope compositions of closely spaced rock samples, even for those collected from within large "shear zones", suggesting small fluid/rock ratios for most of the samples in the high-grade terrane or heterogeneous stable isotopic compositions of the fluids. Furthermore, a similarity in mineral-mineral stable isotope fractionation factors is observed for all the pelitic rocks, including the orthoamphibole gneisses found immediately south of the orthopyroxene isograd. These features preclude the presence of pervasive

fluid infiltration after peak metamorphism. Two implications are, that granulite facies metamorphism in the SMZ terrane was not caused by an influx of mantle derived CO_2-rich fluid and, that the orthoamphibole gneisses are not retrogressed equivalents of the granulites found to the north of the orthopyroxene isograd. It is suggested that this isograd represents a change in the water activities of the rocks during metamorphism.

Apparent disequilibria in mineral - mineral stable isotope fractionations observed amongst different minerals within any one pelitic rock, may be explained by a combination of the crystallization of residual melt within these rocks and oxygen diffusion amongst minerals which have not reached their oxygen-closure. The concordant quartz-plagioclase, quartz-biotite and plagioclase-biotite oxygen isotope equilibration temperatures are taken to represent minimum crystallization temperatures for the melts (~560°C), while successively higher quartz-orthopyroxene, quartz-amphibole and quartz-garnet oxygen isotope equilibration temperatures are a function of increasing closure temperatures for the orthopyroxene, amphibole and garnet respectively. The minimum estimate to peak metamorphic temperatures is given by the quartz-garnet oxygen isotope temperature averaging 736 $\pm$ 52°C. If oxygen diffusion experiments performed in hydrothermal systems are appropriate for the SMZ rocks, then cooling rates for the SMZ terrane could have been as low as 12 to 25°C/My over a temperature range of 480 to 600°C.

Stable isotope modeling of hypothetical fluids that may have been in equilibrium with the high-grade rocks, suggests that a mixture of CO_2 and H_2O, with CO_2/H_2O mole ratios > 0.1 can precipitate both quartz and

carbonate of stable isotope composition similar to those determined for quartz and carbonate from the mineralized Archaean lode gold deposits of the Murchison and Pietersburg greenstone belts. A model involving granulite facies metamorphism, partial melt extraction and subsequent release of fluids, Au, K and S upon crystallization of such melts, appears to be viable for gold mineralization occuring in the adjacent lower grade greenstone belts and in the high-grade terrane of the Southern Marginal Zone.

ACKNOWLEDGEMENTS

Financial support for this work was received through the Cooperative Scientific Programme (CSP), National Geoscience Programme (NGP) of the Council for Scientific and Industrial Research (CSIR). This financial support also allowed for the employment of Ms Dawn Leach, Mrs Move Steven and Ms Nadima Ebrahim as research assistants during the duration of the project. Their assistance in the sometimes tiring task of mineral separation and mass spectrometer analyses is greatly appreciated. In addition, I would like to extend a special thanks to Mrs Move Steven who also completed large parts of the powder briquette and fusion disc separation with meticulous care.

The assistance of other staff members and technicians in the Departments of Geochemistry and Archeology is also appreciated. In particular, I would like to thank John Lanham for the maintenance of the mass spectrometer in the Department of Archeology, Dick Rickard for help with the electron microprobe analyses, Dave Hill for always allowing to be disturbed (even during lunch) in order to help with the computing, Lynn O'Neil for providing help with all sorts of administrative work and Bruce Cairns, who, amongst other help, always managed to fix furnaces on the silicate line just in time for the next reaction. I would also like to thank "shtep-onnit" Jackie van Schalkwyk from the Rand Afrikaans University, for my first introduction to the field area. A special thanks also to Charlie and Patrick for their assistance with the photographic and photocopying work throughout this study. In addition, Charlie also provided a

refreshing updates on the latest "skinner" regarding SA's politics.

While lots of people provided thought-stimulating discussions over the years of research, some people need to be singled out. Dr. H.S. Smith ("Stuey"), as my supervisor and co-worker on this project, commonly provided some refreshing new ideas on all aspects of the work, while Dr. Mike Watkeys, with his extensive knowledge on the Central Zone of the Limpopo Belt, often served as a good "buffer" when discussing the implications of the data.

And then there was Bicentennial Gold 88 in Melbourne, Australia. The work of Prof. Tony Erlank and "Stuey" Smith together with the generous financial aid by the NGP-CSIR and the Australian Convention Travel Services, made the attendance of such a great conference possible. The attendance of this conference provided an excellent learning experience, in that it served as and "eye-opener" to some aspects of geology/geochemistry and, in that it provided first-hand information on the most recent ideas in the more familiar aspects of geology/geochemistry regarding gold mineralization. Furthermore, it provided an excellent opportunity to discuss several ideas with specialists from many branches of geology.

Of course, there is also my most recent office-mate America, sorry, Marshall Otter (yep, like the animal O-t-t-e-r!). Marshall not only supplied some often badly-needed energy in the form of chocolate (including Smarties!!), but he also served as a sponge in absorbing some of my "great" ideas, listening attentatively for long periods of time and bouncing some ideas back at me. In addition, Marshall also convinced me that lunch-time jogging with "dem boys" is

actually healthy (is it?). Many thanks also to Jenny's "sweet secrets" that often silently ended up on my desk (yet another reason for jogging though!).

With regard to the final stages of the thesis work, I would like to thank Dr. "Stuey" Smith, Dr. Chris Harris (my new 2-month "flash-type" supervisor), Dr. Hugh Humphries and the ever-fussy Jon McStay for reviewing earlier drafts of the thesis. Finally, I also want to thank my wife Cora for spending long hours of "beach-potential" weekend days and late evenings typing large volumes (and more) of illiterate text without any complaints (she is also the inventor of several new mineral names and rock species!). When, during "night-hours", my thoughts wandered back to work, Cora also served as and absorbant listener and, in part, is responsible for "sparking-off" some new ideas. Somehow, Cora also knew when exactly it was time for me (and us!) to have a break. Besides, can there be anything nicer than getting a cute smile during the darkest of times?

CHAPTER 1: INTRODUCTION

Metamorphism, in general, refers to the mineralogical and structural adjustment of rocks to physical and chemical conditions prevailing at depths beneath the surface of the earth.

Chemical analysis of metamorphic rocks often fall within the compositional limits of common igneous or sedimentary rocks, except for components such as H_2O and CO_2. While such isochemical behaviour appears to be true on the handspecimen (or larger) scale, ionic diffusion, nucleation and crystal growth testify to microscopic allochemical processes.

Volatile components such as H_2O and CO_2 which are continually released during prograde metamorphism are considered essential for microscopic ionic diffusion resulting in mineralogic crystallization (Carmichael, 1969) as well as possibly being responsible for the macroscopic transfer of metals from the high-grade metamorphic rocks to higher crustal levels (e.g. Kerrich and Fyfe, 1981). In this respect stable isotope studies are a useful method for determining thermal and fluid histories of metamorphic rocks.

1.1 Previous Work and General Geology

The Southern Marginal Zone is commonly considered to form part of the Limpopo Mobile Belt of southern Africa (Fig. 1.1). The Limpopo Mobile Belt is a linear zone of highly metamorphosed and intensely deformed rocks situated between the

Rhodesian and Kaapvaal Cratons (Mason, 1973; Coward et al., 1976) Structurally the belt can be subdivided into Northern and Southern Marginal Zones with predominantly east-north-east trending structures which are separated from a central zone with predominantly northerly trending structures by major east-northeast trending ductile shear zones; the Tuli-Sabi shear zone in the north and the Palala shear zone in the south (Mason, 1973; Du Toit et al., 1983; McCourt and Vearncombe, 1986).

Stratigraphically, the Limpopo Mobile Belt can be divided into a number of domains (Fig. 1.2 and Watkeys, 1983), where the Northern and Southern Marginal Zones can broadly be seen as comprising high-grade cratonic lithologies, commonly thought to represent high-grade granite-greenstone equivalents, whereas the Central Zone is dominated by a different Archaean stratigraphy consisting of high-grade paragneisses, metasediments (pelites, calc-silicates, marbles), layered igneous complexes and rare intrusive granites (Watkeys et al., 1983; Du Toit et al., 1983; Mason, 1973). The difference in the metamorphic grade and lithology of supracrustal rocks, coupled with a complex early Archaean (pre-3000 Ma) history shown within the Central Zone but not in the rocks of the marginal zones suggests the possibility that the Central Zone may be genetically unrelated to the marginal zones (Du Toit et al., 1983; Watkeys et al., 1983; Barton and Key, 1983; Harris and Holland, 1984; van Reenen, 1983, 1986).

The Southern Marginal Zone is represented by two main categories of rocks (Du Toit and van Reenen, 1977; Du Toit et al., 1983): the grey banded and migmatized tonalitic and trondhjemitic gneisses, termed the Baviaanskloof Gneisses, and the pelitic, mafic and ultramafic rocks of the Bandelierkop

Formation (Fig. 1.3). Initial work done by Du Toit and van Reenen (Du Toit, 1979; van Reenen, 1978 and also Du Toit et al., 1983; van Reenen D.D., 1983, 1986) demonstrated that these rocks experienced at least four deformational events, three folding and one shearing event, and were subjected to three metamorphic events, one prograde granulite event (M1), followed by rapid isothermal upliftment (M2) which preserved the granulite assemblage observed at the surface, and a third retrogressive event establishing the orthopyroxene isograd (Fig. 1.3).

While the importance of shearing in the Southern Marginal Zone (and the Limpopo Belt in general) was already recognized fairly early by some workers (Mason, 1973), the relationship between shearing (and thrusting) and metamorphism was established only recently (van Reenen et al., 1986; 1987; 1988)

Commonly members of the Baviaanskloof Gneisses and Bandelierkop Formation are interpreted to represent high-grade equivalents of the lower grade granite-greenstone lithologies of the adjacent Kaapvaal Craton (Du Toit et al., 1983). However, the exact relationships between rocks of the Bandelierkop Formation and the Baviaanskloof Gneisses are as yet uncertain (Du Toit et al., 1983 p.124). Geochronological information, although only scarce, indicates zircon U-Pb minimum ages of 2800 $\pm$ 70 Ma for the Baviaanskloof Gneisses (Burger and Walraven, 1976, 1979a, 1979b) whereas Barton et al. (1983) suggest an age of about 3200 Ma from trends in Rb/Sr and Pb/Pb diagrams. Rocks from the Bandelierkop Formation correspond to an approximate Rb/Sr age of 2650 Ma (Barton et al., 1983) and could, thus, well have been deposited onto a Baviaanskloof "basement".

The lower grade greenstone belt lithologies of the Pietersburg, Sutherland and Rhenosterkoppies greenstone belts are at greenschist facies grade in the south-western parts and increase in grade towards amphibolite facies rocks in the north-east where they are tectonically juxtaposed with the higher grade lithologies of the Southern Marginal Zone. The non-uniform increase in metamorphic grade towards the north within the Kaapvaal craton is subject to the presence of giant "shear zones" dividing the terrane into a number of large blocks (see Fig. 1.3), and also the presence of a retrograde isograd (De Beer et al., 1986; van Reenen et al., 1987; 1988). According to van Reenen (1986) and van Reenen et al. (1987; 1988) the southern portion of the high-grade terrane was infiltrated by retrogressive, CO_2-rich fluids, producing the retrograde orthopyroxene isograd.

Rb-Sr studies of the differentiated and partially deformed Matok complex which straddles the orthopyroxene isograd (Fig. 1.3) yield an isochron of 2620 $\pm$ 75 Ma and an initial $^{87}Sr/^{86}Sr$ ratio of 0.7026 $\pm$ 0.0011 (2σ) for the porphyritic granite facies, with the so-called mafic facies (charnockitic-enderbitic of Du Toit et al., 1983) scattering around the 2620 Ma isochron (Barton et al., 1983). This age is similar to that of the undeformed Moletsi and Lunsklip granites further south (Fig. 1.3; Burger and Walraven, 1976, 1979a, 1979b; Barton et al., 1983) and could imply that the Matok complex is part of a series of plutons emplaced at ~ 2600 Ma. Although the Matok Complex may have been emplaced during deformation of the Southern Marginal Zone it may not be directly related to it. Van Reenen et al. (1987) interpret the Matok complex to have intruded at the time of establishment of the shear zones, the northern

charnockitic facies having been created by fluids moving along and up the shear zones which dip steeply towards the north.

Emplacement of the undeformed 2456 ± 78 Ma ($^{87}Sr/^{86}Sr_o$ of 0.7092 ± 0.0011) Palmietfontein granite may provide a good time marker for the end of the main tectonometamorphic events in the Southern Marginal Zone (Barton et al., 1983).

1.2 Aim of the Study

The bulk of this work forms part of a contribution towards a National Geoscience Program (NGP) entitled "The Relationship Between Mineralization and Craton-Forming Processes in the Higher-Grade Granite-Greenstone Terranes of the Kaapvaal Craton" and sponsored by the Foundation for Research Development (FRD). The working group on the above mentioned project was made up of researchers from various universities and research institutions, each dealing with a particular aspect of the project. The stable isotope work undertaken at the University of Cape Town was aimed at delineating the significance of metamorphic fluids to gold mineralization processes.This task was approached by dividing the work into two sections, one dealing with the stable isotope and geochemical characteristics of rocks in the mineralized shear zones within lower grade rocks, and the other section was confined to the geochemical and stable isotope characteristics of the adjacent high-grade terrane. The work represented in this study covers the latter high-grade section.

From the previous section on the general geology of the Southern Marginal Zone it becomes evident that this area is geologically complex. This fact, coupled with the rather poor exposure of the metamorphosed supracrustal rocks severely complicates geologic interpretations. However, the generally increasing metamorphic grade found within the terrane adjacent to lower grade mineralized greenstone belts, provides an attractive background to test the significance of metamorphic fluids in gold mineralizing processes, particularly as such fluids have been identified from stable isotope work on Au-Sb mineralization in the Murchison greenstone belt (Smith, 1986).

Recent models on gold mineralization have proposed a close link between "lower crustal maturation", granulitization and gold mineralization processes (e.g. Colvine et al., 1988; Fyon et al., 1988). In the light of the above, the aim of this study is to characterize the possible fluids that coexisted with the amphibolite/granulite facies rocks of the Southern Marginal Zone. Whole rock and mineral analyses from the pelitic, mafic and ultramafic rocks of the Bandelierkop Formation are examined in order to determine the following:

1. Temperatures of fluid-flow determined from cation and anion geothermometry and the extent of fluid-rock interactions.

2. The type of fluid-flow and the extent of fluid-rock interactions.

3. The importance and stable isotope composition of fluids in granulite facies metamorphic rocks of the Southern Marginal Zone.

4. The importance and stable isotope composition of possible retrograde

fluids in this terrane.

5. Possible mechanisms of fluid, ore and mobile element transfers, if any, from metamorphic terranes to zones of mineralization.

6. The implications of the above for gold mineralization in adjacent greenstone belts.

CHAPTER 2: ANALYTICAL BACKGROUND

2.1 Sampling

The sampling of supracrustal rocks from the Bandelierskop Formation followed a pattern of regional sample collection of rocks. Pelitic, mafic and ultramafic rocks from both north and south of the orthopyroxene isograd, as mapped by du Toit et al. (1983), were obtained (see Figure 2.1 for sample localities). In addition, several samples from the large shear zones such as represented by the Hout River Transition (du Toit et al., 1983; van Reenen et al., 1987) and from the adjacent greenstone belts (e.g. Pietersburg and Rhenosterkoppies belts) were collected for comparison purposes. While the bulk of the samples were collected during April 1986, further sampling was undertaken during visits to specific localities within the high-grade terrane. In all localities visited, care was taken to note the general appearance of the sampled rock in outcrop, that is presence or absence of large scale veining, pegmatite intrusions and contact relationships with surrounding rock types. This task was often complicated by the poor exposure of the rocks in the field.

The size of the samples collected depended on the grain size of the particular rock. Thus, for the pelitic rocks it was estimated that once the weathered surfaces are removed, about 4 to 5kg of material would be left for sample preparation and mineral separation, whereas for the somewhat finer grained and mineralogically homogeneous mafic and ultramafic rocks about 3 to

4kg samples were considered sufficient. From the ~ 80 samples collected in the field, a total of 53 samples were subsequently selected for thin section, microprobe, stable isotope and X-ray fluorescence (XRF) analysis described below.

2.2 Major and Trace Element Analysis by X-Ray Fluorescence

The samples selected for XRF analysis were split to remove all weathered material and were subsequently crushed and powdered using a carbon-steel swingmill at the Geochemistry Department of the University of Cape Town. Once ground to about 300# (~80 micrometres) sized powders, fusion disks and pressed powder briquettes were made. All major elements, except Na, were obtained by analysis of lithium tetraborate fusion discs according to the method of Norrish and Hutton (1969). Powders used for the fusion discs were dried overnight at 110°C, the recorded loss in weight being attributed to loss of adsorbed water (H_2O-). Subsequently, these powders were ashed at 1000°C overnight with the recorded weight reported as loss on ignition (LOI). For samples P5C and P6C, the weight after ashing at 1000°C was found to be higher than prior to the ashing procedure. This is considered to be caused by oxidation of FeO to Fe_2O_3, indicating a very reduced state for samples P5C and P6C. Sodium and the trace elements were obtained by analysis of pressed powder briquettes. The operating conditions used were those adopted for routine analysis in the Department of Geochemistry and described by Willis et al. (1971; 1972). Some estimates on the absolute average errors and the detection limits obtained for the adopted

counting statistics are given in Table 2.1. The values given in Table 2.1 are the average values obtained for the analysis of the pelitic, mafic and ultramafic rocks. As the absolute errors and the detection limits vary with the whole rock geochemistry (i.e. background to the element analyzed), the values for the errors and detection limits should theoretically be quoted for each rock or for each group of chemically similar rocks. However, for the purpose of the following discussions it suffices to quote the average errors and detection limits, particularly as the differences in absolute values of the errors and detection limits between the major rock groups (i.e. pelites, mafics and ultramafics) are relatively small compared to the analyzed element contents in each group.

2.3 Electron Microprobe Analysis

The mineral compositions were obtained using a 4-channel, fully automated Cameca Camebax Microbeam at the Department of Geochemistry, University of Cape Town. For all minerals, except plagioclase, a focused beam (2 micrometre; 40nA) with an accelerating voltage of 15 kV was used. For plagioclase a "defocused" (10-20 micrometre, 20nA) beam was used at the same accelerating voltage. All analysis were performed on graphite-coated, glass mounted polished rock sections. The x-ray intensities were calibrated against a set of both natural and synthetic mineral standards, where the standards showed element concentrations similar to those in the sample. Natural standards used were chromite (Chr), fluorite (Flu), Kakanui hornblende (K-H), Kakanui pyrope (K-P), Lake County Oregon labradorite

(Lac), Marjulahti olivine (M-O), Nunivak Ireland plagioclase (Nun), orthoclase (Orl) and scapolite (Sca). Synthetic standards were diopside (Dio), magnesium-alumina spinel (MGA), nickel silicate (NIS), rhodonite (Rho) and rutile (Rut). The raw counts were corrected for dead time and background, with the resulting nominal concentration being corrected using the ZAF procedure. Generally for minerals whose oxides should sum to $\simeq$ 100%, values of between 99 to 101% were accepted, except for Fe-rich garnet and orthopyroxene, where values somewhat higher than 101% were accepted as this is considered to be a function of the ZAF correction procedure for high-Fe samples.

A summary of the standards used, the errors and the detection limits for various analyzed mineral species is given in Tables 2.2 and 2.3. Counting time on peaks for all the analyzed elements was 10 seconds except for F and Cl in biotite, where counting times used were commonly 100 seconds. As the counting error and detection limits are functions of counting time and of element concentration, the errors and detection limits given in Tables 2.2 and 2.3 are quoted for a typical analysis of the given mineral species in the rocks of this study.

The microprobe analyses given in subsequent sections are commonly referred to as core and rim analyses. Rim analyses were taken as close as possible towards the edge of the mineral grains (~5 to 10 micrometres). Core analyses have been taken more than 30 to 50 micrometres from the edge for small grains and towards the centre of larger grains, in either case well away from fractures. While the analyses given in subsequent sections are commonly obtained from one spot within the specific grain, in the case of more than one rim or

core analysis having been obtained, the values were found to be well within the errors quoted in Tables 2.2 and 2.3 for unzoned mineral grains. The given values are thus considered representative for the minerals analyzed.

2.4 Stable Isotope Analysis

2.4.1 Mineral Separation

Routine mineral separation was performed on 60 to 90# sized sample fractions washed in distilled H_2O and dried overnight at 110°C. In the case of coarse-grained rocks with inclusion-free constituent minerals, the 40 to 60# fraction was used. After an initial magnetic separation using the Frantz isodynamic separator, subsequent mineral purification was obtained by hand picking under binocular microscopes. Because of the difficulty in distinguishing quartz from plagioclase in the non-magnetic fraction, these fractions were suspended above HF vapours, derived from 35% HF liquid held at 90°C, for 1 to 2 minutes in a small Pt-pan. This pan was filled with a thin layer of sample only (~1 grain size in thickness; van der Plas, 1966). Afterwards the etch-residue was fixed on the surface of the particles by a 400°C heat treatment in an electric furnace for 5 minutes, resulting in a "milky" plagioclase surface. For K-feldspar determination the etched aliquots were inserted into a saturated sodium cobaltinitrite solution for about 2 minutes and then washed with distilled water, leaving yellow K-feldspar grains. Magnetite was separated by hand magnet from a finer than 120# crush suspended in distilled water. Graphite

was separated from 60 to 90# sample fractions by a combined method of water floatation and subsequent hand picking. All mineral separates were more than 95% pure as determined by visual estimation with the aid of binocular microscopes.

2.4.2 Oxygen Isotope Analysis

Oxygen was extracted from the minerals and whole rocks in the Department of Geochemistry at the University of Cape Town using ClF_3 as reagent and an extraction method similar to that described by Borthwick and Harmon (1982). Prior to extraction, the mineral separates were crushed in acetone until finer than about 120 to 200#, except for garnet, magnetite and whole rocks, which were crushed until finer than about 300#. The crushed samples were then dried for a minimum of 15 minutes at 110°C, weighed and transferred into the reaction vessels using a loading stick. For silicates and whole rocks about 10mg of sample were reacted with about 7 times the stoichiometrically required amount of ClF_3 reagent for periods of 12 to 14 hours. For magnetite about 15 to 20mg of sample were used with the same running conditions as for the silicate minerals. All minerals were analyzed in duplicate whereas for whole rocks on average every second sample was analyzed in duplicate only.

The extracted oxygen was converted to CO_2 by passing it over a hot, platinized carbon rod. After manometrically measuring the amount of CO_2 produced, the CO_2 was analyzed for its oxygen isotope composition using a VG Micromass 602E double collecting ratio mass spectrometer housed in the Department of Archaeology. For oxygen analysis the mass-46 peak was measured

relative to the combined mass-45 + mass-44 peaks. This ratio, expressed relative to that of the mass spectrometer reference gas as $\delta 46$, was subsequently corrected for the effects of the mass spectrometer background on the peaks (e.g. Deines, 1970) and for mass-45 contributions (^{13}C and ^{17}O in CO_2) to the mass-44 peak (Craig, 1957). The $\delta^{18}O$ values were all calculated relative to Standard Mean Ocean Water as given by Gonfiantini (1978; V-SMOW scale), using the conventional definition for δ:

$$\delta^{18}O_{Sample} = \left(\frac{^{18}O/^{16}O_{Sample}}{^{18}O/^{16}O_{Standard}} - 1 \right) * 1000 \qquad (2.1)$$

and adopting a NBS-28 (quartz) value of 9.64‰ relative to V-SMOW. The theoretical yields of CO_2 were calculated from the microprobe analysis of the minerals within each rock and using the general formula:

$$\frac{1000\ (0.5 * \text{no. of atoms of oxygen in formula})}{\text{formula weight}} \qquad (2.2)$$

For minerals where no microprobe analysis were available, the micromole/milligram values for the same mineral species in compositionally similar rocks were used.

Table 2.4 summarizes the number of extractions, the reaction temperatures used, average oxygen yields and the average errors in $\delta^{18}O$ about the mean from duplicate analysis. For most of the minerals the yields are between 98 and 102% and reproducibility is better than $\pm$ 0.1‰ about the mean of duplicate

analysis. Notable exceptions to this are orthopyroxene, cordierite and orthoamphiboles, where the former two show yields lower than 98% while the latter has yields higher than 102%. For the orthoamphiboles from sample P38C the oxygen yields were found to be consistently high at 107%. Omitting this orthoamphibole pair then the average oxygen yields for the orthoamphiboles is lowered to 101.6% (s.d. 1.66). The reason for these high yields is unknown but could be related to the volatile contents or the Fe oxidation state of the orthoamphiboles as this is not determinable from the microprobe analysis. The reason for the low oxygen yields of the orthopyroxenes (both enstatites from the ultramafics and orthopyroxenes from the pelites) and the cordierites are unknown although the latter may also be a function of volatile estimates in the mineral. Another possible explanation for these low yields could be incomplete oxygen liberation as will be discussed later.

Because of the difficulty in distinguishing quartz from plagioclase, the non-magnetic sample fraction containing both of these minerals was etched with HF vapours (see above). Effects of this etching on the plagioclase isotopic composition were tested for plagioclase separated from the mafic rock M3A. Thin section analysis for this rock indicated an absence of quartz and thus plagioclase could be separated without etching. Four non-etched plagioclase analysis provided an average $\delta^{18}O$ of 9.43 $\pm$ 0.07‰. A small aliquot of the same plagioclase which was etched for about 3 minutes provided a mean of 9.55 $\pm$ 0.08‰ (n=2), suggesting that no significant difference in $\delta^{18}O$ is introduced with etching of the feldspars.

2.4.2.1 Reaction Experiments for some Silicate-ClF_3 Reactions

Because of the similarity in optical and density properties between quartz and feldspars, mineral separation of these two is complicated. The etching of feldspars, producing a "milky" etched surface on grains, can be expected to have a chemical effect on the feldspar. While it was shown above that the etching of feldspars by the HF vapours did not have a significant effect on the isotopic composition of the feldspar (to within the current analytical uncertainty), this may not necessarily be the case for strongly zoned feldspars. An alternative method for quartz-feldspar oxygen isotope analysis is to sequentially react a quartz-feldspar sample mixture with reagent (e.g. BrF_5 or ClF_3), first at a low temperature to react with the feldspar and subsequently at a higher temperature to react with the residual quartz in the mixed sample (H.S. Smith pers. commun.; see also Clayton and Mayeda, 1963; Crowley and Giletti, 1983). This idea led to a series of reaction-temperature and reaction-time experiments conducted using ClF_3 reagent. It is worth noting at this point that during temperature calibrations of the Lindberg electric heating elements (type 73-KS) it was established that it took approximately 15 $\pm$ 5 minutes for the nickel reaction vessels (outside diameter 19mm, internal diameter ~12mm) to reach the set temperature.

The results of such experiments for the minerals of quartz (NBS-28 and Murchison quartz), plagioclase (An_{38}-M3A and An_{70}-Bushveld Igneous Complex), biotite (NBS-30), garnet (Alm_{60}-Pyr_{35}-P14C), clinopyroxene (Di_{82}-Hd_{18}-Busveld Igneous Complex), and olivine (Fo_{90}-San Carlos) are given in Tables 2.5 to 2.7 and are summarized in Figures 2.2a and b. The most important features

from these experiments are the following:

1. Quartz, clinopyroxene and biotite remain more or less unreacted until a certain temperature limit is reached. For temperatures exceeding these temperature limits (T>300°C) the reaction between these minerals and ClF_3 proceeds more or less spontaneously.

2. In the case of plagioclase and garnet a more steady increase in yield is observed with increasing temperature. For plagioclase, however, the reaction starts at temperatures as low as 100°C and is completed at temperatures of around 450°C whereas for garnet these temperatures are 250°C and 600°C respectively. If reacted at temperatures considerably higher than 450°C (i.e. 550°C), the reaction between plagioclase and ClF_3 proceeds more or less spontaneously. Experimentally this could not be established for the garnet as at temperatures exceeding $\pm$ 650°C the Ni reaction vessels will react with the ClF_3 (e.g. Borthwick and Harmon, 1982).

3. High-Mg olivine remains largely unreacted even at temperatures as high as 650°C and reaction times of 14.5 hours.

4. For all minerals, except garnet, a positive relationship of increasing $\delta^{18}O$ with increasing oxygen yield was observed. Generally for yields higher than 90% the $\delta^{18}O$ values were found to be indistinguishable, to within the analytical uncertainty, from those for a complete reaction. The unreacted quartz was re-reacted with ClF_3 at 550°C after the extraction of oxygen produced during low temperature runs. The oxygen

extracted from the re-run was found to compliment the initially (light $\delta^{18}O$) extracted oxygen. For olivine $\delta^{18}O$ was found to increase with yield but lack of a complete reaction prohibits comparison with 100% yield $\delta^{18}O$ values.

5. The $\delta^{18}O$ of oxygen extracted from vessels with unreacted garnet was found to be heavier than that for completely reacted garnet, in reverse to the above minerals. However, after only ~50% oxygen yield the $\delta^{18}O$ is found to be representative of 100% yield values.

An important implication of the above is that if the low cordierite and orthopyroxene oxygen yields are caused by a lack of complete mineral-ClF_3 reaction, then the $\delta^{18}O$ values of the cordierite and orthopyroxene should still be representative for the $^{18}O/^{16}O$ compositions of these minerals as their oxygen yields were commonly larger than 95%. The possibility that these low yields are a function of contamination by other mineral species is not considered valid, particularly as the mineral separates were better than 95% pure. In the case of high-Mg, colourless cordierite, quartz and plagioclase may represent possible contaminating phases that could have remained undetected. However, such a contamination would largely increase the oxygen yields of the cordierite which is not observed.

Furthermore, the above experiments imply that the reaction conditions used for the whole rock analysis (i.e. 600°C, 12 hours) should provide representative oxygen isotopic compositions for the pelitic and mafic rocks of this study. This may not be the case for the ultramafic rocks containing high-Mg olivine, unless olivine gives representative oxygen isotopic values even at low

yields (e.g. ~30%). It is also interesting to note that the garnets analyzed in this study using ClF_3 as a reagent do not indicate incomplete reactions as is the case for some garnets reported in the literature (e.g. Huebner et al., 1986).

No attempt was made to determine the effect of mineral grain size on the rate or temperature of the reactions. It is, nevertheless, interesting to note that quartz, feldspar and biotite showed rapid reactions with ClF_3 even for the relatively coarse-grained size fractions used (see Tables 2.5 to 2.7). This was not the case for garnet and olivine which were crushed until the powder floated in acetone (~300#).

2.4.3 Carbon Isotope Analysis

As little or no carbonate is present in the majority of rocks, carbon isotope measurements were performed only on graphite flakes present in the pelitic rocks. About 2mg (milligrams) of graphite flakes (0.1 - 1mm in size) were thoroughly mixed with 100mg cupric oxide (CuO) in a crucible. The mixed powder was inserted into a quartz tube, evacuated to about 10^{-3}mbars, sealed and combusted to CO_2 in a furnace set at 800°C for 12 hours. Manometric yields of the analyzed samples varied between 80 and 105% relative to theoretically calculated values. A blank sample of 100mg CuO also heated to 800°C for 12 hours showed no measurable gases when analysed. Low yield samples were optically examined for residual graphite but none was detected. Loss of graphite during mixing and/or partial silicate contamination are therefore considered the most

likely explanations for the low yields in some samples.

CO_2 was analyzed both for $\delta 45$ ([mass-45/mass-44]$_{sample}$/[mass-45/mass-44]$_{reference\ gas}$) and $\delta 46$ (see above) on the VG Micromass 602E mass spectrometer in the Department of Archaeology. After corrections for oxygen interference (^{17}O) on the $\delta 45$ values, the $\delta^{13}C$ values were calculated relative to the PDB standard (Peedee Belemnite carbonate - Gonfiantini, 1978).

CHAPTER 3: PETROGRAPHY AND MINERALOGY

3.1 Introduction

In the section to follow the textural and mineralogical features of selected samples from the Bandelierkop Formation of the Southern Marginal Zone (SMZ) are described in more detail. This description will be related to the paragenesis, to mineral reactions occuring and, if possible, to the degree of textural and chemical equilibrium attained in the rocks under consideration. All of these features form the basis to subsequent discussions on the geochemistry of the SMZ rocks. In addition, a comparison of the observed mineral reactions to experimentally calibrated reactions involving similar mineral phases in chemically similar systems allows for some crude estimates on the pressure-temperature (P-T) and perhaps water activity conditions (expressed as partial H_2O pressure or $P(H_2O)$ relative to the total pressure, P(total)) experienced by the SMZ rocks. The results of this independent estimate of P-T conditions are subsequently compared to the P-T conditions as obtained from cation and anion thermometry in an attempt to quantify the metamorphic history experienced by the SMZ rocks.

This section largely concentrates on the high-grade rocks (for sample localities refer to Fig. 2.1). Thus while samples from various lithologies of the Pietersburg and Rhenosterkoppies greenstone belts, the Baviaanskloof gneiss, charnockites of the Matok area, as well as a granodiorite have also been

analyzed for their major and trace elements, they are not described in this section. However, brief mineralogic-petrographic descriptions of these rocks can be found in Appendix A.

Bandelierkop Formation rocks outcrop as large, relict blocks, surrounded by the characteristic grey, migmatitic gneisses termed the Baviaanskloof Gneiss (Fig. 3.1). Chemically these gneisses are tonalitic to trondhjemitic in composition and are mainly composed of quartz, plagioclase, biotite, orthoclase and/or hornblende (Appendix A - G9C; Du Toit and van Reenen, 1977; Du Toit et al., 1983). Because of poor exposure, contact relationships between the grey gneisses and rocks of the Bandelierkop Formation are poorly understood. However, in zones such as the Hout River Transition (or Hout River shear zone; see Fig. 1.3) where contact relationships are visible, a leucocratic granitic melt is present at the contact (Fig. 3.2). Foliations within larger lenses and boudins are generally found to be parallel in orientation to the fabric of the grey gneisses (see also du Toit et al., 1983).

Rocks of the Bandelierkop Formation can be divided into metamorphosed ultramafic, mafic, and metasedimentary members, the latter including minor metamorphosed iron formations and metaquartzites. The petrology of these members is discussed in more detail below.

3.2 Ultramafic Rocks

In the field, ultramafic rocks are recognised as dark brown pods and lenses, commonly forming small hillocks. When somewhat carbonated and serpentinized, the colour is grey to grey-brown. Although often cross-cut and intruded by leucocratic veins and pegmatites, the ultramafic bodies are generally not found in contact with any other rocktype of the Bandelierkop Formation. Petrographically the ultramafic rocks collected for this study can be subdivided into peridotites, pyroxenites and, when intensely retrogressed, serpentinites (see Appendix A and Table 3.1). In all rock types the original textural features of the igneous rocks have been replaced by coarse-grained metamorphic textures.

Peridotites consist predominantly of large grains of enstatite with lesser amounts of olivine, tremolitic hornblende, colourless chlorite, green spinel, minor carbonate and serpentine (Fig. 3.3). Olivine, spinel, chlorite and tremolite can occur as inclusions in enstatite. Both olivine and enstatite are also found replacing larger flakes of chlorite. Serpentine together with fine-grained green chlorite are found as retrograde alteration assemblages along fractures of olivine and enstatite. Only one pyroxenite was sampled (U10A) and consists of finer grained, equigranular enstatite, tremolite, chlorite, green-brown spinel and small amounts of anthophyllite commonly found replacing the enstatite. All constituents show good equilibrium textures, that is, all minerals are in contact with each other and show 120° contact angles.

3.2.1 Metamorphic Reactions and Discussion

Metamorphism of ultramafic rocks is commonly represented in the system CaO-MgO-Al_2O_3-SiO_2-H_2O (e.g. Evans, 1977). The only other major constituent in ultramafic systems is FeO. Because of the formation of magnetite (or spinel) during initial serpentinization of metamorphic rocks (Jolly, 1982; Winkler, 1976 p. 163) and its stability in higher metamorphic grades, little FeO is available for substitution of MgO in silicate minerals. Furthermore because of the relative ease of Fe-Mg substitutions, the errors introduced by omitting FeO from experimental systems are considered to be less than the uncertainties in the experimental determinations of equilibrium conditions (Evans, 1977; Winkler, 1976 p. 163; Turner, 1980 p. 169).

In the above mentioned system, the formation of enstatite occurs according to the reaction:

$$\text{talc} + \text{forsterite} = \text{enstatite} + H_2O \qquad (3.1)$$

(Chernosky, 1976; Evans, 1977) and would indicate upper amphibolite to granulite facies metamorphism (600°-750°C). In a system somewhat richer in alumina, the talc is presumably replaced by chlorite.

Textural evidence for the breakdown of chlorite to enstatite and olivine (Fig. 3.4) would indicate the following reaction:

$$\text{chlorite} = \text{forsterite} + \text{enstatite} + \text{spinel} + H_2O \qquad (3.2)$$

which indicates granulite facies conditions (Fawcett and Yoder, 1966; Chernosky,

1974; Trommsdorf and Evans 1969), with the chlorite being stabilized by Al_2O_3 presence in the ultramafic rocks. The presence of prograde tremolite in equilibrium with olivine would indicate that temperatures for a two-pyroxene paragenesis have not been attained (Evans, 1977 eqn. 2 in Fig. 3). The P-T conditions implied by the above reactions are summarized in Figure 3.19.

Somewhat lower grades of metamorphism could be indicated by the pyroxenite U10A where the presence of idioblastic anthophyllite limits pressures to below about 5kbars (Chernosky, 1976) and temperatures below 600°C (Evans, 1977). Alternatively the anthophyllite in this rock is of retrograde origin, an interpretation which is compatible with the textural evidence.

3.3 Mafic Rocks

Mafic rocks can be identified in outcrop by their green-brown to black colour. They can be both massive and banded with alternating leucocratic and melanocratic bands. Veins varying in size from centimeters to meters can be rich in biotite, amphibole, or amphibole and quartz, all of which are commonly coarse-grained relative to the medium-grained host rocks. Veins show both concordant and discordant characters. Although mafic lithologies were commonly sampled close to pelitic lithologies, no direct contacts between these lithologies were found. However, du Toit et al.(1983) report lenses of ultramafic, pelitic and banded iron formation interlayered with the mafic lithologies.

All the mafic rocks from the high-grade terrane selected for this study are of amphibolitic nature. They vary from true amphibolites composed solely of hornblende + oligoclase with lesser amounts of quartz and titanite via pyroxene amphibolites with hornblende + andesine + clinopyroxene + opaques $\pm$ quartz to two-pyroxene-hornblende gneisses with clinopyroxene + orthopyroxene + labradorite + hornblende (Table 3.2, Fig.'s 3.5 and 3.6).

Increasing anorthite content in plagioclases of the amphibolites is paralleled by an increase in volume percent of pyroxenes and opaques, and a concomitant decrease in hornblende and quartz. Furthermore, the hornblende in the true amphibolites is commonly blue-green whereas in the pyroxene-hornblende gneisses it is brownish-green. In detailed studies of compositionally similar amphibolites in the Adirondack Mountains (Engel and Engel, 1962), and in the central Alps (Wenk and Keller, 1962) such mineralogical and textural changes are ascribed to increasing metamorphic grades.

3.3.1 Metamorphic Reactions and Discussion

The breakdown of hornblende by the generalized reaction:

hornblende + quartz = orthopyroxene + clinopyroxene + plagioclase + H_2O (3.3)

is commonly recognized as separating two subfacies of the granulite facies (de Waard, 1965). However, reaction (3.3) strongly depends on the chemical composition of the hornblende as well as on the oxygen fugacity (fO_2) and $P(H_2O)$ relative to P(total) (Sen and Ray, 1971; Winkler, 1976, p. 260; Spear,

1981; Wells, 1979) and is therefore not commonly used for geothermometry.

Spear's (1981) experiments on the stability of hornblende in a rock of similar bulk composition compared to the Adirondack amphibolites (Engel and Engel, 1962), Indian amphibolites (Raase et al., 1986) and the amphibolites considered in this study, determined that at $P(H_2O)$ = P(total) = 1kbar and fO_2 = QFM (QFM=quartz-fayalite-magnetite), clinopyroxene first appears at 794°C, with the upper thermal stability limit of amphibole being around 910°C (Fig. 3.19). In natural assemblages at granulite facies conditions the complete dehydration of amphibole has been determined to occur at estimated temperatures of 730° $\pm$ 30°C for the Adirondack amphibolites (Stoddard, 1976) and at 722° $\pm$ 22°C for the Indian amphibolites (Srikantapa et al., 1985). This discrepancy between experimentally determined temperatures and those derived for the natural assemblages is most likely to be due to $P(H_2O)$ being much less than P(total) under granulite facies conditions (Spear, 1981; Raase et al., 1985).

Assuming metamorphic conditions suggested for the amphibolites from the Adirondacks and India (i.e. $P(H_2O) \leq$ P(total) and $fO_2 \leq$ QFM - Engel and Engel, 1962; Spear, 1981; Lamb and Valley, 1984; Bhattacharya and Sen, 1986; Edwards and Essene, 1988) to hold true for the amphibolites considered in this study then the assemblage clinopyroxene, orthopyroxene, labradorite and hornblende could indicate peak temperatures of between 700 and 780°C. The temperature would not be expected to be much higher as no olivine is observed and as some hornblende is still present in the SMZ rocks.

Locally the above mentioned changes can however be inverted by retrograde reactions with two-pyroxene-hornblende gneisses being converted to hornblende + andesine amphibolites. Evidence for this retrogression is found in textures where the hornblende partially surrounds the pyroxene, occasionally showing inclusions of the pyroxene (Fig. 3.5). Retrogression is particularly common in veins and fractures cross-cutting the rocks (e.g. M37C and vein in M27C), where blue-green hornblende is found to replace brown-green hornblende of the host rock, the former occuring together with quartz and oligoclase feldspar. However, the blue-green hornblende is never replaced by chlorite and actinolite assemblages, implying that retrogression must have occured above the upper chlorite stability limit (~ 550°C - Liou et al., 1974). Similar retrogressive hornblende growth has been described by Edwards (1957) on a regional scale and by Engel and Engel (1962) on a shear zone scale (10's of meters).

3.4 Metasedimentary Rocks

3.4.1 Pelitic Rocks

the pelitic rocks vary in colour from grey-brown to dark reddish-brown, can be texturally massive or, more commonly, show fine to coarse gneissic banding defined by alignment of biotite, orthoamphibole and/or felsic segregations. The segregations give the rocks a migmatitic character. Both concordant and discordant felsic segregations and veins are present, occasionally displaying

large garnets (up to 7cm; Fig. 3.7). The segregations form rounded patches, lenses, or distinct veins in a finer grained matrix. Whenever pelitic and mafic rocks were found close together in the field, contact relationships were obstructed by the presence of felsic, pegmatitic material.

The pelitic rocks can be divided petrographically into five groups (Table 3.3). Groups names given below are adopted from van Reenen and du Toit (1977) and are listed here in order of increasing petrographic complexity.

1. Garnet-biotite gneisses consisting of garnet, biotite, plagioclase, quartz, minor opaques and Al_2SiO_5 polymorphs.

2. Orthoamphibole gneisses consisting of the above mineralogy with additional gedrite, anthophyllite and occasional cordierite.

3. Garnet granulites consisting of the same minerals as group 1 above with additional orthopyroxene.

4. Cordierite-garnet granulites which are mineralogically the same as group 3 above with additional cordierite, minor spinel and K-feldspar.

5. Cordierite granulites are identical to group 4 rocks but lack garnet (or only a trace left).

Occasional graphite was also detected as an accessory phase in all these rock types.

The migmatitic character of these rocks as observed in the field, as well as in thin section, together with abundant pods and lenses of coarse-grained

quartz and antiperthitic feldspar commonly found surrounding larger skeletal garnet (Fig. 3.7) and orthopyroxene provides evidence for the involvement of partial melting reactions. Whether these reactions occured under fluid-absent or fluid-present conditions is more difficult to determine. However, as the segregations observed in the field as well as those having recrystallized as small pods on thin section scale contain anhydrous mineral assemblages, it is likely that conditions were close to fluid-absent. Identical textural relationships have been ascribed to anhydrous partial melting reactions (e.g. Fediukova and Suk, 1979; Tracy and Robinson, 1983; Waters and Whales, 1984; Waters, 1988). The general absence of K-feldspar from the product assemblages is, however, suggestive of fluid-present melting (e.g. Clemens and Wall, 1981; Grant, 1985). Initial melting could therefore have occured under fluid-present conditions. If only small amounts of fluid were present within these rocks before the high-grade event, this fluid would presumably have entered the first melt formed and subsequent prograde melting will then be fluid-absent. For consistency with previous studies, it is considered best to model these reactions as dehydration melting reactions (c.f. Thompson, 1982) or as vapour-absent melting reactions (c.f. Grant, 1985). Considerations of fluid-absent reactions rather than fluid-present reactions will tend to maximize the P-T estimates (e.g. Clemens and Wall, 1981). It must be emphasized though, that the above described anhydrous product assemblage does not exclude the occurrence of dehydration reactions not involving partial melting, nor does it exclude the possibility of fluid-present partial melting reactions. An alternative explanation, equally valid in describing the presence of an anhydrous mineral assemblage in the segregations, would be that the fluids released from the

crystallization of the melts were expelled along well-defined channelways. Such a fluid release would largely inhibit retrograde hydration reactions.

Texturally most of the rocks indicate a complex metamorphic history and the mineral paragenesis is best considered separately for different groups of rocks.

3.4.1.1 Garnet-Biotite Gneisses

Rocks belonging to this group (P17C, P41C) generally have a simple mineralogy, where textural and mineral inclusion information (refer to Appendix A) would suggest a paragenesis of garnet growth after biotite. This reaction could well have been a partial melting/recrystallization reaction as suggested by the migmatitic character of the rocks, both in outcrop and in thin section (Fig. 3.9). The coarse-grained anhydrous assemblage of quartz, plagioclase and skeletal, poikioblastic garnet makes up the leucosome.

The general absence of a free Al_2SiO_5 polymorph would exclude sillimanite (or kyanite) as being a reactant or, alternatively, suggests that the aluminosilicate has been consumed during the reaction. Fine needles of what is believed to be sillimanite are found intergrown with and replacing the biotite, particularly in places where the biotite occurs close to segregations. These aluminosilicate needles are therefore considered to be of retrograde origin. However, according to Carmichael (1969), these needles could represent an intermediate stage in the breakdown of biotite where immobile Al^{3+} ions form sillimanite while more mobile components (K^+, OH^-, Fe^{2+}, Mg^{2+}, etc.) are removed or added from elsewhere before garnet can crystallize. This

interpretation is considered invalid as the product garnet is higher in Al-content relative to the biotite and also largely accomodates the Fe and some of the Mg released from the biotite breakdown.

The absence of a potassic phase in the anhydrous assemblage could imply that the K-component was incorporated in the melt.

3.4.1.1.1 Mineral Reactions and Discussion

In the light of the above textural evidence, the following reactions can be deduced:

biotite + quartz + plagioclase + Al_2SiO_5 + H_2O = garnet + melt (3.4)

or, if anhydrous conditions existed then K-feldspar presence is required (Powell, 1983):

biotite + quartz + plagioclase + Al_2SiO_5 = garnet + K-feldspar + melt (3.5)

Owing to the Fe-Mg exchange between garnet and biotite these reactions are continuous and both phases may change their compositions and be stable over a wider temperature range. As K-feldspar is not present in these rocks it could imply:

1. that hydrous melting occured according to reaction (3.4) above,
2. that anhydrous melting occurs, but that the K_2O content of the melt is too small to allow K-feldspar to crystallize (c.f. Powell, 1983).

The latter case could be explained by the low bulk rock K_2O contents observed for these rocks, indicating that reactions such as (3.5) represented in K_2O-FeO-Al_2O_3-SiO_2-H_2O (KFASH) and K_2O-MgO-Al_2O_3-SiO_2-H_2O (KMASH) diagrams of Thompson (1982, reaction 48) as written may not be applicable to the K_2O depleted rocks of the SMZ. Small amounts of K_2O can, upon crystallization of the melt be incorporated into the plagioclase forming antiperthite (see for example sample V6D). This speculation would be consistent with the observation that large, recrystallized plagioclase is commonly antiperthitic (see Appendix A).

Assuming as a maximum temperature estimate dehydration melting of biotite to produce garnet, and using the P-T projection of Clemens and Wall (1981) for biotites of similar composition (Fe/Fe+Mg ~ 0.4, refer to Chapter 5), temperatures of between 700 to 770°C can be estimated for pressures of between 6 to 8kbars for the garnet-biotite gneisses (see also Fig. 3.19). In melting experiments on assemblages of biotite, quartz and plagioclase, Hoschek (1976) observed the first formation of garnet at temperatures of around 725°C at $P(H_2O)$ = 4kbars and QFM buffering, which is in good agreement with the estimated temperatures of >675°C by Tracy and Robinson (1983) for the fluid-absent melting of biotite forming garnet in felsic segregations and also with the temperatures given by Clemens and Wall (1981). It is interesting to note though that the starting assemblages used by Hoschek (1976), did not include any aluminosilicate. In that case the Al_2O_3 required for garnet formation may have been derived from the breakdown of feldspar. The absence of an aluminosilicate phase from a starting assemblage of biotite, quartz and

plagioclase, therefore, does not appear to influence the progress of the reaction to form garnet.

The presence of garnet in some rocks (Fig. 3.7) and of cordierite in other rocks closeby (Fig. 3.8), is likely to be a function of the Fe/Mg ratio in the biotite as the only ferromagnesian phase in these rocks prior to partial melting (Thompson, 1982 p. 1586/7). However, the large cordierites observed in some outcrops are not generally surrounded by felsic segregations as is observed for the rocks containing garnet. As the rocks outcrop only several meters apart, one can assume that the P-T conditions for these rocks were very similar. The absence of melts during cordierite formation would agree with the observations of Thompson (1982) that partial melting in Fe-rich rocks can be concurrent with simple dehydration reactions in Mg-rich rocks at temperatures of around 700°C.

3.4.1.2 Orthoamphibole Gneisses

The rocks classified as orthoamphibole gneisses cover a wide compositional range (see Chapter 4) and thus show various metamorphic assemblages. In general they are characterized by the presence of fibrous to coarse-grained gedrite and lesser anthophyllite in addition to biotite and garnet (Table 3.3). In the Fe-rich rocks such as samples P5C and P6C only trace amounts of biotite are left as inclusions within garnet and no free biotite is present. In these rocks garnet and gedrite show clean contacts. However, in rocks richer in MgO where biotite is present, garnet is not found in textural equilibrium with either biotite (Fig. 3.10) or gedrite (Fig. 3.11). In most rocks fibrous gedrite is found

replacing the biotite, and as biotite forms a common inclusion in coarser grained gedrite, growth of gedrite after biotite is indicated. In addition to fine-grained gedrite, small aluminosilicate needles have also been identified within the biotite-gedrite intergrowths. Cordierite grains within these rocks were observed in the biotite-gedrite intergrowths, as well as between garnet-biotite contacts (Fig. 3.11). Cordierite can show small spinel inclusions.

3.4.1.2.1 Mineral Reactions and Discussion

Textural relationships for these rocks suggest the following reactions:

biotite + garnet = orthoamphibole + K-feldspar + H_2O (3.6)

or, in the more magnesian rocks:

biotite + garnet = orthoamphibole + cordierite + K-feldspar + H_2O (3.7),

(e.g. Grant, 1981).

In the case of the Fe-rich rocks (P5C, P6C and P42C), complete removal of biotite results in a stable coexistence of garnet and orthoamphibole. In all other orthoamphibole gneisses, disequilibrium textures observed on ferromagnesian mineral contacts, together with the fibrous nature of the biotite-orthoamphibole intergrowths, implies incomplete reaction progress.

Absence of K-feldspar as a reaction product may suggest that the above reactions were accompanied by partial melting processes. By analogy to the reactions forming garnet (e.g. reactions (3.4) and (3.5) above), the K-feldspar

component may be incorporated into the melt phase. The occurrence of partial melting has also been used by Grant (1968) to explain cordierite-orthoamphibole bearing assemblages similar to those observed in these SMZ rocks. In addition, Knabe (1970a) and Hoschek (1976) observed orthoamphibole formation in experimental runs with starting assemblages of biotite, quartz and plagioclase but no garnet (experiments at $P(H_2O) = P(Total)$). In the reaction suggested by Knabe (1970a):

biotite + quartz + plagioclase = gedrite + K-feldspar + H_2O (3.8),

the K-feldspar component together with quartz and plagioclase is considered to make up the melt. However, these experiments were performed under hydrous conditions. Under essentially dry conditions the H_2O available will presumably be taken up by the melt and orthopyroxene instead of orthoamphibole is expected to be formed (Knabe, 1970b; Grant, 1981). Reaction (3.8) could explain the common biotite-gedrite intergrowths observed in these rocks.

It is therefore concluded, that the orthoamphibole (and cordierite) in these rocks formed from the breakdown of biotite or biotite and garnet. If the reaction was accompanied by partial melting, then such melting occured under fluid-present conditions. While not producing the typical fluid-absent melting textures (e.g. Tracy and Robinson, 1983; Waters and Whales, 1984; Waters, 1988), such melting is consistent with the general migmatitic character of these rocks.

Knabe (1970a) and Hoschek (1976) observed orthoamphibole formation in experimental runs with starting assemblages of biotite, quartz and plagioclase to occur at temperatures of 650 to 725°C and fluid pressures of 2 and 4kbars

respectively.

Coarse-grained orthoamphibole could be identified as both gedrite and lesser amounts of anthophyllite, both of which were in direct contact with each other. Spear (1980) estimated the crest of the solvus between anthophyllite and gedrite to occur at approximately 600 $\pm$ 25°C. These somewhat lower temperatures compared to those of Knabe (1970a) and Hoschek (1976) may suggest that orthoamphibole formation started at temperatures as low as ~ 620°C in rocks of suitable bulk composition. However, because of Fe-Mg exchange amongst the ferromagnesian phases, the above reactions are continuous and thus all phases are stable over a wider temperature interval. The reason for the incomplete reaction and disequilibrium textures is not known, but could be related to melt removal and/or rapid changes in metamorphic conditions subsequent to the start of the reactions outlined above.

3.4.1.3 Garnet Granulites

Only one rock could be identified as a garnet granulite in this study (P25C). This rock is mineralogically similar to those of group 1 above except that it contains additional orthopyroxene of similar poikioblastic texture as the garnet. Inclusion mineralogy of the garnet and orthopyroxene would indicate growth of garnet and orthopyroxene after biotite, quartz and plagioclase (Fig. 3.12). All phases show good equilibrium contacts (120° triple junctions).

3.4.1.3.1 Mineral Reactions and Discussion

The breakdown of the biotite in this rock can be envisaged as a two stage process. In this process the garnet may be produced via reactions (3.4) or (3.5) as described above. Due to the Fe-Mg exchange between biotite and garnet, these reactions are continuous reactions and both phases can change their compositions and be stable over a wider temperature interval. Thus, after partial melting and production of garnet, the biotite, now somewhat more magnesian in composition (Ellis, 1982), may coexist stably with its product phase, until a further temperature increase occurs. Subsequently the biotite may break down to form orthopyroxene according to:

biotite + quartz + plagioclase = orthopyroxene + K-feldspar + melt (3.9).

A further composition change of the biotite may result in its stable coexistence with both the garnet and the orthopyroxene at temperatures above the formation temperatures of orthopyroxene, provided the biotite is in excess of other reactant phases. This biotite breakdown may be analogous to that of hornblende in mafic systems (reaction (3.3) above; Spear, 1980), except that textural evidence implies the involvement of partial melting instead of simple dehydration. In analogy to the above systems the K-feldspar component may enter the melt.

In partial melting experiments on assemblages of biotite, quartz and plagioclase, Hoschek (1976) showed that the mineral products formed by the breakdown of biotite critically depend on the Al-Mg-Fe composition of the biotite. Garnet and orthopyroxene are restricted to more Fe-rich compositions,

cordierite is limited to Mg-rich biotite compositions, whereas orthoamphibole appears in rocks with medium Fe/Mg and high Al contents in the biotite. He also indicated that the biotite solid solution is shifted towards medium Al contents and medium to high Mg/Fe ratios and that these biotites can exist stably to temperatures which are in excess of those of initial melting. Temperatures of first formation of orthopyroxene in Hoschek's (1976) experiments varied from 675 to 750°C, depending on biotite and/or plagioclase compositions (temperatures at $P(H_2O)$ = 4kbars). Hoffer and Grant (1980) experimentally determined coexistence of orthopyroxene and liquid to occur at temperatures as low as 675°C at hydrous pressures of 6 to 8kbars. However, these somewhat lower temperatures, when compared to those of Hoschek (1976), may be explained by the experimental conditions used, as Hoffer and Grant (1980) included seeds of orthopyroxene in their starting assemblages of quartz, albite and biotite.

Clemens and Wall (1981; see also Fig. 3.19) approximated the fluid-absent formation of orthopyroxene, as illustrated in reaction (3.9) above, to temperatures of about 750°C at 4kbars and 780°C at 8kbars, which is in good agreement with the experiments of Hoschek (1976).

An alternative to the two-stage process is the coeval formation of garnet and orthopyroxene:

biotite + quartz + plagioclase = garnet + orthopyroxene + K-feldspar + melt (3.10)

which, according to the experiments of Hoschek (1976) can occur at about 750°C for biotites of the correct compositions.

Both Knabe (1970a, b) and Hoschek (1976) demonstrated, that for assemblages of biotite, quartz and plagioclase (i.e. for relatively K_2O poor rocks) the K-feldspar component enters the melt phase and is not necessarily an anhydrous product of biotite breakdown reactions as illustrated elsewhere (e.g. Thompson, 1982; Grant, 1985). The possible incorporation of K_2O into plagioclase is evidenced by the observation that large, probably recrystallized plagioclase tends to be antiperthitic in character (e.g. V6D in Appendix A).

3.4.1.4 Cordierite-Garnet Granulites

The cordierite-garnet granulites are mineralogically and texturally the most complex rocks. They contain biotite, cordierite, garnet, and orthopyroxene as ferromagnesian phases together with quartz and antiperthitic plagioclase.

Orthopyroxene and garnet can have a similar appearance as in group 3 rocks, occuring as clusters or stringers and/or as poikioblastic grains with inclusions of biotite, quartz, and plagioclase. In some cases garnet is surrounded by fine intergrowths of biotite, cordierite and orthopyroxene. Biotite can be partially replaced by needles of aluminosilicate (analyzed as kyanite by van Reenen, 1978) and in places is found to be replaced by cordierite. Pseudomorphs of cordierite after biotite (Fig. 3.13) and inclusions of biotite and garnet within cordierites (Fig. 3.15), indicates the growth of cordierite after biotite and garnet. In addition, cordierite commonly shows small spinel inclusions. Potassium feldspar is limited to large antiperthitic grains or to a vermicular intergrowth involving plagioclase and quartz (Fig. 3.14). Crystals of an

aluminosilicate in these rocks are found in intergrowths with biotite, or if cordierite is present to an intergrowth with cordierite and biotite, and to feldspar-feldspar and feldspar-quartz boundaries, as well as rimming cordierite grains. In all cases the growth of aluminosilicate crystals is texturally interpreted to have occured after the initial formation of biotite, feldspar, quartz and cordierite crystals. As such the aluminosilicate crystals may be retrograde in origin (see also Vernon and Flood 1977).

3.4.1.4.1 Mineral Reactions and Discussion

Textural evidence in these rocks is therefore taken to suggest the following melting reactions:

biotite + garnet + quartz + plagioclase = cordierite + orthopyroxene + K-feldspar + melt (3.11)

(e.g. Reinhardt, 1968; Grant, 1973; 1985) or, if some aluminosilicate was present as a reactant phase:

biotite + Al_2SiO_5 + quartz + plagioclase = cordierite + spinel + K-feldspar + melt (3.12).

For both reactions, the K-feldspar component produced is considered to be incorporated into large recrystallized plagioclase grains forming antiperthite. Alternatively it is removed with the melt.

In terms of the ferro-magnesian minerals, reaction (3.11) could represent the fluid-absent equivalent to reaction (3.7) described for orthoamphibole gneisses of identical bulk major element composition (see Chapters 4 and 5). Cordierite formation from partial melting of a biotite, quartz and plagioclase assemblage was also observed by Hoschek (1976) for magnesian biotites. By analogy to the formation of garnet in the garnet-biotite gneisses, the Al_2O_3 required for the formation of cordierite must have been derived from the reactant plagioclase component.

In Hoschek's (1976) melting experiments the first formation of cordierite occured at 750°C ($P(H_2O)$ = 4kbars and QFM buffering). This agrees well with the tentatively placed univarient equilibria of equation (3.11) as shown by Grant (1985, Fig. 3.15; temperatures of 720 to 780°C at pressures of 3 to 5kbars) and with temperatures of about 750°C at pressures of 5kbars as determined by Waters (1986) for pelitic rocks in Namaqualand. Harris and Holland (1984) estimated temperatures >675°C and pressures of around 4.5 $\pm$ 0.8kbars for assemblages of garnet, cordierite, orthopyroxene and sillimanite from rocks of the Central Zone of the Limpopo Belt.

Experiments by Hoffer (1978) and Hoffer and Grant (1980) placed the fluid-present equivalents of reaction (3.12) and (3.11) respectively at temperatures of 650 to 680°C (at $P(H_2O$ = 6kbars and QFM buffering). The discrepancy between these experiments and those of Hoschek (1976) may be explained by the experimental procedures used. Hoffer (1978) and Hoffer and Grant (1980) used seeds of product phases in their reactant mixtures, thereby allowing for relatively easy product crystal growth.

3.4.1.5 Cordierite-Granulites

The cordierite-granulites are mineralogically identical to the cordierite-garnet granulites of group 4, except that they lack garnet, or in the case of sample P8C only contain trace amounts of garnet.

While biotite, plagioclase and quartz have a similar appearance as in the previous group of rocks, this is not necessarily the case for cordierite and orthopyroxene. The coarse-grained cordierite and orthopyroxene show similar textural appearance as in group 4 rocks. Elsewhere within these rocks the cordierite and orthopyroxene form an intergrowth texture which pseudomorphs garnet (Fig. 3.16) with small, commonly vermicular orthopyroxene surrounded by somewhat larger cordierite grains. Garnet may occur as a corroded relict phase surrounded by such intergrowth zones. Small biotite laths are always present within these intergrowths, while quartz and feldspar grains are rarely observed within such intergrowths. Biotite inclusions are confined to cordierite crystals. In addition, small green spinels may form inclusion trails within the cordierite.

These textures have been described in more detail by van Reenen (1978, p. 77 to 79; 1983) in SMZ rocks and by Reinhardt (1968) in regional metamorphic cordierite-gneisses of Canada and by Schreyer and Abraham (1980) in a contact metamorphic terrane. Texturally these pseudomorphs after garnet would thus indicate that cordierite, orthopyroxene, garnet, biotite, and possibly also spinel may be involved in the symplectite formation (see also van Reenen, 1978 p. 79).

3.4.1.5.1 Mineral Reactions and Discussion

The complete removal of garnet from these Mg-rich rocks can be represented by the following reaction:

biotite + garnet = cordierite + orthopyroxene + K-feldspar + H_2O (3.13).

In the case of silica deficiency (Schreyer and Abraham, 1978):

garnet = cordierite + orthopyroxene + spinel (3.14)

In the rocks considered by Reinhardt (1968), the breakdown of garnet as illustrated by equation (3.13) represents the last stage of prograde metamorphism for his cordierite-gneisses. According to van Reenen (1978, 1983) the breakdown of garnet did not necessarily involve biotite, even though it is the most common inclusion in such intergrowths (van Reenen, 1978 p. 79) but instead involved only quartz:

quartz + garnet = cordierite + orthopyroxene (3.15).

The presence of small green spinels, commonly as inclusion trails within cordierite would argue against excess quartz having been present during the formation of some parts of the symplectite. However as some, although only very minor in abundance, quartz and plagioclase do occur within the symplectite intergrowths (Fig. 3.17) and as spinel occurrence is not ubiquitous, reactions (3.13), (3.14) and (3.15) may be combined to give a resultant reaction similar to (3.11) above, with or without spinel as a product, depending on the local conditions of silica saturation. The K-feldspar and H_2O are presumably

incorporated into a melt phase, the presence of which is indicated by larger felsic segregations within these samples, and also recognizable as coarse-grained quartz and feldspar in thin section. The presence of larger segregation type quartz in the vicinity of coarse-grained orthopyroxene commonly found surrounding these symplectites would argue for enhanced diffusion of ions across melt phases.

Estimated temperatures for the symplectite formation would therefore be similar to those suggested in section 3.4.1.4.1 above.

3.4.2 Banded Iron Formations

Sample B4A, outcropping close to the mafic rocks M2A and M3A (Fig. 2.1), consists of quartz and magnetite in approximately equal proportions with lesser amounts of pigeonite and grunerite. high-grade iron formations according to Klein (1983) largely consist of quartz and magnetite with additional pyroxene and possible small amounts of fayalite and garnet. Although abundant in medium-grained iron formations (Klein, 1983), grunerite is only present in small amounts in high-grade iron formations, as it breaks down to form pyroxenes and/or fayalite at temperatures of 700 to 800°C (Klein, 1983).

An assemblage similar to that of sample B4A has been observed by Vaniman et al. (1980) in a contact metamorphic rock where the formation of orthopyroxene by inversion from pigeonite is considered to indicate peak metamorphic conditions of higher than 800°C at pressures of above 2kbars. Experiments of Simmons et

al. (1974) and Smith (1972) indicate that at higher pressures and higher Mg-contents of the pyroxene, higher temperatures are needed to stabilize pigeonite relative to its inversion products of augite and orthopyroxene. Pigeonite in sample B4A is uninverted (Fig. 3.18) which, assuming similar compositions of B4A to the banded iron formation of Vaniman et al. (1980), may indicate temperatures significantly higher than 800°C at pressures of higher than the 2kbars inferred by Vaniman et al (1980). The uninverted character suggests that P-T conditions after crystallization of the pigeonite must have changed rapidly, that is fast cooling and/or rapid uplift, or alternatively post-peak metamorphic conditions must have been very dry, thereby inhibiting diffusion within this sample (Cox et al., 1979). Another alternative could be that the pigeonite is very Fe-rich, implying somewhat lower stabilization temperatures (~800°C) and due to the sluggish inversion of Fe-rich pigeonite (Podpora and Lindsley, 1979; Cox et al., 1979) no rapid changes in P-T conditions need to be invoked.

Grunerite is more commonly developed in medium grade banded iron formations and its presence in B4A as separate, isolated grains may indicate that the upper thermal stability limit of grunerite has not been reached (temperatures of <850°C; Klein, 1983).

3.5 General Discussion and Conclusions

Mineral textures of ultramafic, mafic and metasedimentary rocks collected from the Southern Marginal Zone (see Fig. 2.1 for sample localities) allow an

interpretation of the prograde metamorphic imprints to be made. A comparison of mineral reactions deduced from textural evidence of these rock groups with those reported from the literature for the metamorphism of compositionally similar natural and experimental assemblages, indicates that peak metamorphic conditions reached were presumably of the order of 750 $\pm$ 70°C at pressures of 5 to 8kbars (see Fig. 3.19). The peak pressures are not well constrained due to the lack of pressure sensitive reactions in the rocks considered. For the rocks south of the orthopyroxene isograd (Fig. 1.3) higher partial pressures of H_2O are suggested by the formation of orthoamphibole (+ cordierite) after biotite and garnet, relative to the formation of cordierite and orthopyroxene after biotite and garnet for the granulites found north of the isograd. The orthopyroxene isograd is therefore interpreted to be a prograde (decreasing $P(H_2O)$) feature. However, both north and south of the isograd, metamorphic conditions during initial melting may be described as fluid-present. This is implied by the absence of free K-feldspar from the product assemblage. Minor K-feldspar is present only as antiperthite in the cordierite-bearing rocks (high MgO rocks), suggesting subsequent fluid-absent melting.

Many of the prograde textures have been modified by subsequent retrograde effects. Such modifications include:

1. Partial hornblende rimming around pyroxenes and formation of secondary hornblende veins within mafic rocks.

2. Fibrolitic growth of aluminosilicate within biotite, surrounding cordierite grains and along feldspar-feldspar grain boundaries in pelitic

rocks.

3. Embayments of segregation garnet by quartz, biotite and aluminosilicate within pelitic rocks.

4. Partial replacement of cordierite by gedrite and aluminosilicate assemblages (see also van Reenen, 1986).

5. Partial serpentinization of metamorphic olivine and enstatite along fractures within these minerals in the ultramafic rocks.

In the case of ultramafic and mafic rocks, such retrograde effects are common only along veins cutting the rocks, or if rocks are relatively small xenolithic fragments within leucocratic material. For the pelitic rocks such retrogression is particularly common next to felsic segregations, both on the outcrop scale and on thin section scale.

This spatial association between retrogressive features and felsic segregations could indicate that the fluids released upon crystallization of the segregation material may have enhanced local retrogression (Corbett and Phillips, 1981; Watkeys et al., 1988). In the case of the pelitic rocks, presence of small pockets of a melt phase may have caused the establishment of local chemical gradients due to the enhancement of diffusion in the vicinity of the melt phase, resulting in the establishment of a diverse mineralogy and texture over the scale of millimeters.

If retrogression is caused by the crystallization of melts formed during the prograde stage, then this may be related to cooling beyond the granitic

solidus (curve H in Fig. 3.19) and as such could represent a separate metamorphic event. Small retrograde aluminosilicate crystals identified as kyanite by van Reenen (1978), growing within Al-containing silicates, combined with the location of the granitic solidus could imply isobaric cooling of the terrane. Such retrograde, isobaric cooling has been described for other Precambrian terranes by Corbett and Phillips (1981), Warren (1983) and Waters (1986). The occurrence of disequilibrium textures, incomplete mineral reactions and, in some pelitic rocks, the presence of at least four ferromagnesian phases (reactant and product phases) may suggest overstepping of metamorphic assemblages and the existence of metastable phases during subsequent metamorphic events. These features, collectively, suggest rapid changes in metamorphic conditions or open system behaviour, that is, removal of some components during metamorphism (e.g. melt removal).

The conclusions given above are in marked contrast to those of van Reenen (1978; 1983; 1986) for the SMZ rocks. According to van Reenen (1983), the cordierite-orthopyroxene symplectite after garnet formed during retrograde decompression. In addition, van Reenen (1986) suggests that retrogressive replacement of orthopyroxene and cordierite formed the orthoamphibole now observed in the orthoamphibole gneisses. These gneisses are thus interpreted by van Reenen (1986) to be retrogressed granulite facies rocks. For reasons discussed below these interpretations are considered to be incorrect.

The retrograde character for the cordierite-orthopyroxene symplectite is deduced from the assumption that stable coexistence of garnet and cordierite occured in the cordierite-garnet granulites at pressures of above 9.5kbars as

based on experiments by Henson and Green (1972), together with the presence of kyanite intergrown with biotite (van Reenen 1983, p. 165). These pressures are considered invalid for reasons listed below:

1. Recent work by Holdaway and Lee (1977) and Martignole and Sisi (1981) has indicated that cordierite is stabilized towards higher pressures by both the Mg-content and H_2O content. Thus cordierite may be used as a geobarometer only if both temperature and $X(H_2O)$ are known, invalidating the geobarometry of Currie (1971) and Hensen and Green (1972) as used by van Reenen (1983). The cordierite contained in the rocks of this study are generally optically positive which suggests that they are fairly CO_2 rich (Armbruster and Bloss, 1980). If this is indeed the case, then the upper P-T stability limit of Mg-rich cordierites of this study (see Chapter 5) could be estimated to fall below ~7.5kbars, assuming $X(CO_2) = X(H_2O)$ at temperatures of ~750°C (curve G in Fig. 3.19; Martignole and Sisi, 1981), indicating that cordierite and garnet must have coexisted at pressures below 7.5kbars.

2. The occurrence of fine-grained needles of an Al_2SiO_5 polymorph both within the biotite and within the cordierite (never as separate crystals) has been identified as kyanite by van Reenen (1978, 1983). The difference in grain size of needles within the biotite and of those within cordierite (fine-grained) has led van Reenen (1983) to conclude that the kyanite within the biotite is prograde whereas that in cordierite is part of the retrogressive event replacing the cordierite by gedrite + kyanite intergrowths (van Reenen 1986). This difference in grain size of the

aluminosilicate in the biotite and the cordierite may be due to easier nucleation and growth of the aluminosilicate in the relatively large, open structure of the biotite compared to the smaller void spaces within the cordierite. Results on experimental investigations in the Al_2SiO_5 system indicate that the Al_2SiO_5 polymorphs show extremely slow reaction rates, resulting in poor nucleation and crystallization (e.g. Richardson et al., 1969; Holdaway, 1971). Thus, in experimental runs coarse-grained aluminosilicate crystals are used as nucleation centers for further growth of the same or other polymorphs thereof (Holdaway, 1971). In natural systems, Al-containing minerals such as biotite, plagioclase and cordierite could have served as nucleation centers. Once nucleated, the aluminosilicate crystals can then grow adjacent to these minerals or, in the case of minerals with fairly open structures, may project into the minerals. It is interesting to note that the fine needles observed along feldspar-feldspar and quartz-feldspar boundaries are even finer grained than those within the cordierite which may lead to the conclusion that all the aluminosilicates present are probably retrograde in origin and cannot be used as proof of high pressures during prograde metamorphism.

In the light of the above, the existence of a hypothetical M1 metamorphic event ($P \geq 9.5$kbars, T ~800°C) as proposed by van Reenen (1983), is not supported by this study.

It was concluded above that retrogression has, to some extent, modified the prograde mineral assemblages. However, the occurrence of coarse-grained orthoamphibole is not considered to have formed solely by retrogression of

orthopyroxene and cordierite as indicated by van Reenen (1986), for the following reasons:

1. Partial replacement of cordierite occurs throughout the whole terrane (north of the isograd; van Reenen, 1986), occasionally pseudomorphing the cordierite.

2. Cordierite is also found in the orthoamphibole gneisses.

3. Gedrite is found replacing biotite in the orthoamphibole gneisses and both biotite and orthoamphibole define the strong foliation within these gneisses. Orthoamphibole formation after biotite would involve the loss of H_2O. This would not be expected if retrogression was caused by the infiltration of fluids (van Reenen, 1986). In addition, replacement orthoamphibole as envisaged by van Reenen (1986), where the orthoamphibole replaces orthopyroxene and cordierite, would not be expected to grow parallel to the foliation in the rock, particularly as van Reenen's M3 isograd (1986) is not followed by any fabric-forming event (du Toit et al., 1983 p. 140).

4. Extraction of at least some of the segregation material and its crystallization distant from its place of origin would inhibit complete retrogression.

5. Presence of local chemical gradients (millimetre scale) may be indicative of rapid prograde reactions involving partial overstepping, creating metastable phases and removing some of the product phases in the form of a

melt. Intense retrogression as envisaged by van Reenen (1986) would tend to destroy such local chemical gradients.

CHAPTER 4: WHOLE ROCK GEOCHEMISTRY

4.1 Introduction

In the following section the major and trace element geochemistry of the three members of the Bandelierkop Formation are discussed. The principal aim is to compare the geochemistry of the high-grade rocks in this study to the geochemistry of similar rock types from unaltered, less metamorphosed lithologies elsewhere, in order to establish what the geochemistry of the pre-metamorphic equivalents to these high-grade rocks could have been, and to try and assess the changes in composition, if any, that could have affected these rocks during metamorphism.

For analytical techniques used and estimated analytical errors refer to Chapter 2. All variation diagrams and compositional comparisons are based on recalculated volatile-free data given in Appendix B.

4.2 Ultramafic Rocks

In the past, it has been suggested that the ultramafic and mafic rocks of the Bandelierkop Formation form part of a high-grade supracrustal sequence (e.g. du Toit et al., 1983). However, the absence of fine-grained igneous volcanic textures which may be preserved even at high-grade metamorphism (e.g. Arndt et

al., 1979) in combination with the generally isolated outcrop pattern of the ultramafic rocks relative to other rocks of the Bandelierkop Formation, suggests an intrusive origin for these ultramafic rocks. The major and trace element compositions of the ultramafic rocks (Table 4.1) have therefore been compared to the major and selected trace element ranges of some Archaean komatiitic (i.e. volcanic) and intrusive harzburgitic rock groups selected from the literature (Table 4.2 and Fig.'s 4.1 and 4.2a, b and c).

The comparison to komatiitic rocks indicates that the SMZ ultramafic rocks tend to be depleted in TiO_2, FeO, MnO, and CaO but enriched in MgO, Ni, and Cr. If it is assumed that the SMZ ultramafics were originally komatiitic, then these compositional differences could be due to the following:

1. original magmatic differences existed and the rocks behaved as closed systems during metamorphism to high-grades,

2. differences were induced by alteration processes prior to metamorphism and the rocks behaved as closed systems during metamorphism,

3. differences are caused by an open system behaviour during metamorphism,

4. a combination of two, or possibly all three of the above.

While the first alternative is impossible to test, estimates on the possible effects of the second alternative can be made by reference to alteration studies on rocks of basaltic composition (e.g. Condie et al., 1977; Robinson et al., 1977; Seyfried et al., 1978; Donelly et al., 1980; Beswick, 1982; Smith et al., 1984). These studies commonly indicate loss of, amongst others, Fe and Ca if

epidote, iron oxides or iron sulphides and carbonates are not stabilized. Hynes (1980) also observed mobility of Ti in special cases of CO_2-rich alteration fluids where Ti concentrations can be affected by the formation of CO_3^{2-} - Ti^{4+} complexes, with high Ti contents being reflected by high carbonate contents.

The interpreted Fe, Ti, Ca depletion of the SMZ rocks could therefore indicate the formation of serpentine and chlorite as dominant alteration minerals, with only minor carbonate and possibly Fe-sulphides rather than Fe(-Ti)-oxides. With initial metamorphism, the Ca-carbonate and Fe-sulphide components may then break down to release much of the Ca and Fe whereas Mg (and Ni, Cr) is fixed in the mafic phases created. Removal of FeO, MnO, CaO and TiO_2 by the alteration fluid would result in a relative increase in the residual oxide concentrations of the komatiitic precursor. A problem with this hypothetical komatiitic alteration model is that the enrichment in MgO as shown by the high-grade rocks relative to the komatiitic rocks is not reflected by increased concentrations of the other oxides (i.e. SiO_2, Al_2O_3, Na_2O, K_2O and P_2O_5). In addition, the high trace element content of Ni and Cr, elements which are reported to be immobile during alteration processes (Condie et al., 1977; Smith et al., 1984), cannot be explained by such an alteration process. Pre-metamorphic alteration processes therefore appear to be unlikely explanations for the differences in chemical composition of the SMZ ultramafics relative to komatiitic rocks.

A detailed chemical comparison of the high-grade ultramafic rocks with Archaean intrusive ultramafic rocks is largely limited to rocks from the

Barberton greenstone belt (Table 4.2). Nevertheless, the major element similarity of the high-grade rocks with harzburgitic rocks from the Barberton area (Viljoen and Viljoen, 1970; Anhaeusser, 1979) and with peridotitic-pyroxenitic igneous rocks in general (e.g. Cox et al., 1973; not shown) is in support of an intrusive origin for the high-grade ultramafics. In this case no special alteration events are required in order to explain the bulk chemistry of the high-grade rocks.

A comparison of the serpentinite (U6B - Appendix B) with the average volatile free composition of the high-grade rocks (Table 4.2) indicates nearly identical compositions. This may be interpreted to imply that the chemical changes occuring during metamorphism are negligible (except for a loss in H_2O and CO_2). Such an isochemical behaviour during metamorphism of ultramafic rocks has also been observed by Jolly (1980) and Pearton (1982).

4.3 Mafic Rocks

For reasons similar to those given above for the ultramafic rocks, the compositions of the high-grade mafic rocks of this study (Table 4.3) are compared to those of volcanic and intrusive Archaean mafic rocks selected from the literature (see Table 4.4). Chemical comparisons with rocks of apparent volcanic origin are also illustrated in Figures 4.1, 4.2a, b and c.

A comparison with volcanic tholeiitic rocks from the Kaapvaal craton and to other Archaean tholeiitic rocks (e.g. Condie et al., 1976; Jolly, 1980; not

shown) indicates that the compositional range of the amphibolites extends to significantly lower TiO_2, Al_2O_3, FeO and Zr concentrations, with higher MgO, CaO, Cr and Ni values. As for the ultramafic rocks, these compositional differences could be due to alteration and/or open system metamorphic processes or it may suggest that the amphibolitic rocks were not originally of tholeiitic affinity. In Figures 4.1 and 4.2 the amphibolitic rocks are found to plot within a number of compositionally distinguishable fields, partially straddling the boundary between the tholeiitic and komatiitic fields. While this could suggest that the amphibolitic rocks were derived from rocks of originally different affinities, that is, tholeiitic and komatiitic affinities, the approximate linearity of the trends in combination with the continuity of samples along the trends formed by the amphibolites in chemical variation diagrams (Fig. 4.1, 4.2 and others - not shown), could be taken to imply the derivation of amphibolitic rocks from an originally continuous magmatic series (e.g. komatiitic basaltic, high-Mg basaltic). Furthermore, the high MgO, Ni and Cr contents of the amhibolites, where these elements are commonly observed to be more or less immobile during seawater/hydrothermal alteration processes (e.g. Condie et al., 1974; Donnelly et al., 1980; Smith et al., 1984), would tend to argue against significant shifts in composition caused by pre-metamorphic alteration.

The amphibolitic rocks have also been compared to rocks of high-Mg basaltic and komatiitic affinities as well as to some intrusive gabbroic rocks (Table 4.4). From such a comparison it becomes evident that the amphibolitic rocks show very similar compositional ranges to those of the high-Mg basaltic, basaltic komatiitic and intrusive gabbroic series, for all oxides and trace elements

considered. This compositional similarity suggests that the precursor material to these rocks could have been rocks belonging to the high-Mg basaltic series (e.g. Hallberg and Williams, 1972, not shown; Nisbet et al., 1977) or rocks similar to the basaltic komatiites of Viljoen and Viljoen (1969b) or, alternatively, to gabbroic, intrusive rocks (Anhaeusser, 1979; Srikantappa et al., 1984). The compositional range covered by high-Mg basalts and gabbroic rocks is fairly large, making further chemical distinction difficult. However, both of these magmatic series are commonly found closely associated with ultramafic rocks (c.f. Viljoen and Viljoen, 1969; Hallberg and Williams, 1972; Nisbet et al., 1977; Anhaeusser, 1979; Srikantappa et al., 1984).

The mineralogy of sample M11B, which was collected from the Pietersburg greenstone belt (see Fig. 2.1), indicates greenschist facies grade of metamorphism. Compositionally it is very similar to the amphibolites and, because of its relatively high Ni, Cr and MgO contents, may also be of a high-Mg basaltic affinity. In this regard it is interesting to note that M11B was sampled from a pillow unit within the Pietersburg greenstone belt.

The above mentioned compositional similarities between the amphibolites, the high-Mg basaltic rocks and M11B, indicates that metamorphism for these mafic rocks could be approximated as a closed system process (except for H_2O, CO_2). Compositional changes of the amphibolites with increasing metamorphic grade such as observed by Engel and Engel (1962) could not be detected for this small sample population.

Another sample of interest is M52C, as it shows low MgO, FeO, but high SiO_2, CaO, Ni and Cr contents. Assuming Ni and Cr to be relatively immobile (Condie et al., 1977; Smith et al., 1984), then its high contents of these elements may indicate that it was also originally of high-Mg basaltic composition. Field and textural evidence suggests that this sample was retrogressively altered (see Appendix A).

4.4 Pelitic Rocks

The major and trace element composition of the pelitic rocks, together with that of the pegmatitic rocks, is given in Table 4.5. The rocks termed "pelitic" rocks (adapted from du Toit and van Reenen, 1977) show an unusual chemistry in that they are rich in FeO and MgO, and poor in K_2O relative to common sediments (e.g. McLennan, 1982; McLennan and Taylor, 1984). Indeed, this unusual chemical character may lead to the idea that the rocks termed "pelitic" rocks from the SMZ do not represent sediments after all. However, some geochemical features supporting a sedimentary origin are the low CaO for a relatively high Al_2O_3, high MgO, FeO, Cr, Ni with a high SiO_2 contents, the high Ba with a low K_2O contents and the whole rock oxygen isotope composition. These features, collectively, are unlike those reported for altered rocks of basaltic origin (i.e. rocks with similar MgO, Ni, Cr contents - Condie et al., 1974; Donnelly et al., 1980; Hynes, 1980; Smith et al., 1984). Accepting a sedimentary origin, for the purpose of the following discussions, it is of interest to determine whether the rocks are of coarse-grained, clastic

sedimentary origin or of an argillaceous, shale-type origin. Figures 4.3 and 4.4 summarize some major element relationships for the two most likely groups of sedimentary source rocks. The fields outlined in these Figures were defined from an analysis of more than 900 variably metamorphosed detritial sediments of Palaeosoic age sampled in the Pyrenees (de la Roche, 1966). For reference purposes an igneous rock trend line is also shown. In both diagrams, the pelitic rocks of this study can clearly be seen to fall well away from both the shale and greywacke compositional fields, except for the garnet-biotite gneisses which are found to plot within or close to the greywacke compositional fields. In general the metasediments are found to be more MgO, Al_2O_3 and FeO rich compared to those considered by de la Roche (1966). The chemical separation of most of these rocks from common greywackes and shales may be due to a compositionally different source area for these pelitic rocks.

Archaean sedimentary rocks are reported to show major and trace element compositions that are different to those of post-Archaean rocks (Cameron and Garrels, 1980; McLennan, 1982; McLennan and Taylor, 1984). In Table 4.6 and Figure 4.5, the average pelitic rocks of this study are compared to various other Archaean sedimentary rocks. When compared to Archaean greywackes, the average SMZ pelite is found to be enriched in Al_2O_3, FeO, MgO, Sc, Ni and Cr, but depleted in CaO, Na_2O, K_2O, P_2O_5, Sr, Zr and Rb. However, a comparison of the garnet-biotite gneisses (SMZ B in Table 4.6 see also Fig.4.4) with Archaean greywackes indicates a closer compositional similarity, with the two garnet-biotite gneisses being only somewhat enriched in SiO_2, Al_2O_3, Na_2O, Cr and depleted in FeO, CaO, Ni and MgO relative to the greywackes. A

comparison of SMZ A to the average Archaean shales from India and Canada (chosen because of the availability of both major and trace element data) indicates that the SMZ rocks are enriched in MgO, Ni, Cr and depleted in K_2O, P_2O_5, Zr, Rb and to a lesser extent in CaO, that is, an enrichment and depletion pattern that is similar to that for the greywacke comparison mentioned above.

The compositional difference between the average SMZ metasediments and other Archaean sedimentary rocks could be related to compositional differences of the provenance rocks to the sediments. While the greywackes of the Bellvue Formation in the Barberton greenstone belt do not indicate major differences in the chemistry of the source provenance relative to the Indian greywackes, this is not the case for the Fig Tree shales (also from the Barberton greenstone belt) relative to the Indian shales (Table 4.6). Unlike the Indian shales, the Fig Tree shales compare well with the SMZ pelites in terms of MgO, CaO, K_2O, P_2O_5 and Rb, but are, however, enriched in FeO and depleted in Al_2O_3. In this regard it is interesting to note the peculiar composition of the magnesiopelites from the Murchison greenstone belt (Murch-Pel in Table 4.6 - Pearton, 1982). Like the SMZ metasediments, these rocks are enriched in FeO, MgO and depleted in CaO, Na_2O and K_2O relative to other Archaean metasediments. Pearton (1982) interpreted these compositions as being a function of a predominantly ultramafic source provenance, in combination with deep water sedimentation of argillaceous material. These sedimentation conditions allow time for leaching during erosion, transport and particularly depositional processes, accounting for the low Ca, Mn, Sr and Na contents.

From the above it can be concluded that the rocks termed "pelitic" rocks in this study, represent a sequence of greywacke-type sediments to deep-water shales, with sediments being derived from a predominantly ultramafic source terrain. However, in view of the abundant petrographic evidence for some partial melting of the metasediments, part of the compositional variations for the pelitic rocks can be expected to be caused by melting processes and the removal of the melts thus formed. The extent of provenance rock control and partial melting control on the composition of the pelites will be considered in more detail below.

4.4.1 Source Area Control

Compositional differences in sediments are controlled by the physical and chemical stability of sediment particles. Thus besides the source control, the type of sedimentation process (e.g. high energy - greywacke; low energy - shale) is also important for the ultimate chemical composition of the sediment (see also above). The high Al_2O_3 with a low CaO and Na_2O component of the metasediments indicates that the precursor rocks were shales. In contrast, the low K_2O, Rb and low K_2O/Na_2O imply a greywacke type precursor (Mclennan, 1984; Scott and Argast, 1986). Consequently, the following discussion will be based on a comparison with both greywackes and shales.

Greywackes are composed of varying proportions of quartz (including chert), feldspars (plagioclase and microcline), rock fragments and to a lesser extent mica, chlorite, serpentine, minor carbonates and opaques, the latter making up

the matrix component in the greywackes (Condie et al., 1970; McLennan, 1984). Rock fragments are commonly chert, felsic volcanic, granitic with lesser amounts of mafic and sedimentary/metamorphic fragments. Ultramafic components are generally included in the matrix (Condie et al., 1970) of Archaean greywackes. The abundance of each of these components is extremely variable.

Least squares mixing models based on Bryan et al. (1969) were used to obtain an estimate on the possible proportions of different source rocks and on the material that could have made up a greywacke-type sediment with a major element composition similar to the average of the pelitic rocks in this study. The choice of mixing phases is based on the lithological components observed in Archaean greywackes (Condie et al., 1970; McLennan, 1984), where the tonalitic/trondhjemitic phase together with muscovite make up the feldspar and felsic rock component, quartz includes chert, and the mafic/ultramafic component is represented by chlorite (of intermediate Fe/Mg) and serpentine.

If most of the muscovite, chlorite and serpentine make up the matrix, then the results of such an approximation (Table 4.7) are in good agreement with the modal proportions given by Condie et al. (1970) and McLennan (1984). The large proportion of matrix component (muscovite + chlorite + serpentine) may reflect relatively good sorting during sedimentation and labile clastic components such as calcic plagioclase are destroyed causing low CaO content in the sediment. In addition, the low CaO content of the SMZ pelitic rocks suggests the absence of carbonates, which may be a function of early Archaean sedimentation processes (Cameron and Baumann, 1972).

A mixed source consisting of 70% tonalitic gneiss, 10% basaltic rocks, 5-10% ultramafic rocks and 5-10% sericitic, feldspathic and ferruginous quartzites has been proposed by Naqvi et al. (1988) for the Indian greywackes. The modeling illustrated in Table 4.7 indicates a combined mafic/ultramafic component of about 30% which is at least 10% to 15% more than that for the Indian greywackes and could explain the MgO, Cr, Ni and Sc enrichment observed. Complimentary smaller amounts of a tonalitic component can explain the low CaO, Na_2O, K_2O, P_2O_5, Zr, Rb and Sr contents observed in the SMZ pelites.

While it is more difficult to determine source material proportions for shales, the good sorting during sedimentation and diagenesis results in shales being predominantly made up of mica, chlorite, quartz and various clay minerals, resulting in very CaO poor, but Al_2O_3, FeO, MgO and K_2O rich bulk compositions. From Figure 4.5c it becomes clear that there is a good agreement between shales and the SMZ pelites for most major and trace elements shown. However, the MgO, Ni, Cr and Sc enrichment of the SMZ pelites is still evident, necessitating an ultramafic rich source provenance to these sediments. The K_2O and Rb poor character for the SMZ pelites may imply the general scarcity of K-rich granitic rocks from the source provenance.

In summary, it is possible to explain the average chemical composition of the pelitic rocks of this study in terms of a specific source area for the original sediments. This source area must have been substantially different to that for other Archaean sediments which may be a function of age and changes in crustal composition with geologic time (e.g. Lowe, 1980; McLennan, 1982; McLennan and Taylor, 1984), or a function of the local sedimentary environment

to these rocks. It is interesting to note that no felsic volcanics, or metamorphic equivalents thereof, have been recognized so far in the Southern Marginal Zone. Felsic volcanic fragments commonly make up a large proportion of the rock fragments found in other Archaean greywackes.

If the chemical variation amongst the pelitic rocks can also be satisfactorily explained by variations in source components, then metamorphism of the sediments may be interpreted as a closed system process. Internal chemical variation within the pelitic rock suite will be considered in more detail below.

4.4.2 Partial Melting Control

As mentioned above, an alternative explanation for the mafic character of the pelites is given by partial melting processes. In the preceding section on the petrography of the pelitic rocks, various melt-producing reactions were discussed. Such reactions would, if the melt is allowed to leave the system, result in the formation of a more basic restite relative to the precursor rock. While the migmatitic character of the pelitic rocks, together with closely associated pegmatitic and larger granitic bodies (see du Toit et al., 1983) provides visual evidence for the occurrence of partial melting, the possible extent and importance of such processes will be discussed in the following section.

Figure 4.6 summarizes the major element variations for the pelitic rocks and the spatially associated pegmatitic rocks. Most elements show negative

correlation with SiO_2. Exceptions are CaO and Zr, showing a more or less flat trend with varying SiO_2 contents, and Na_2O, which has a positive correlation with SiO_2. Trace elements such as Sc (Fig. 4.6i), Ni, Cr, V, Co and Zn (not shown) have good negative correlations, paralleling MgO.

If the compositional variations shown by the pelitic rocks are interpreted to be caused by variations in the relative amounts of ultramafic/mafic and felsic (tonalitic-trondhjemitic-granitic) source components, then for immature clastic sediments one would expect a good positive correlation between SiO_2 and Na_2O, K_2O and Zr, and a negative correlation between SiO_2 and all other major oxides, as crustal felsic rocks tend to be enriched in SiO_2, Na_2O, K_2O, Zr relative to basic volcanic rocks. More mature sediments (such as shales) tend to show lower Na_2O as sodium is taken up by the seawater, but higher K_2O and Al_2O_3, both of which are fixed in clay minerals (e.g. illite) or in muscovite (Mason and Moore, 1982). Poor correlation between K_2O and Al_2O_3 (Fig. 4.6j) indicates that K_2O is not necessarily controlled by illite and/or muscovite only. A positive K_2O versus SiO_2 correlation similar to that of Na_2O versus SiO_2 would be expected if the K_2O was of a clastic sedimentary origin. Thus, variations in ultramafic + mafic relative to felsic source proportions cannot explain the negative K_2O-SiO_2 correlation, nor the flat CaO-SiO_2 and Zr-SiO_2 trends against a positive Na_2O-SiO_2 correlation. An alternative explanation could be provided by partial melting processes.

4.4.2.1 Mineralogic Control on Melt Compositions

It has been shown earlier that melting reactions involve biotite, quartz and plagioclase with product phases being garnet, orthoamphibole, orthopyroxene and cordierite. As biotite, together with quartz and plagioclase still occurs within all the pelites (except P5C and P6C which lack biotite), it implies either that none of the reactant phases have been exhausted during melting or, that some of the reactant phases have been exhausted, but because of the high viscosity of such granitic melts not all the melt was removed from the system. Upon recrystallization, phases such as quartz and plagioclase will then precipitate within the rocks. The Fe and Mg rich nature of the pelitic rocks (even of SMZ B) suggests that biotite occured in excess of quartz and plagioclase. Support for quartz and plagioclase being recrystallized phases in these rocks is given by the textures of some of the rocks (Chapter 3).

Geochemical implications of such melting reactions would be the retention of TiO_2, Al_2O_3, FeO, MnO, MgO and even K_2O together with associated traces of Sc, Ni, Cr, Y, Zn and Rb, Ba in the residual pelitic rocks in phases such as biotite, garnet, orthopyroxene, orthoamphibole and cordierite, accounting, in particular, for the good Sc (and Ni, Cr, Zn) versus SiO_2 trends observed for the SMZ pelites. CaO may become enriched in the residue as the plagioclase commonly gets more anorthositic during melting (Knabe, 1970a, b; Winkler, 1976; Sawyer, 1987) and some minor CaO can be incorporated in the garnet as grossular component. Complete melting of plagioclase should largely remove the CaO together with Na_2O from the residue. Such processes may explain the more or less flat CaO trend (i.e. melt CaO is approximately the same as

residue CaO) and the positive trend of Na_2O relative to SiO_2 which also enters the melt.

Figure 4.6k and l illustrate the typically low K/Rb and K/Ba ratios with a good positive correlation between K_2O and Rb or Ba implying that these elements are controlled by biotite as the only major K_2O-bearing phase. Such low K/Rb and K/Ba ratios are identical to the low grade greywacke and shale ratios (Table 4.6), but are atypical of granulite facies rocks (e.g. Rollinson and Windley, 1980; Barbey and Cuney, 1982; Jahn and Zhang, 1984). This atypical character is caused by residual biotite. In rocks richer in K_2O and poorer in (FeO + MgO), the breakdown of biotite to form K-feldspar, with K-feldspar showing lower distribution coefficients for Rb and Ba, results in higher K/Rb and K/Ba ratios in the residues to partial melting (Hanson, 1978; Barbey and Cuney, 1982; Sawyer, 1987).

Comparing the K/Rb and Rb/Sr ratios of the SMZ pegmatitic rocks to those of the SMZ pelites (Table 4.5), then the pegmatitic rocks could well have been derived from the pelites by partial melting with biotite as a residual phase. Sr is largely incorporated into the melt as the plagioclase breaks down. In samples such as P5C, P6C and P42C, there is little or no biotite. Yet the K/Rb ratio in these samples is preserved, indicating that biotite is the only controlling phase for both K_2O and Rb. Thus, upon removal of the biotite, both the K_2O and the Rb enter the melt in equal proportions as they occured in the biotite. The K/Ba ratio is, however, very low in the case of P5C and P6C and may indicate Ba enrichment in feldspar. It is also interesting to note that these rocks are rich in garnet, with lesser orthoamphibole and residual quartz

and plagioclase, indicating that Fe-rich biotite in these samples was the minor phase relative to excess quartz and plagioclase (Knabe 1970a, b; Hoschek, 1976).

4.4.2.2 Melt Composition

Simple mass balance calculations involving major elements have been determined using the following equations:

$$xM + yR = S \qquad (4.1)$$

where $x + y = 1$ x, y = weight fractions in the melt and residue.

and M, R, S = weight percent of oxide in melt, residue and source respectively.

Solving for R and eliminating y:

$$R = (S - xM)/(1 - x) \qquad (4.2)$$

Equation (4.2) has been used to determine the theoretical chemical composition of the residue left after extracting 25%, 50% and 70% of a melt that has a composition similar to the "minimum" melt of White and Chappel (1977). The results of such theoretical mass balance calculations, given in Table 4.8, indicate that the K-bearing phase (biotite in the SMZ rocks) would be depleted after about 25% partial melting. As the residue left at 25% partial melting does not show any compositional similarity to the theoretical residue of SMZ C, this could imply the following. Either the "minimum" melt composition of White

and Chappel (1977) is not representative for melts extracted from metasediments having initial compositions similar to SMZ B or, melting in excess of 25% will remove melts of "non-minimum" melt compositions as the K-bearing phase is depleted. It has been deduced above, that biotite, in general, is the excess phase relative to the other reactant phases during partial melting processes. It is therefore reasonable to assume that the "minimum" melt composition of White and Chappel (1977) is not applicable to these rocks. Knabe (1970b) also observed that for starting assemblages consisting of quartz, plagioclase and biotite (such as P17C and P41C - SMZ B), minimum melts are more granodioritic in composition relative to melts in the systems containing K-feldspar and/or muscovite in addition to plagioclase, quartz and biotite (i.e. system considered by White and Chappel (1977)).

Rearranging equation (4.2) and solving for M results in the following equation:

$$M = (S - R(1 - x))/(x) \qquad (4.3)$$

This enables the determination of melt compositions which must be removed from SMZ B (average of greywacke-type pelites P17C and P41C - Fig. 4.4) in order to arrive at the most basic endmember-average as represented by SMZ C in Table 4.8. The model melt shown in Table 4.8 has been derived for 70% partial melting, as this shows good agreement with the minimum melt of White and Chappel (1977) in terms of SiO_2 and Al_2O_3, both of which are critical components in the normative quartz - albite - orthoclase granitic system (Winkler, 1976 p. 320). Besides SiO_2 and Al_2O_3, good agreement with White and Chappel's (1977)

minimum melt is also shown by MgO and MnO. The model melt does, however, show higher FeO, TiO_2, CaO, Na_2O, P_2O_5 and in particular lower K_2O contents, that is, a melt of more granodioritic composition in agreement with the experiments by Knabe (1970b). The normative quartz : albite : orthoclase ratio for the model melt is 46 : 41 : 13 (see Fig. 4.7) which compares well with the range of Qz : Ab : Or ratios obtained by Knabe (1970b) and also shown by Winkler (1976 p. 322). The Ab/An ratio of 3.6 for the model melt also falls within the given range of 2.9 to 3.7 as given by Knabe (1970b).

Little is known about the behaviour of FeO, MgO, and related traces during melting in granitic systems. However, from the experiments of Hoschek (1976), it can be estimated that in these relatively quartz-poor and biotite-rich samples (as indicated by their geochemistry - see above), the FeO will preferentially enter the melt phase as biotite becomes more magnesian with increasing amounts of melting. The released FeO can form, together with SiO_2 and Al_2O_3, orthopyroxene and garnet (e.g. Knabe, 1970a; Hoschek, 1976). As most SiO_2 is used up for the formation of the anatectic melt, it leaves little SiO_2 behind for the formation of orthopyroxene or garnet (or orthoamphibole - Knabe, 1970b), resulting in the incorporation of FeO into the melt.

In a detailed study on the geochemistry of anatectic leucosomes in a migmatitic terrane, Sawyer (1987) determined that most of the leucosomes are either fractionated (negative Eu-anomaly), or partial cumulates (positive Eu-anomaly and Al_2O_3 rich), with quartz and feldspar being the major fractionating phases. Only a few leucosomes were identified as representing unfractionated partial melts. The position of the model melt relative to the

projected cotectic surfaces (Fig. 4.7), indicates that quartz and plagioclase would be the first phases to crystallize. If it is assumed that the pegmatitic rocks represent partial melts derived from the pelitic rocks, then the lower SiO_2 and higher Al_2O_3 relative to the model melt is in agreement with quartz and feldspar crystal fractionation. As such, the pegmatitic rocks may not represent minimum melts but partial cumulates (see also Appendix A - V6D).

4.4.3 Conclusions for Partial Melting Processes

In conclusion it may be stated that partial melting processes as outlined above could well be used to account for the geochemical variation observed amongst the pelites of this study. Such melting processes are consistent with the textural and mineralogical interpretations for these rocks (Chapter 3).

In order to explain the major element geochemical variation amongst pelites, extraction of a model melt with partial melting of up to 70% by weight is proposed. Compositionally this model melt compares favourably with the minimum melts of Knabe (1970a) and Winkler (1976, p. 322), however, the degree of partial melting may be debatable. Clemens and Vielzeuf (1987) and Waters (1988) predict that for common pelitic rocks large amounts of melting (>30%) can only occur with a complete breakdown of the hydrous phase present (i.e. biotite). The geochemistry of the SMZ rocks, even that of the lowest (FeO + MgO) rocks implies biotite-rich precursory rocks. Thus, unlike the more common pelitic rocks considered by Clemens and Vielzeuf (1987) and Waters (1988), the amounts of partial melting in the SMZ rocks could be limited to the

quartz and feldspar available. Experiments by Knabe (1970a) for similar biotite-rich rocks predict that initial melts may be as much as 50% by weight with little biotite actually breaking down relative to the quartz and plagioclase.

If the amounts of partial melting were less than 70% by weight, it would imply that the precursor rocks to the high (FeO + MgO) rocks were originally richer in the mafic components. Smaller amounts of partial melting would then have enhanced the pre-existing, source related correlation of FeO, MgO, Al_2O_3, Sc, Ni, etc. with SiO_2, but melting was sufficiently large to cause rotation of a positive K_2O, CaO and Zr correlation to form negative correlations (K_2O vs. SiO_2) or flat trends in CaO, Zr versus SiO_2 diagrams (Fig. 4.6).

The occurrence of partial melting processes and their possible effects on the geochemistry of these pelitic rocks may lead to the development of locally inconsistent isograds in the residues to partial melting. As non-isochemical behaviour is implied with the removal of melts, such isograds may not reflect variations in metamorphic grade.

4.5 Conclusions

From the discussion on the major and trace element compositions of the various

members from the Bandelierkop Formation the following can be deduced:

1. The ultramafic rocks of the Southern Marginal Zone compare favourably with peridotitic-pyroxenitic igneous rocks and are thus likely to be of intrusive origin rather than of komatiitic origin.

2. Geochemically the mafic rocks of this study show strong similarities to high-Mg basaltic rocks (or komatiitic basaltic rocks of Viljoen and Viljoen (1969)) and to intrusive gabbroic rocks commonly found associated with ultramafic intrusives.

3. For both the ultramafic and mafic rocks closed system metamorphism appears to be applicable (except for volatiles such as H_2O and CO_2).

4. The metasediments of this study, may represent a sequence of metamorphosed greywacke-type sediments to deep water shales, derived from a source terrain that shows a high proportion of ultramafic rocks (~20 to 30%).

5. Some of the chemical variations observed for the pelitic rocks are best explained by the occurrence of partial melting processes, implying that the pelitic rocks of this study did not behave as closed systems during metamorphism to high-grade conditions.

6. Geochemically the pegmatitic rocks of this study may well represent partial cumulates derived from the partial melts of the metasediments.

The major and trace element geochemistry of some rocks analyzed in this study but not discussed above is given in Table 4.9 and Appendix B.

CHAPTER 5: CHEMICAL MINERALOGY

5.1 Introduction

In this section the chemistry of the dominant minerals of the ultramafic, mafic and pelitic rocks will be discussed briefly. Emphasis is placed on those properties that may vary systematically with metamorphic grade. For more detailed descriptions on the mineral chemistry for mafic and pelitic rocks of the Southern Marginal Zone, the reader is referred to the study of van Reenen (1978). The experimental conditions used for the electron microprobe analyses of these minerals are described in Chapter 2.

5.2 Ultramafic Rocks

Tables 5.1, 5.2 and 5.3 summarize the composition of various constituent minerals of the ultramafic rocks U10A and U17B.

5.2.1 Olivine

The olivines analyzed for U17B range in composition from $Fo_{89.4}$ to $Fo_{90.3}$ (Table 5.1) which is common for metamorphic olivines in ultrabasic rocks (Trommsdorff and Evans 1969, 1974; Srikantappa, 1985), as well as for olivines of igneous komatiitic affinity (e.g. Nisbet et al., 1977; Arndt et al., 1977).

Similarly, the NiO contents of the olivines, for the given Fo compositions are similar to those of other metamorphosed and unmetamorphosed ultrabasic rocks.

5.2.2 Orthopyroxene

Orthopyroxenes from samples U10A and U17B are enstatitic in composition (X_{Mg} = 0.88 - 0.91) and even in samples containing green to brown spinel (hercinitic spinel), have a low tschermak component (Al = 0.026 - 0.095 atoms per formula unit) compared to high-grade metamorphic orthopyroxenes in rocks of similar bulk chemistry from southern India (Srikantappa et al., 1984; 1985). The Ti, Mn, Ca and Cr contents of these orthopyroxenes are commonly low, in agreement with those observed for the orthopyroxenes from southern India. The low Al-contents of the orthopyroxenes may be somewhat surprising, particularly as the solubility of aluminium in orthopyroxene coexisting with olivine and spinel is found to increase with increasing metamorphic grade (e.g. Wood, 1974; Danckworth and Newton, 1978). Such Al-solubility is found to be suppressed by increasing Ca, Fe and Cr contents (Lee and Ganguly, 1988). As the SMZ orthopyroxenes are comparable to other high-grade orthopyroxenes in terms of Ca, Fe and Cr, and as the whole rocks have similar Al_2O_3 contents, the low Al-contents of the orthopyroxenes may be a function of the stabilization of Al-rich chlorite in the SMZ rocks.

5.2.3 Chlorite and Amphibole

Chlorite is typically sheranditic in composition with high Al_2O_3 (Al_{Total} = 4.70 - 4.97), high MgO and Cr_2O_3 (Table 5.3) contents. Frost (1975) and Trommsdorff and Evans (1974) reported a maximum of 2.4 Al_{IV} atoms per 8 tetrahedral sites for chlorite at its breakdown temperature with lower values at correspondingly lower grades. The Al^{IV} of the chlorite in U10A is 2.64 whereas those for U17B vary at around 2.43 (assuming only Si and Al in tetrahedral sites). Chlorites thus show compositions interpreted to occur at their breakdown temperature, which is in good agreement with reaction (3.2) (see Chapter 3) and the textural interpretations for the breakdown of chlorite.

The analyzed amphibole, with an Al^{IV} content of 1.201 atoms per 8 tetrahedral sites and $Al^{IV}+Fe^{3+}+Ti \geq 0.6$ (depending on the Fe^{3+}/Fe^{2+} ratio, can be classified a hornblende or magnesio-hornblende (Leake, 1978). This is the amphibolite facies equivalent to tremolite, replacing the latter by complex substitutions of the tschermakite and pargasite endmembers (Frost, 1975; Evans, 1977; Srikantappa et al., 1985.)

5.3 Mafic Rocks

5.3.1 Plagioclase

Representative plagioclase analyses are given in Table 5.4. Compositionally, the plagioclase is found to vary from oligoclase-andesine in hornblende rich samples

to labradorite in the two-pyroxene mafic rock (M27C), with a total range from An_{28} to An_{62}. The variation in anorthite content within single samples was commonly less than 10 mole% both for grain to grain and for core-rim variations, except for sample M1A. This latter sample, collected from a xenolithic fragment situated within a felsic, migmatitic host rock along the Hout River Transition (Fig. 2.1 and Appendix A), showed plagioclase compositions ranging from An_{39} to An_{74} (Table 5.4).

The overall range in An-content closely corresponds to trends reported from other metamorphic terranes for amphibolite and granulite facies terranes (e.g. Wenk and Keller, 1969; Raase et al., 1985), and has also been reported for the Southern Marginal Zone by Van Reenen (1978, 1983). However, the fairly large variations in anorthite content within some of the samples may reflect variable retrogression, particularly in cases of more albitic rims to some grains. Alternatively it could suggest a lack of equilibrium within such samples due to local chemical gradients. In sample M27C, a vein of retrogressive hornblende after pyroxene cuts the rock (Appendix A), yet the feldspar still indicates similar An-contents to that analyzed well away from such a vein, implying that local retrogression of pyroxene has not significantly affected the plagioclase composition. Only in intensely altered sections is the plagioclase found to be sericitized to a considerable degree.

5.3.2 Amphibole

The amphiboles analyzed from the mafic rocks can be classified as hornblende or

pargasitic hornblende (Table 5.5, Fig. 5.1a; Leake, 1978). The change from common hornblende to pargasitic hornblende is related to the progressive breakdown of amphibole and the resultant formation of pyroxene and plagioclase according to reaction (3.3) (Chapter 3), with the plagioclase becoming more anorthositic in composition. Such a compositional change of the amphiboles is commonly found to occur with increasing grade of metamorphism (Raase, 1974; Srikantappa et al., 1985; Raase et al., 1986) and is related to $Si = Al(Na+K)$ substitutions. Raase (1974) determined that the Ti-contents of amphiboles also increases with metamorphic grade. This relationship is illustrated in Figure 5.1b. A positive correlation is found between modal abundances of pyroxene and the TiO_2 content of the amphiboles. According to reaction (3.3) (Chapter 3), this implies that the amphibole becomes more TiO_2 rich as the foreward reaction proceeds, until the amphibole becomes Ti-saturated and ilmenite is precipitated. Small opaques (ilmenite?) have been identified along cleavage planes within some amphiboles (see Appendix A) and are taken to indicate the presence of prograde Ti-saturated amphiboles.

A comparison of the amphibole compositions of M27C, to that of the other mafic rocks, indicates that it has both low Al^{IV} and (Na + K) content (Fig. 5.1a), while still showing a fairly high Ti content (Fig. 5.1b). In view of the above, this would appear to be contradictory as the low pargasite content of the amphibole may indicate lower metamorphic grades while high Ti-content may indicate relatively high metamorphic grade relative to the other amphibolites. A possible explanation for this observation is that the amphibole composition is controlled by the bulk chemistry of the rock, particularly as both the whole

rock and the amphiboles of M27C show low K_2O abundances. Alternatively, the amphibole analyzed in M27C may have been of retrograde origin, replacing pyroxenes, with the amphibole composition being controlled by that of the pyroxenes (i.e. low K-content and low TiO_2 content). If such retrogression did occur for sample M27C, then the plagioclase composition may have remained unaffected by retrogression as its An-content is still fairly high. By analogy to the studies of Wenk and Keller (1969), this may suggest higher metamorphic grades.

5.3.3 Pyroxene

The chemical variation observed in the pyroxene compositions (Table 5.6) are summarized in Figure 5.2, the latter illustrating that the clinopyroxenes can be classified as diopside whereas the orthopyroxenes of sample M27C are enstatites (Morimoto et al., 1988). Furthermore Figure 5.2 illustrates that the clinopyroxenes analyzed from various mafic rocks show rather limited compositional variation, with Mg (atomic) ranging from 0.69 to 0.80 and Al of 0.05 to 0.11 and low contents of Ti, Cr and Mn, comparing favourably with other high-grade pyroxenes (e.g. Raase et al, 1986).

Sample M27C is the only rock having orthopyroxene, together with a clinopyroxene of similar composition to that analyzed from the other mafic members. Owing to a higher bulk rock MgO content when compared to the other pyroxene-rich rocks (e.g. M8A, M11C), the occurrence of both pyroxenes in M27C is probably related to the bulk chemistry of this sample.

From the core-rim analysis of single grains (Table 5.6) it can be seen that the pyroxenes may show weak compositional zoning, the compositional trends differing from sample to sample and even from grain to grain within one sample. In sample M27C, the clinopyroxene shows an increase in Mg-content towards the rim, suggesting some retrogressive Fe/Mg exchange (Wells, 1979).

5.4 Pelitic Rocks

5.4.1 Plagioclase

In Table 5.7 the plagioclase composition of the pelitic rocks can be seen to vary from An_{20} to An_{42}. The lowest An content is observed in the biotite-garnet gneisses (P17, P41C - for P17 see also Table 3.3, An-contents determined optically), with values of around An_{22}, whereas the biotite-poor but FeO-rich rocks of P5C and P42C have the highest An-contents of around An_{41}.

In the case of core-rim analyses of single plagioclase grains within the pelitic rocks, the rims are generally observed to be more calcic than the cores, with observed maximum shifts of up to 4 mole-percent An. Such increases are in agreement with melting reactions involving the albite component of the plagioclase (Knabe, 1970b; Winkler, 1976; Sawyer, 1987).

5.4.2 Biotite

Biotite compositions are given in Table 5.8 and summarized in an expanded section of the "ideal biotite plane" after Guidotti (1984), representing the Mg/Fe exchange and the tschermak exchange $(Mg, Fe^{2+}) + Si^{IV} = Al^{VI} + Al^{IV}$ and plotted as Al^{VI} versus Mg/Mg+Fe in Figure 5.3. Group denotations refer to the mineralogic classification of Chapter 3. The biotites analyzed for this study show a range of (Mg/Mg+Fe)*100 from about 57 up to 77 and have Al contents between 0.23 and 0.76 atoms per six octahedral sites. These compositional ranges are given for all the analyzed biotites, including rim compositions of biotites in contact with other ferromagnesian phases, together with compositions of biotites occuring as inclusions in such phases. As the biotites are compositionally zoned (see below), the compositional ranges quoted above can be expected to be reduced if only core compositions are considered. However, this was not observed to be the case as is illustrated in a comparison of the (Mg/Mg+Fe) values in Figures 5.3a and 5.3b. In Figure 5.3a only core compositions of matrix biotites have been plotted for clarity, while in Figure 5.3b all analyzed biotites are plotted. From the comparison between Figure 5.3a and b it can thus be seen that the M ranges are not significantly changed, whether considering only core biotite compositions or all the analyzed biotites. The same is also true for the Al^{VI} and Ti ranges (Table 5.8). Inspection of Figure 5.3 reveals that for a given value of Mg/Mg+Fe for the biotite, there is a decreasing sequence in Al^{VI} from the garnet-biotite gneisses, via the orthoamphibole gneisses, the cordierite-garnet granulites to both the cordierite granulites and the garnet granulites. The Ti variations are

complimentary to this in that they increase in the same sequence for a given Mg/Mg+Fe in the biotite.

Most of the biotites analyzed in this study showed detectable F content (up to 1.5wt% - P41C; Table 5.8), but only small amounts or no detectable Cl. A closer inspection of the fluorine content for the orthoamphibole gneisses yields an average of 0.19wt% (standard deviation (s.d.) = 0.06 for 22 analyses) compared to values of 0.35 (s.d. = 0.06, n = 10) for the garnet granulite and 0.28wt% (s.d. = 0.06, n = 11) for the cordierite granulites.

While no detailed study of compositional zoning for the biotites was undertaken, the core-rim relationships reported in Table 5.8 do indicate that biotite zoning is of variable character. In terms of Mg/Fe compositions there may be a weak increase in Mg and an accompanying decrease in Fe towards the rim (M values vary by about 2 only). In the orthoamphibole gneisses little or no significant zoning of the biotite was observed. In contrast however, variations in M values for different biotite grains within the same rocks can be considerably higher than core-rim variations within single grains (Table 5.8). This is particularly well exemplified by sample P17C where variations in M can be as high as 15, with the highest Mg-biotite close to or in contact with garnet while lower values are shown with distance from the garnet (P17C-1C to P17C-6C; Table 5.8).

5.4.2.1 Discussion of Biotite Compositions

In a recent review on metamorphic biotites, Guidotti (1984) observes that

amphibolite facies biotites commonly show Al^{VI} values lower than 0.7 for rocks lacking coexisting musovites, with Mg/Mg+Fe ranges of between 0.3 and 1. For granulite facies biotites in rocks of similar composition, the Al^{VI} is reported to be commonly less than 0.55. This decreasing Al^{VI} content in the high grade biotites is described as being accompanied by an increase in Ti content from about 0.25 atoms per 22 oxygens in the granulite-grade biotites. In Figure 5.3 the range of Ti-content for the biotites can be seen to extend from 0.17 up to 0.65 atoms per 22 oxygens. Some of these differences in biotite compositions may certainly be controlled by the bulk chemical composition of the rocks and/or the modal biotite abundances in the rocks. This was tested by plotting the biotite Ti-contents against the bulk rock TiO_2 content and the biotite Ti/M ratio against the bulk rock TiO_2/(MgO/MgO+FeO) (Fig. 5.4a and b). Figure 5.4 illustrates that for a similar range in bulk rock TiO_2 contents, the orthoamphibole gneisses tend to show a lower Ti-content in biotites relative to that for the other rock groups. As the modal abundance in biotite shown by the orthoamphibole gneisses is similar to that of the other rock groups in general, the lower Ti-content in the biotite is either a function of the orthoamphibole presence (as another Ti-bearing phase) or of different metamorphic grades (e.g. Guidotti, 1984). An exception is the orthoamphibole gneiss P42C which shows a high biotite Ti-content and yet has low bulk rock TiO_2 content (Fig. 5.4a). The most likely explanation is its low modal biotite contents, with TiO_2 concentrating in residual biotite during its breakdown reactions (Chapter 3). By analogy, the difference in Ti-content between the biotites of P21C and P1D may be explained by lower modal biotite abundance in P21C relative to P1D (Fig. 5.4 and Table 3.3). In general though, by comparison

to the review study of Guidotti (1984), the biotites of this study show typical amphibolite facies to granulite facies compositions in terms of Al^{VI}, Mg/Fe and Ti-contents.

In a recent study on the biotite compositions from charnockites and metapelitic rocks in India (Madras), Bhattacharya and Sen (1986) revealed an inverse relationship between $a(TiO_2)$ (activity of TiO_2) and $a(H_2O)$ (activity of water). Extending these ideas to the biotites of this study, the variation in Ti contents between the orthoamphibole gneisses and the granulites could be related to variations in $a(H_2O)$ and need not necessarily be a function of metamorphic pressures and temperatures only.

From studies of F and Cl content in biotites (e.g. Munoz, 1984; Guidotti, 1984), it has been determined that both F and Cl tend to concentrate in hydrous phases such as biotite with increasing metamorphic grade. Such an enrichment is, however, reported to be highly variable and depends on the amount of chlorides in the bulk rock, the modal biotite abundances, as well as on the activities of these components within the fluid. The lower F-content in the orthoamphibole gneisses is unlikely to be a function of modal % biotite, as is exemplified by a comparison of samples P50C and P14C, with these two samples showing similar modal abundances of biotite but different F-content (P50C- orthoamphibole gneiss, P14C- cordierite-garnet granulite). In addition, the lower F-content is unlikely to have been caused by retrogressive re-equilibration of F in the biotite as this would require large fluid/rock ratios of ~1000:1 according to Wood and Walther (1986), which are not indicated by the oxygen isotope compositions (see Chapter 7). Thus, using the above information,

then the biotite compositions of the orthoamphibole gneisses suggest significantly lower metamorphic grades relative to the other rock groups.

5.4.3 Garnet

Garnet compositions analyzed from the pelitic rocks are given in Table 5.9. These garnets are iron-rich almandine-pyrope solid solutions containing 54 to 70 mole% almandine, 22 to 41% pyrope and usually less than 6% grossular and 2.5% spessartine. While this range in garnet compositions overlaps with those observed in other high-grade Precambrian pelitic rocks (e.g. Reinhardt, 1968; Dallmeyer, 1974; Stephenson 1979), the garnets of this study tend to be of somewhat higher pyrope content, possibly being a reflection of the Mg-rich bulk rock composition of these rocks.

The compositional variations within single rock samples are commonly less than 4 mole% in terms of almandine or pyrope components, with core-rim differences seldom exceeding 2 mole% for these components. Furthermore, a comparison of garnet core compositions between the various groups of rocks does not reveal any significant differences in garnet compositions. This is illustrated in Figure 5.5a where only some selected core compositions, representing the extreme endmember compositions (for samples with 2 or more analyses) were plotted for each sample. While the garnets from the cordierite-garnet granulites and particularly from the garnet-granulite (groups 4 and 3 respectively) do show pyrope compositions extending to somewhat higher pyrope mole% values (i.e. higher Mg in Fig. 5.5a), there is a considerable overlap in

garnet composition between these groups and the orthoamphibole gneisses (group 2). This overlap is likely to be caused by differences in bulk chemistry, which in turn controls the garnet composition. A comparison of chemically similar rocks (e.g. P7D and P14C of groups 2 and 4) does, however, reveal a slight but significant difference in mole% pyrope of their garnets (P7D - pyrope mole% = 31.8 s.d. = 1.7 n = 5 cores; P14C - pyrope mole% = 35.1 s.d. = 1.0 n = 7 cores). Van Reenen (1978, 1986) observed increasing pyrope contents from the orthoamphibole gneisses to the cordierite-garnet gneisses, with this increase being ascribed to increasing metamorphic grades.

From the core-rim analysis given in Table 5.9, it can be seen that the general zonation in garnets is a Mg-depletion and an accompanying Fe-enrichment towards the rims. Such zonation, if present, is commonly weak. No Mn zoning is observed for most samples whereas Ca zoning is variable, with Ca contents both increasing and decreasing towards the rim. Figure 5.5b, illustrates this weak type of zoning profile in a garnet analyzed from sample P21C. Note the absence of significant zoning, particularly in the core sections. For P50C (a group 2 rock), garnet zonation was in reverse to the above, with an increase in Mg content towards the rim (in contact with biotite) and a decrease in both Fe and Mn; and in one profile also a decrease in Ca towards the rim. Sample P7D (also a group 2 rock) showed variable garnet zonation, with profiles reversing for different garnets within the rock.

The garnets analyzed in P42C show grossular contents of 7.7 to 12.1 mole%, which are considerably higher than those of any other sample in this study.

These high values may be explained by the high bulk CaO content of this sample relative to the other rocks.

The common zonation profile (higher Fe/Mg in rims) is best described by some minor retrogressive Fe/Mg re-equilibration between garnet and, in particular, biotite but also between garnet and orthopyroxene and/or cordierite. This small scale re-equilibration is supported by the fact that matrix garnet (i.e. those not surrounded by other mafic phases) commonly show no zonations in terms of Fe/Mg, which is typical for high-grade garnets (e.g. Woodsworth, 1977).

5.4.4 Orthoamphibole

The orthoamphiboles of the pelitic rocks (Table 5.10) can be classified as gedrite ($Al^{IV} + Na > 1$, for 23 oxygens) or as anthophyllite ($Al^{IV} + Na < 1$) and alumino-anthophyllite ($Al^{VI} > 0.5$) using the nomenclature of Leake (1978). The range in Al^{IV} and A-site cation (i.e. Na) is shown in Figure 5.6, with the orthoamphiboles from pelitic rocks forming a linear trend extrapolating from anthophyllite through to gedrite compositions. For most minerals, the actual position along this trend may be a function of bulk rock composition (particularly Al_2O_3 and Na_2O; e.g. compare P38C and P32C or P50C in Table 4.5). However, for sample P50C coexisting gedrite and anthophyllite were analyzed, with these orthoamphiboles being separated by the miscibility gap as described by Spear (1980). Similarly, in samples P7D and P38C two orthoamphiboles could be identified by their different pleochroic schemes. For sample P5C, the orthoamphibole shows Al^{IV} contents of 1.0 to 1.3 atoms per 8

tetrahedral sites and A-site occupancy of 0.2 to 0.3 atoms per site. These ranges, when compared to Figure 14 of Spear (1980) would roughly coincide with compositional ranges expected to be found for orthoamphiboles close to the crest of the miscibility gap. If the temperature estimates of 600 $\pm$ 25°C for the crest of the miscibility gap as derived by Spear (1980) are assumed correct, then it would imply that the orthoamphiboles of sample P5C formed at temperatures above 600 $\pm$ 25°C, whereas those of sample P50C formed below these temperatures.

5.4.5 Orthopyroxene

Orthopyroxene analyzed from the pelitic members can be classified as enstatite according to their (Mg/Mg+Fe)*100 ratios (Table 5.11; Morimoto et al., 1988). Orthopyroxene from the garnet granulite (P25C) shows an average enstatite component of 69.5 mole%, that of the cordierite-garnet granulites varies from 58.6 to 64.5 while in the cordierite granulites it varies from 66.2 to 71.3 mole%. The enrichment in Mg-content of the orthopyroxene from the cordierite-garnet granulites to the cordierite granulites parallels the bulk rock compositional differences observed between these rock groups.

The Al_2O_3 content in orthopyroxenes ranges from 3.4 to 6.0 weight% in these rocks, and there does not seem to be a significant difference in Al_2O_3 content of orthopyroxenes between the various groups of rocks. Furthermore, the orthopyroxenes from within single rocks are homogeneous in composition and in only a few cases, when adjacent to garnet, did the orthopyroxene show

significant zoning, with an increase in Mg-content and an accompanying decrease in Fe-content towards the rim. There was also no significant compositional difference between the small, fine-grained and finger-like orthopyroxene and the coarse-grained orthopyroxene outside the cordierite-orthopyroxene intergrowths.

5.4.6 Cordierite

Cordierite analyses from the cordierite-garnet granulites and the cordierite granulites are shown in Table 5.12. In general, these cordierites are more Mg-rich (X_{Mg} range from 79.7 to 89.3) when compared to cordierite in pelitic rocks from other high-grade metamorphic terranes (e.g. Ashworth and Chinner, 1978; Waters and Whales, 1984) and reflect the Mg-enriched character of the SMZ rocks.

Comparing the (Mg/Mg+Fe)*100 ratios (M in Table 5.12) for cordierites in the group 4 rocks to those in the group 5 rocks, then no significant difference can be detected. A possible explanation for this is that the range of cordierite compositions observed within one rock may vary by as much as 10% in terms of (Mg/Mg=Fe)*100 (e.g. P19C - Table 5.12). Within one rock, the most Fe-rich cordierites are found in conjunction with biotite while the most Mg-rich cordierites are found replacing the garnets. This heterogeneity of the cordierite may imply cordierite growth during two separate events, with no chemical re-equilibration of the cordierite within the scale of a single rock (even single thin section). Alternatively the cordierites grew during the same event and the chemical heterogeneity is caused by the existence of local

chemical gradients as evidenced by the occurrence of small inclusions of spinel in some, but garnet inclusions in other cordierites (see Chapter 3; Fig. 3.15). The zoning within individual cordierites was found to be insignificant, regardless of the mineral (garnet, orthopyroxene, biotite) with which the cordierite was found to be in contact.

5.5 Discussion and Conclusions

For both the mafic and ultramafic rocks the compositions of the constituent minerals are consistent with upper amphibolite to granulite facies conditions. In the case of the mafic rocks, the mineral chemistry of samples M8A, M11C and M27C, all sampled north of the isograd (Fig. 2.1), suggests higher metamorphic grades (higher P-T and/or lower $a(H_2O)$) relative to the samples south of the isograd. Evidence of retrogressive processes in the ultramafic and mafic rocks is limited to single samples or even to only a single group of minerals adjacent to veins within some rocks (e.g. M27C).

The pelitic rocks are chemically and mineralogically complex systems, making interpretations in terms of metamorphic conditions difficult. The effects of bulk chemistry on the mineralogy are illustrated in Figure 5.7. In terms of the parameters chosen for Figure 5.7, the group 2 rocks (excluding P5C, P6C and P42C) can be seen to be chemically similar to the group 4 rocks. The difference in mineralogy between these groups can therefore be explained in terms of varying metamorphic conditions (P, T or $a(H_2O)$). Mineralogical changes

between these rock groups involve the breakdown of the biotite-garnet assemblage to give orthoamphibole or orthoamphibole and cordierite in the group 2 rocks, but orthopyroxene and cordierite in the group 4 rocks (Fig. 5.7; see also Chapter 3). In the Fe-rich orthoamphibole gneisses biotite has been removed as a reactant, resulting in the stable coexistence of garnet and orthoamphibole (e.g. P5C, P6C, P42C). In the Mg-rich rocks (group 5) garnet removal is complete (Fig. 3.16). The replacement of orthoamphibole found in the group 2 rocks by orthopyroxene in the granulites is considered prograde in origin (increasing P-T and/or decreasing $a(H_2O)$). Because of the Fe-Mg exchange amongst the ferromagnesian phases, the replacement reactions are continuous and the reactant phases may change their composition to be stable over a wider P-T-$a(H_2O)$ interval.

In the case of the group 3 rock (P25C), the low Al_2O_3 content did not stabilize cordierite (Fig. 5.7). Similarly in group 1 rocks the absence of cordierite and/or orthopyroxene may be related to their bulk chemistry.

The chemistry of biotite in the pelitic rocks indicates typical amphibolite facies conditions in the group 2 rocks compared to the granulite metamorphic conditions in the group 3, 4 and 5 rocks. The fluorine variations in biotites of these groups indicate that the lower metamorphic grade conditions are unlikely to be the result of retrogressive fluid infiltration. If so, then large amounts of fluid would be required.

In a detailed study on the orthoamphibole gneisses of the SMZ, van Reenen (1986) concludes that the formation of orthoamphiboles is retrogressive in

origin, but temperature estimates for this event are considerably higher than the crest of the miscibility gap defined for the orthoamphibole by Spear (1980). This disagreement in terms of temperature is explained by van Reenen (1986) as being caused by varying fluid compositions during formation of the orthoamphiboles of the SMZ relative to those considered by Spear (1980). However, the calculations done by van Reenen (1986) were based on the reaction anthophyllite = enstatite + quartz + water as experimentally determined in the system MgO-SiO_2-H_2O (Greenwood, 1963). This rather simple system may not be applicable to the more complex chemistry shown by the pelitic rocks in this study. The existence of at least three compositionally different orthoamphiboles within the orthoamphibole gneisses, with the alumino-anthophyllite compositions coinciding with the expected crest for the miscibility gap, can be taken to suggest that orthoamphibole formation occured over a wide temperature interval.

The large Fe/Mg variation shown by different grains compared to small variations in single grains of biotite and cordierite, indicates localized chemically heterogeneous behaviour during retrogression. Garnet and orthopyroxene, in contrast, do not show large compositional variations within any one sample. The difference in behaviour of biotite and cordierite relative to garnet and orthopyroxene may be a function of cation (Fe^{2+}, Mg^{2+}) diffusivity variations for the different minerals.

CHAPTER 6: CATION GEOBAROMETRY AND GEOTHERMOMETRY

6.1 Introduction

In the following sections, pressure (P) and temperature (T) conditions are evaluated from the mineral chemistry of various coexisting minerals in the Bandelierkop Formation members. The calculated P-T estimates will be compared to the experimentally determined mineral reaction conditions (as described in the petrography section) and also form the basis for a cation-anion (oxygen isotope) thermochemical comparison described later (Chapter 9).

Details on the terminology and the equations used for P-T determinations are given in Appendix C.

6.2 Ultramafic Rocks

In the ultramafic rocks no detailed microprobe analysis was undertaken for thermobarometric purposes. In respect of the limited analytical data, the only analysis that renders itself to some further discussion is the alumina content in the orthopyroxenes of rocks U10A and P17B. From Table 5.2 it can be seen that the alumina content of orthopyroxene ranges from 1.39 to 2.32 weight% Al_2O_3 in sample U10A and from 0.63 to 1.54 weight% in P17B. If one assumes the simple MgO-Al_2O_3-SiO_2 ternary system of Danckwerth and Newton (1978) to be

applicable to the SMZ rocks, then a maximum Al_2O_3 content of 2.32 wt% would correspond to about 680°C (at 10kb's) in the enstatite Al_2O_3-isopleth diagram where enstatite coexists with forsterite and spinel (Danckwerth and Newton, 1978 - Fig. 7). However, the stability of chlorite as an additional Al-containing phase besides spinel in the SMZ rocks, together with the presence of components such as FeO and CaO diluting for Al_2O_3 in orthopyroxene, may result in a low Al_2O_3 content of the SMZ orthopyroxenes. As a result, the temperature estimate of 680°C may represent a minimum temperature for peak metamorphic conditions recorded by the ultramafic rocks.

6.3 Mafic Rocks

For the given mineral assemblages of the mafic members, only the Ca-Fe-Mg distribution between ortho- and clinopyroxene has been calibrated as a geothermometer (Wood and Banno, 1973; Wells, 1977; Powell, 1978; Lindsley, 1983), which limits cation temperature estimates to sample M27C of this study. However, detailed comparisons of the temperatures obtained from Wood and Banno (1973) and from Wells (1977) to other thermometers have commonly led to the conclusion that the given two-pyroxene temperatures are too high and displayed considerable scatter (e.g. Bohlen and Essene, 1979; Essene, 1982; Lindsley, 1983; Srikantappa et al., 1985). Bohlen and Essene (1979) ascribe the high two-pyroxene temperatures to factors such as a non-ideality of cation exchange, uncertainties in extrapolations from experimental reversals on end-member compositions at high temperatures down to metamorphic temperatures, analytical

error and both an underestimation of and a lack of knowledge about thermodynamic factors (e.g. activity coefficients, site allocations) at metamorphic temperatures.

In an attempt to overcome assumptions of ideal mixing in the pyroxenes, Powell (1978) established a two-pyroxene geothermometer which makes allowance for the interference of Ca and Na on M_2 sites of the pyroxenes. For the graphical thermometer of Lindsley (1983), the orthopyroxene-clinopyroxene solvus is represented in the Ca-Mg-Fe quadrilateral (see Fig C.1 in Appendix C). Pyroxene components not represented in the quadrilateral are empirically approximated and are subtracted from the quadrilateral Ca-Mg-Fe components. This process largely eliminates the effects of non-quadrilateral components on the activities of wollastonite, enstatite and ferrosilite.

The average temperature derived for M27C by using the thermometer of Powell (1978) is 702 $\pm$ 70°C. While the formulation of this thermometer still involves the extrapolation of high temperature experimental reversals to lower metamorphic temperatures, the average temperature obtained is similar to estimates of granulite metamorphic conditions for mafic rocks elsewhere (e.g. Bohlen and Essene, 1979; Srikantappa et al., 1985). The thermometer of Powell (1978) was, however, found to be critically dependant on accurate analysis of Ca in orthopyroxene. Thus small variations of Ca content in orthopyroxene may lead to large differences in calculated temperatures.

The graphical method of Lindsley (1983), results in temperature estimates from clinopyroxene core compositions averaging 535 $\pm$ 120°C while those

estimated from coexisting orthopyroxene cores average 589 ± 120°C (Appendix C). These temperatures are considerably lower than temperatures expected for granulite facies rocks (T ≥ 680°C; Winkler, 1976). Such low temperatures would be consistent with retrograde Ca-Mg-Fe exchange (Essene, 1982). The wide range in temperatures obtained by this graphical thermometer is presumably a result of the slope of the pyroxene solvus at these temperatures. Only small errors in the wollastonite component result in large temperature differences (Fig. C.1).

It is concluded that while the calibration of Powell (1978) yields average temperatures expected for granulite metamorphic conditions, further information is needed to establish whether this temperature represents a true metamorphic temperature or not.

6.4 Pelitic Rocks

6.4.1 Geobarometry

By comparison to geothermometry, the choice of mineralogic geobarometers is rather limited. This is caused by a combination of a lack of pressure sensitive mineral exchange reactions and, if present, by insufficient experimental and/or thermodynamic information for such reactions (e.g. Essene, 1982; Newton and Perkins, 1982; Bohlen, 1987). For the SMZ rocks promising geobarometers are provided by coexisting garnet and less dense aluminous minerals such as

cordierite, plagioclase and aluminous pyroxene. The use of the garnet-plagioclase-Al_2SiO_5-quartz geobarometer (Newton and Haselton, 1981) is excluded on the basis of the absence of a free, prograde Al_2SiO_5 polymorph (see Chapter 3). Furthermore, the lack of agreement between experimental and semi-empirical calibrations of the garnet-cordierite-Al_2SiO_5-quartz assemblage (Currie, 1971; Hensen and Green, 1973; Thompson, 1976; Holdaway and Lee, 1977; Martignole and Sisi, 1981) excludes this assemblage as an accurate geobarometer until such discrepancies can be solved. Available thermodynamic and experimental data thus limits mineralogic geobarometry to the mineral assemblage plagioclase-orthopyroxene-garnet-quartz (Newton and Perkins, 1982) and the solubility of alumina in orthopyroxene coexisting with garnet (Harley and Green, 1982). These barometers are reported to give reasonably accurate pressures for granulite facies rocks (Newton, 1983; Bohlen et al., 1985; Bohlen, 1987; Moecher et al., 1988). Pressures calculated from the latter two geobarometers are presented in columns A and B of Table 6.1.

From Table 6.1 it can be seen that the range of pressures obtained by either barometer is within the average quoted precision limits ($\pm$ 1500bars for Newton and Perkins, 1982; $\pm$ 1kbar for Harley and Green, 1982). However, the Harley and Green (1982) barometer tends to show somewhat lower pressures when compared to those obtained by using Newton and Perkins (1982; average pressures of 5.2 and 6.1kbars respectively). The range of pressures calculated from several mineral analyses within one sample, were commonly found to be within the precision limits for the calibration of Newton and Perkins (1982), but not necessarily for that of Harley and Green (1982). The existing differences in

pressures, as observed particularly for sample P14C (see Appendix C), may be explained by small compositional variations in the analyzed phases. Thus in the cordierite-garnet granulites, the garnet and orthopyroxene were commonly analyzed in the vicinity of cordierite, as garnet is seen to be replaced by orthopyroxene and cordierite (Chapter 3). In cases where the garnet and orthopyroxene were analyzed distant from any cordierite (e.g. P14C - T4 and P19C - T2), the orthopyroxene showed a distinctly higher enstatite component (X_{Mg}) and a somewhat lower Al-content, while garnet only showed a small decrease in pyrope component (see Appendix C). These compositional differences result in the derivation of lower pressures when the barometer of Newton and Perkins (1982) is used but in higher pressures for the Harley and Green (1982) barometer. The latter barometer was found to be more sensitive to small compositional changes in the orthopyroxene which resulted in a wider range of calculated pressures within one sample.

Sample P25C (a garnet granulite) does not contain any cordierite. For this sample the observed range in calculated pressures is found to be well within the expected precision range of either barometer. Analyses of orthopyroxene and garnet in P25C showed a higher X_{Mg} for both phases when compared to these minerals in the cordierite-garnet granulites. This results in the average pressure for this sample being very similar to that of the cordierite-garnet granulites.

6.4.1.1 Discussion of Geobarometry

An average pressure of around 6.1 $\pm$ 1.5kbars as obtained from the Newton and Perkins (1982) barometer is in agreement with the mineral paragenesis (see Fig 3.19) as well as with pressures derived for other Archaean granulite terranes (e.g. Phillips, 1980; Harris and Holland, 1984; Bohlen et al., 1985). Such pressures disagree, however, with the pressures obtained for the SMZ-pelitic rocks by van Reenen (1978; 1983) which are in the range of 7.2 to 8.2kbars. The pressures obtained by van Reenen (1978; 1983) are largely based on the cordierite-garnet geobarometers of Currie (1971) and Hensen and Green (1973). When applied to the rocks of this study they yield similar temperatures and pressures (T-range of 640 to 800°C for Currie (1971); 400 to 720°C for Hanson and Green (1973) and pressures of 6.3 to 8.7kbars for both calibrations; not shown) to those obtained by van Reenen (1978; 1983;). In the light of more recent information on the stability of cordierite (e.g. Holdaway and Lee, 1977; Newton and Wood, 1979; Martignole and Sisi, 1981) and because of the conflicting experimental results of Currie (1971) relative to the results of Hensen and Green (1973) (i.e. disagreements in the change of K_D values with temperature for garnet-cordierite reactions as reflected by the different resultant temperatures quoted above), the cordierite-garnet calibrations of Currie (1971) and Hensen and Green (1973) are inherently suspect. Wood (1973), Holdaway and Lee (1977) and Martignole and Sisi (1981) indicated that knowledge on the hydration state of cordierite (or $P(H_2O)$) is a necessary requirement before attempting to use cordierite for geobarometric purposes.

The lower pressure stability of cordierite relative to garnet + Al_2SiO_5 + quartz may be taken to indicate that the breakdown of garnet to cordierite and orthopyroxene (see equations 3.13 to 3.15, Chapter 3) proceeds with decreasing pressures in rocks of the appropriate composition (van Reenen, 1983). As the garnet and its breakdown products would be expected to re-equilibrate during the progress of the continuous reaction, it is expected that the rocks not showing any garnet breakdown at all, such as P25C, should show higher metamorphic pressures. This does not seem to be the case though (Table 6.1). Alternatives proposed by van Reenen (1983) for the continuous breakdown of garnet are an increase in the partial pressures of water or increasing temperature. These possibilities will be discussed in subsequent sections.

6.4.2 Geothermometry

Cation Fe-Mg mineralogic exchange reactions between coexisting ferro-magnesian phases have been widely used for thermometry. Small volume changes involved in most Fe-Mg exchange reactions make such exchange reactions largely independant of pressure. In high-grade pelitic rocks such thermometry has been used with varying success (e.g. Ghent et al., 1982; Hodges and Spear, 1982; Martignole and Nantel, 1982; Harris and Holland, 1984; Edwards and Essene, 1988; Battacharya et al., 1988). Factors controlling the success are: (a) the accuracy of the calibration used, which depends on whether or not additional components have been accounted for in a sufficient manner and on the extrapolation in chemistry needed to apply a given thermometer, (b) the extent to which peak metamorphic conditions have equilibrated amongst coexisting phases, (c) the extent of

retrogressive re-equilibration of phases (e.g. Essene, 1982). These factors will be discussed in somewhat more detail in the light of various experimentally and naturally calibrated geothermometers applied to the minerals in this study. The results of the thermometers used are summarized in Table 6.1 while more detailed descriptions of each thermometer are given in Appendix C.

6.4.2.1 Garnet - Orthopyroxene Thermometry

Garnet-orthopyroxene thermometry is potentially attractive as it involves intercrystalline Fe-Mg exchange amongst two phases that are commonly considered to be fairly refractory phases (Freer et al., 1982; Cygan and Lasaga, 1985). In addition, the simple chemistry of orthopyroxene allows it to be regarded as an ideal Fe-Mg mixture (Newton and Perkins, 1982; Harley, 1984; Sen and Bhattacharya, 1984). The low Mn-content in garnet justifies a ternary Ca-Fe-Mg mixing model for the garnet.

The results of the orthopyroxene-garnet thermometry using the calibrations of Harley (1984) and Sen and Bhattacharya (1984) are summarized in columns C and D of Table 6.1 respectively. While the two different thermometers show temperatures that are largely within their accepted errors (~60°C), the calibration of Harley (1984) always yields temperatures lower than those for Sen and Bhattacharya (1984). Nevertheless, both thermometers indicate that sample P25C (cordierite free garnet granulite) equilibrated at somewhat lower temperatures when compared to the cordierite-garnet granulites. Peak temperature estimates from contiguous garnet-orthopyroxene cores fall at around 675°C for

P25C whereas temperatures of 780°C are estimated for P21C (cordierite-garnet granulite; Sen and Bhattacharya, 1984).

6.4.2.1.1 Discussion of Garnet - Orthopyroxene Thermometry

The temperature difference between the two garnet-orthopyroxene thermometers (Table 6.1) is likely to be related to the different thermochemical parameters used for these calibrations. In particular, the higher interference factor for Ca in garnet in the Sen and Bhattacharya (1984) calibration relative to that of Harley (1984; 3300 versus 1400 cal/mol.site - Appendix C) results in higher absolute temperatures and in a larger range in temperatures for small differences in the grossular component of the garnet.

The lower temperature estimates for sample P25C relative to the cordierite-garnet granulites is surprising, particularly as there did not appear to be a significant difference in pressure between P25C and the cordierite garnet granulites, where the barometers were based on similar thermochemical parameters and activity-composition relationships as the garnet-orthopyroxene thermometers used. However, a closer inspection of the range in temperatures obtained for the different mineral pairs in sample P14C reveals that the garnet-orthopyroxene pair analyzed well away from any cordierite grains yields a lower value for the equilibrium constant K, owing to a higher Mg-content in the orthopyroxene and thus a resultant lower apparent equilibration temperature (P14C-T4 in Appendix C). Assuming that garnet has largely remained closed during retrogression (Chapter 5, see also Woodsworth, 1977), then the presence of

cordierite in garnet-orthopyroxene rocks provides a Fe-Mg phase with which the orthopyroxene may re-equilibrate during retrogressive cooling. In terms of the garnet-orthopyroxene geothermometer of Sen and Bhattacharya (1984) a temperature of 675 $\pm$ 60°C may thus represent the closest estimate to a peak metamorphic equilibrium temperature preserved for the granulites. Alternatively, if cordierite has no adverse retrograde effects on other Fe-Mg phases, then peak temperatures could have been as high as 780°C.

Simple Fe^{3+} estimates for orthopyroxene and garnet (Papike et al., 1974; Essene, 1982) indicate that Fe^{3+} corrections can only change temperatures by ~30°C. In fact, in many cases lower temperatures are obtained as such simple calculations can give higher Fe^{3+}/Fe^{2+} ratios for orthopyroxene relative to those for garnet. This is in reverse of what is generally expected for orthopyroxene relative to garnet (Harley, 1984). The reason for this is unknown but may be related to the re-equilibration of the orthopyroxene with phases such as cordierite and/or biotite or with a melt phase (Chapters 3 and 4) during retrogression.

6.4.2.2 Garnet - Biotite Thermometry

Garnet-biotite assemblages are common to many metamorphic rocks of various metamorphic grades. In the present study it is of particular interest as this assemblage is present in rocks both north and south of the orthopyroxene isograd, ideally allowing for a comparison of temperature conditions across the isograd.

The cation exchange reaction:

Fe-garnet + Mg-biotite = Mg-garnet + Fe-biotite (6.1),

representing Fe-Mg exchange amongst biotite and garnet has been calibrated on natural assemblages (Thompson, 1976) and also experimentally for a restricted range of mineral compositions (Ferry and Spear, 1978). However, while the Ferry and Spear (1978) thermometer has yielded results consistent with phase equilibria in medium grade rocks (e.g. Ghent et al., 1982), it has been shown to give erratic temperatures in high-grade rocks. This is commonly attributed to the restricted compositional range of the experimental calibration relative to natural high-grade assemblages, to non-ideal mixing of phase components and to retrograde resetting (e.g. Harris and Holland, 1984; Indares and Martignole 1985a, b; Edwards and Essene, 1988). To overcome these problems Indares and Martignole (1985a, b) suggest the use of core garnet and matrix-biotite analysis where the biotite is isolated from garnet (and other Fe-Mg phases) and therefore not affected by late Fe-Mg exchange (Tracy et al., 1976). Furthermore, they also extend the thermometer of Ferry and Spear (1978) to make allowance for departures from ideality caused by the effects of Ca and Mn on Fe/Mg in garnet and Al^{VI} and Ti on Fe/Mg in biotite. Such corrections resulted in obtaining temperatures for granulitic rocks, compatible with the semi-empirical calibration of Thompson (1976) but lower than those of Ferry and Spear (1978).

In a recent study by Chipera and Perkins (1988), a series of garnet-biotite thermometers were compared. It was found that the experimental calibration of Perchuk and Lavrenteva (1983) yields the most precise and accurate results. This calibration is derived from experiments conducted both on synthetic and

natural assemblages corresponding to mixtures of garnet, biotite and cordierite. The wider compositional range covered by this thermometer relative to that of Ferry and Spear (1978) and the presence of cordierite in the experimental runs made this thermometer particularly attractive for use on the SMZ rocks. In this study the thermometers of Perchuk and Lavrenteva (1983) and Indares and Martignole (1985b) were used. For comparative purposes the results of Ferry and Spear (1978) are also shown in Table 6.1 and Appendix C.

Columns E, G and H in Table 6.1 summarize the average temperatures obtained from garnet and matrix-biotite cores. Temperatures from garnet and biotite cores with phases in contact are given in column F for the Perchuk and Lavrenteva (1983) thermometer only (Table 6.1). A close inspection of the garnet-biotite temperatures given in Table 6.1 and Appendix C indicates the following general patterns:

1. Garnet core and matrix-biotite compositions (biotite analyzed away from any other Fe-Mg phase) generally yield higher temperatures than when the two mineral phases are in mutual contact.

2. Garnet rim and biotite rim compositions with both phases in contact always yield lower temperatures than the respective core compositions. Exceptions are samples P50C and P7D where the reverse can be the case or core and rim temperatures are identical.

3. The temperatures derived by using Ferry and Spear (1978) can be up to 140°C higher than those derived by using Perchuk and Lavrenteva (1983) or Indares and Martignole (1985b). The former also show a much wider

scatter in temperature values within the same sample and within a separate group of rocks.

4. Garnet and matrix-biotite temperatures in group 4 rocks are considerably higher than those in group 2 rocks when the calibration of Ferry and Spear (1978) is used. This temperature difference between these two rock groups decreases considerably for the Perchuk and Lavrenteva (1983) calibration and even more so for the calibration of Indares and Martignole (1985b). The temperature difference is absent for garnet-biotite contact pairs (column F in Table 6.1).

5. Ferry and Spear (1978) temperatures higher than ~770°C have $Al^{VI}+Ti/(Al^{VI}+Ti+Fe+Mg)$ ratios that fall outside the calibration range of that thermometer (>0.15 - Appendix C). Most other rocks have values of $(Al^{VI}+Ti)/(AL^{VI}+Ti+Fe+Mg)$ of ~0.15.

6.4.2.2.1 Discussion of Garnet - Biotite Thermometry

In Chapter 5 it was determined that Fe/Mg zonation within garnets was limited to small increases in Fe/Mg in narrow rim zones of the garnet (Fig. 5.5b). Such compositional homogeneity of garnet is typical for high-grade garnet (e.g. Woodsworth, 1977) and suggests the attainment of chemical equilibrium for the garnet at some stage during its metamorphic history. Because of the refractory ionic diffusion style of garnet (Loomis, 1975; Cygan and Lasaga, 1982), this homogeneous character is commonly preserved. In contrast, the Fe/Mg variations in biotite are more significant, in particular the variations shown

by different grains within the same thin section (e.g. P17C-1C to 6C - Chapter 5). Biotite is commonly considered less refractory than garnet. If it is assumed that equilibrium was attained at some stage during prograde or at peak metamorphism, then the zonation style observed for biotite in garnet-biotite pairs is generally attributed to local re-equilibration of Fe/Mg during cooling from peak temperatures (e.g. Tracy et al., 1976; Indares and Martignole, 1985). The extent of Fe-Mg re-equilibration within biotite is presumably a function of its surface contact with adjacent Fe-Mg phases or even of its distance from such phases. The latter is particularly well exemplified in sample P17C for garnet-biotite pairs (Chapter 5). In the case of the presence of other Fe-Mg exchanging phases, the relative tendency of minerals to concentrate either Mg or Fe with decreasing temperature, in addition to the ease of Fe-Mg exchange of the ferromagnesian phases becomes important for thermometry considerations. For the ferromagnesian phases in these rocks, the observed order of decreasing Mg/Fe ratios is cordierite, biotite, orthopyroxene ~orthoamphibole and garnet. Therefore, if the matrix-biotite but not the garnet exchanges retrogressively with cordierite, then the garnet and matrix-biotite temperature will be higher than the peak metamorphic temperature as the biotite is enriched in Fe during retrogression. Garnet and biotite will then not represent an equilibrium assemblage. The effect on temperature will be reversed if biotite exchanges with orthopyroxene or orthoamphibole, that is, the garnet and matrix-biotite temperatures may underestimate peak metamorphic temperatures. Similarly, minimum peak temperature estimates will be obtained for garnet-biotite pairs where biotite occurs in contact with garnet and where some parts of the garnet have exchanged (e.g. rim parts).

In this regard it is interesting to note that for both the group 2 (orthoamphibole gneisses) and the group 1, 3 and 4 rocks the garnet and contact-biotite temperatures are identical (point 4 above). This may be taken to suggest similar closure-temperatures for the minerals in the different groups of rocks. For the average garnet and martix-biotite temperatures of compositionally similar rocks such as groups 2 and 4, no significant differences (change in T larger than ~50°C) exist for the Indares and Martignole (1985b) thermometer which corrects for Al^{VI} and Ti interference on Fe/Mg mixing in biotite. As such, the difference in the average peak temperature estimates between group 2 and group 4 rocks could be caused by a combination of different biotite chemistry and retrograde matrix-biotite - cordierite exchange in the group 4 rocks. Effects of matrix-biotite Fe/Mg exchange with cordierite will be minimized for garnet-biotite contact pairs.

It is therefore concluded that garnet core and matrix-biotite core compositions may, in the absence of any other Fe-Mg exchanging phases, represent a close approximation to peak metamorphic conditions (see also Tracy et al., 1976; Indares and Martignole, 1985; Edwards and Essene, 1988). Using the calibration of Perchuk and Lavrenteva (1983) then peak metamorphic equilibration temperatures can be estimated from the garnet-biotite gneisses to about 720 $\pm$ 50°C. Average garnet and matrix-biotite core temperatures (Perchuk and Lavrenteva, 1983) are shown next to the sample positions in Figure 6.1. While the relatively small temperature population does not allow for any detailed conclusions, it does seem to indicate that there is no significant temperature gradient present. The large temperature difference between sample P17C (723°C;

a garnet-biotite gneiss) and P1D (620°C; a cordierite-garnet granulite) which was sampled close to it, illustrates the effect of retrograde re-equilibration of biotite in the presence of other ferromagnesian phases such as orthopyroxene and cordierite.

6.4.2.3 Garnet - Cordierite Thermometry

Fe-Mg partitioning between coexisting garnet and cordierite is represented by the following exchange reaction:

Mg-cordierite + Fe-garnet = Fe-cordierite + Mg-garnet (6.2).

The dependance of this Fe-Mg exchange on P-T-a(H_2O) conditions has been subject to much debate. Experimental results of Currie (1971) and Hensen and Green (1973) provided contradicting results for the temperature dependance of the Fe-Mg distribution amongst these phases. Subsequently, this contradiction was explained by variations in P(H_2O) during the different experiments (Wood, 1973), with P(H_2O) affecting the Fe-Mg partitioning and therefore also the stability limits of the cordierite endmembers (Holdaway and Lee, 1977; Martignole and Sisi, 1981). Studies based on natural samples (e.g. Thompson, 1976; Holdaway and Lee, 1977, Bhattacharya et al., 1988) not only show an agreement with the experiments of Hensen and Green (1973) in terms of the T versus $\ln k_D$ slope, but also show temperatures which are similar to those of Hensen and Green (1973) (e.g. Thompson, 1976; van Reenen, 1978, 1983; Ashworth and Chinner, 1978). For the present study, the calibration of Bhattacharya et al. (1988) is used as its data base includes naturally occuring garnet and

cordierite of composition similar to those found in the SMZ rocks. In addition, this thermometer does not assume ideal mixing of Fe-Mg in garnet and interfering cations have been accounted for. For consistency, the experimental garnet-cordierite calibration of Perchuk and Lavrenteva (1983) has also been used.

In columns J and K of Table 6.1, average temperatures derived from garnet core and adjoining cordierite core compositions have been calculated from the thermometers of Perchuk and Lavrenteva (1983) and Bhattacharya et al. (1988) respectively. The poor agreement in temperature between the two calibrations could be related to a combination of assumed ideal mixing and non-equilibrium of cordierite-garnet pairs in the experimental calibration of Perchuk and Lavrenteva (1983). In the course of their experiments, Perchuk and Lavrenteva (1983) observed large variations in the cordierite compositions and only sluggish garnet-cordierite exchange, suggesting that equilibrium was not attained during their experiments.

From Table 6.1 minimum estimates of peak metamorphic equilibrium temperatures for garnet core and adjoining cordierite core compositions can be placed at 685 $\pm$ 65°C (Bhattacharya et al., 1988). Somewhat higher temperatures (~730°C) can be estimated from garnet and matrix-cordierite core compositions (Appendix C, P14C-T7 and T8).

6.4.2.3.1 Discussion of Garnet - Cordierite Thermometry

In order to obtain best estimates on peak metamorphic temperatures, it is important to choose the correct K_D values. It was argued above that the

garnet, being of refractory character (Loomis, 1975), has largely preserved its chemically homogeneous character. The cordierite, however, while being compositionally homogeneous within single grains, shows large compositional changes from one grain to the next, even within a thin section. In this respect cordierite is analogous to biotite. Thus, by analogy to the garnet-biotite system, best temperature estimates would be given by garnet-matrix cordierite pairs. Owing to the tendency of both cordierite and biotite to concentrate Mg relative to garnet, then, in the absence of garnet and matrix cordierite pairs, the garnet-cordierite pairs with cordierite adjacent to biotite should yield the best estimate of peak metamorphic temperatures. This is indicated by the garnet-cordierite temperatures obtained for P14C, where temperatures of 730°C are recorded for pairs T7 and T8.

Temperatures given in Table 6.1 are only somewhat higher (20-50°C) than those calculated from the calibrations of Hensen and Green (1973) and Thompson (1976) for garnet and adjoining cordierite cores (not shown; see also van Reenen, 1983 for temperatures derived by the latter calibrations).

6.5 Conclusions to the Thermobarometry

The results of a careful choice of microprobe analysis for the Fe-Mg phases in pelitic rocks allows for an estimate of peak metamorphic temperatures of 730 $\pm$ 65°C for the group 1, 3, 4 (and 5?) rocks at pressures of 6.1 $\pm$ 1.5kbars. Such temperatures are deduced from core analysis of garnet-orthopyroxene, garnet-

biotite and garnet-cordierite mineral pairs, where, if possible, the minerals were not in contact with each other, nor with any other Fe-Mg exchanging phase. The temperatures derived from the cores of contiguous mineral pairs and from the rims of contiguous mineral pairs are successively lower than for the non-contiguous mineral pairs, and are interpreted as representing temperatures at which sections of minerals attained their "closure" in terms of Fe/Mg exchange during retrogression. The peak metamorphic temperature derived for the pelitic rocks of groups 1, 3, 4 (and 5?), is also in agreement with a temperature of 702 $\pm$ 30°C for the mafic rock M27C, and with temperature estimates for the ultramafic rocks.

For the group 2 rocks (orthoamphibole gneisses) peak metamorphic temperatures are estimated at 620 $\pm$ 50°C from the garnet-biotite thermometry of Perchuk and Lavrenteva (1983). In samples P50C and P7D, the occurrence of two separate orthoamphiboles (gedrite and anthophyllite) at predicted temperatures of ~600°C is in good agreement with the result of Spear (1980), who places the crest of the miscibility gap at 600 $\pm$ 25°C. The orthoamphibole gneiss P34C shows a distinctly higher temperature (658°C) when compared to the other orthoamphibole gneisses and may therefore indicate that the mineral assemblage represented by the orthoamphibole gneisses was stable over a wide range of temperatures. While these garnet-biotite temperatures of Perchuk and Lavrenteva (1983) are lower than those for the group 1, 3 and 4 rocks, this is not the case if the calibration of Indares and Martignole (1985b) is used. As the latter calibration corrects for Al^{VI} and Ti interference on Fe/Mg exchange in biotite, this indicates that the difference in garnet-biotite temperatures is

a function of the different biotite chemistry in the group 2 rocks relative to the other rock groups. Such differences in biotite chemistry need not be related to differences in metamorphic temperature only, but could be related to variations in factors such as $a(H_2O)$ (see Chapter 5).

The resultant estimates of peak metamorphic conditions corresponding to 730 $\pm$ 65°C and 6.1 $\pm$ 1.5kbars are shown in Figure 3.19. Before comparing this estimate to the P-T estimates obtained from the given phase relationships (represented by curves A to G in Fig. 3.19) some points are worth noting. Firstly, the curves representing the biotite breakdown to form garnet and orthopyroxene (curves E and F respectively) are for an initially anhydrous system. If a hydrous system is considered both curves are shifted towards lower temperatures (~50°C at 6kbars; e.g. Clemens and Wall, 1981). Hydrous melting would be supported by the lack of K-feldspar from the product assemblages (Chapter 3). For the ultramafic and mafic rocks the curves given in Figure 3.19 (curves A, B, C and D) are determined for $P(H_2O) = P(total)$, or for D at $X(H_2O) = 0.4$). If curves A and B, representing the breakdown of chlorite and of olivine + tremolite (Yoder and Fawcett, 1966; Evans, 1977) show a similar dependance on water content as the hornblende breakdown reaction (Curves C; Wells, 1979), then in a system with $0 < P(H_2O) < P(total)$ the position of curves A and B would be at significantly lower temperatures. Thus, in view of the fairly large errors involved for the positioning of curves A to G, caused by a lack of knowledge on $P(H_2O)$ in natural systems, the P-T estimate obtained from the cation geothermometry is considered to compare favourably with the P-T estimates deduced from the mineral assemblages.

From the foregoing discussion it becomes evident that the geothermometers and geobarometer used in this study have, if the appropriate mineral K_D values are chosen, provided accurate temperatures and pressures for compositionally and mineralogically similar rocks elsewhere in the world. In addition, the various geothermometers and geobarometer used in this study show good agreement with each other. Thus, while certain inaccuracies in the calibrations are inherent from simplifying assumptions, the calculated temperatures and pressures are considered to be correct to within their quoted precisions. Similarly, the choice of selected mineral pair distribution coefficients will largely eliminate any errors in calculated pressures and temperatures which are introduced by retrograde cation exchange.

Van Reenen (1983) suggested temperatures of 780 to 820°C at pressures of 7.2 to 8.2kbars for the second metamorphic event (M2) which is characterized by the development of coronas of cordierite and hypersthene surrounding garnet in the SMZ cordierite-garnet granulites. Furthermore, largely based on the upper stability limit of coexisting cordierite + garnet together with the interpretation of "relict" kyanite intergrown with biotite, van Reenen (1983) suggests the existance of an initial (M1) granulite event with $T > 800°C$ and $P \geq 9.5kb$. Such thermobarometric determinations by van Reenen (1983) were largely based on the calibrations of Currie (1971), Hensen and Green (1973), Wells (1977) and Ferry and Spear (1978). In the light of the more recent developments in thermobarometric calibrations (e.g. Holdaway and Lee, 1977, Martingnole and Sisi, 1981; Powell, 1978; Srikantappa et al.,1985; Indares and Martignole, 1985a, b; Newton and Perkins 1982; Perchuk and Lavrenteva, 1983) the

temperatures and pressures derived by van Reenen (1983) cannot be supported anymore. Furthermore, the possibility of kyanite intergrown with biotite being retrograde in origin (refer to Chapter 3), together with the stabilization of cordierite by H_2O content (Newton, 1972; Holdaway and Lee, 1977; Martignole and Sisi, 1981) may require a reassessment of the M1 event as proposed by van Reenen (1983).

Support for a pressure decrease from M1 to M2 is , according to van Reenen (1983), based upon the continuous reaction garnet + quartz = cordierite + hypersthene where the Fe-Mg phases involved in this reaction are found to increase their Fe/Mg with continued procedure of the above reaction. Possible causes of this shift are increasing temperature, decreasing pressure or increasing $P(H_2O)$ (van Reenen, 1983). The similarity of peak metamorphic pressures and temperatures in P25C (garnet granulite) compared to the cordierite-garnet granulites (P14C, P19C, P21C) suggests that the cause of the Fe/Mg increase in the Fe-Mg phases involved, may be an increase in the $P(H_2O)$. A possible mechanism for a local increase in $P(H_2O)$ is the retrograde crystallization of partial melts produced within the pelites during prograde processes (see Chapters 3 and 4). As such the garnet + quartz replacement by cordierite and orthopyroxene would be retrograde in origin. An alternative explanation for the Fe/Mg shift observed by van Reenen (1983) could be the removal of some of the partial melts formed (see Chapter 4), that is, metamorphism did not occur as a closed system process.

Both the extraction of a melt or the final crystallization thereof, will effectively remove the media for ionic exchange and the mineral phases will

cease to exchange, or diffusion of ions will only be controlled by solid-solid exchange. The importance of fluids during metamorphism of these rocks will be discussed in subsequent sections in the light of stable isotope data for the ultramafic, mafic and pelitic rocks.

CHAPTER 7: STABLE ISOTOPE GEOCHEMISTRY

7.1 Introduction

The importance of fluids during metamorphic processes is twofold. Firstly, the presence or absence of fluids during metamorphism critically controls the rates of ionic diffusion, mineralogic recrystallization (e.g. Carmichael, 1969; Winkler, 1976) and the type of mineral assemblage (i.e. hydrous or anhydrous). Secondly, fluids may gradually leave, or enter rock systems subjected to metamorphism, and can therefore serve as heat transporting media and as agents for the transfer of numerous chemical components or elements.

In the previous sections it was shown that rocks from the Bandelierkop Formations in the Southern Marginal Zone (SMZ) of the Limpopo Metamorphic Complex were subjected to amphibolite and granulite facies metamorphism, and as a result, some fluids must have been released during their prograde path. It is the purpose of this Chapter to examine the stable isotope composition of the high-grade rocks and minerals with a view to establishing the extent of isotopic equilibrium among mineral phases, the fluid-rock interactions, and the nature and extent of fluid flow in the systems under consideration.

In order to understand the significance of oxygen isotopic equilibration amongst minerals, whole rocks and fluids during metamorphism, it is important to define the type and scale of fluid migration that can occur within a metamorphic

domain.

7.2 Principles of Fluid Flow in Metamorphic Rocks

An average pelitic rock during prograde metamorphism may produce about 2 moles of fluid per kilogram of rock, which at 500°C and 5kbar would occupy 12 volume percent of the rock (Walther and Orville, 1982). As the average porosity of metamorphosed pelitic rocks is commonly only a fraction of this volume (e.g. Fyfe et al., 1978; Walther and Orville, 1982), and as retrograde hydration or carbonation is rare, or only observed in some zones (e.g. Winkler, 1976), these fluids must leave the system. Driven by density differences these fluids may rise upward through interconnected pores or a fracture system and upon cooling close to the surface, may return to depth establishing a circulation system (Wood and Walther, 1986). This can only occur if the rock is capable of allowing a hydrostatic pressure gradient to be maintained and will stop if the temperature gradient is too small to support density differences of the fluids. Such systems are common in contact metamorphic environments (e.g. Forester and Taylor, 1976). However, if the lithostatic pressure exerted on the rock is too large, then the pores will collapse until the fluid becomes pressurized to the extent that it exceeds lithostatic pressure. Hydrofracturing of the rock will result and may provide a "single-pass flow" for fluid release (Wood and Walther, 1983). Fluid release is commonly confined to veins and fractures, the presence of which is indicated by quartz segregations and quartz veins (e.g. Walther and Orville, 1982; Yardley, 1983) or carbonate veins (Rye and Bradbury, 1988) on the

smaller scale and, on the larger scale, fluid migration can be concentrated in shear or fault zones (e.g. Kerrich et al., 1984).

The effects of each particular type of fluid migration style mentioned above on the isotopic composition of rocks and minerals may vary considerably. Hence, it is important to consider two end-member cases to fluid flow. Pervasive fluid flow is defined as a fluid that moves independently of structural or lithologic boundaries, permeating equally all rocks and causing isotopic re-equilibration across lithologic boundaries in an open system environment (Valley, 1986). A channelized fluid, in contrast, moves along veins, shear zones, rock contacts and permeable lithologic units, thereby favouring chemical and isotopic heterogeneity, allowing some rocks to remain unaffected by the fluids while others would be considerably altered with respect to their ^{18}O compositions. In nature there is abundant evidence for both types of fluid flow on scales varying from millimetres to kilometers (e.g. Garlick and Epstein, 1967; Black, 1974; O'Neil and Ghent, 1975; Margaritz and Taylor, 1976; Rumble and Spear, 1983; Valley and O'Neil, 1984; Ferry, 1987; Chamberlain and Rumble, 1988; Sharp et al., 1988). Some of the above aspects will be discussed further in the sections to follow.

7.3 Oxygen Isotope Compositions of Whole Rocks and Minerals from the SMZ

The oxygen isotope data for various rock types are summarized in Tables 7.1 to 7.4 and Figure 7.1. For the analytical and experimental procedures used the reader is referred to Chapter 2.

7.3.1 Ultramafic Rocks

Whole rock oxygen isotopic studies on ultramafic igneous rocks in general have indicated average $\delta^{18}O$ values of around 5.7‰, that is values that are indistinguishable from those of fresh tholeiitic rocks. These values represent bulk mantle $\delta^{18}O$ values (e.g. Kyser et al., 1982; Beaty and Taylor, 1982; Smith et al., 1984). While the average value of 5.6‰ for the high-grade rocks of this study is very similar to that quoted above, the range in $\delta^{18}O$ compositions for the six high-grade ultramafic rocks (all except U6B and U10B - see Appendix 1) is fairly large (3.7 to 8.9‰) when compared to $\delta^{18}O$ ranges quoted by Smith et al. (1984) for low-grade ultramafic rocks and to those of Hoffman et al., (1986).

Beaty and Taylor (1982) noted that the whole rock $\delta^{18}O$ values of low grade ultramafic rocks may be closely related to the abundance of secondary minerals and therefore to the degree of alteration. Textural interpretation of the whole rocks in this study indicates that the ultramafic rocks have been variably altered after peak metamorphism. Such alteration is commonly reflected by the growth of serpentine, opaques (magnetite?) and fibrous chlorite along fractures of coarse-grained metamorphic orthopyroxene and olivine (Appendix A). As some chlorite in the high-grade rocks is interpreted to be primary (i.e. prograde), only the modal abundance of serpentine ($\pm$ magnetite) may be taken as an index to the degree of alteration. Inspection of Table 3.1 (Chapter 3) indicates that the high serpentine content of sample U31C is reflected by a low $\delta^{18}O$ value (3.7‰), whereas sample U17B, which texturally indicated no alteration, shows a value of 5.9‰. This suggests

that the values in $\delta^{18}O$ lower than 5.9‰ may be caused by infiltration of an alteration fluid which stabilized the hydrous secondary minerals. To determine the isotopic compositions of such an alteration fluid, the open system equation of Taylor (1977) can be used:

$$W/R = \ln \frac{\delta^{i}H_2O + \Delta - \delta^{i}\text{rock}}{\delta^{i}H_2O - (\delta^{f}\text{rock} - \Delta)} \qquad (7.1)$$

where W/R is the water:rock ratio in atom% oxygen, $\delta^{i}H_2O$ is the initial oxygen isotopic composition of water, δ^{i}rock and δ^{f}rock are the initial and final oxygen isotopic compositions of the rock and $\Delta = \delta^{f}\text{rock} - \delta^{f}H_2O$. To determine $\delta^{i}H_2O$ (=alteration fluid), W/R, Δ and δ^{i}rock and δ^{f}rock must be known or estimated. In this study, it is of interest to determine whether the above-mentioned alteration fluid is of metamorphic origin or not. As metamorphic fluids commonly have $\delta^{18}O$ values heavier than +3‰ (e.g. Sheppard, 1986), the maximum possible $\delta^{i}H_2O$ will be determined as follows: W/R = 100 (an arbitrary but high value); δ^{i}rock = 5.3‰ (average of little-altered high-grade peridotites); δ^{f}rock = 3.7‰ (U31C) and Δ estimated at temperatures of 500°C and 400°C from serpentine-water and magnetite-water fractionations given by Wenner and Taylor (1971; see Appendix D) for a serpentine:magnetite ratio of 10:1 (U31C); Δ = -1.43 and -0.59 respectively. The obtained maximum $\delta^{i}H_2O$ values are 5.1 (at T = 500°C) and 4.3 (at T = 400°C). In reality, the W/R ratio was presumably not very large as is evidenced by the partial retrogression of sample U31C which still shows about 50 modal percent orthopyroxene and olivine, and by the variable

amounts of retrogression in the different high-grade peridotites. In addition, a comparison of the $\delta^{18}O$ compositions of enstatite relative to the whole rocks in the high-grade peridotites (Table 7.1) indicates that residual enstatite (+olivine?) must be heavier than the alteration minerals of serpentine + magnetite and thus δ^{i}rock including some partially altered samples is underestimated; temperatures in the range of 400 to 500°C represent maximum stability temperatures for serpentine (Scarfe and Wyllie, 1967; Wenner and Taylor, 1971) and lower temperature estimates would lower $\delta^{i}H_2O$. Thus at temperatures of about 200°C with W/R ratios of around 5 and $\delta^{18}O^{f}$rock values of around 3‰ the $\delta^{i}H_2O$ value is 1.5‰. In conclusion, alteration of the ultramafic samples was probably not caused by metamorphic fluids, nor magmatic fluids ($\delta^{18}O > 5$‰, Sheppard, 1986) but presumably by fluids approaching ~1.5‰ at geologically reasonable conditions of serpentinization (Wenner and Taylor, 1971). Such low values of fluid $\delta^{18}O$ could imply a large seawater ($\delta^{18}O$ ~0 $\pm$ 1‰, Sheppard, 1986) or meteoric water ($\delta^{18}O \leq 0$‰) component to the alteration fluid.

While alteration can suitably explain the low $\delta^{18}O$ values of the ultramafic rocks analyzed in this study, this cannot account for the high value shown by sample U10A. Texturally, this sample indicates growth of enstatite after chlorite. If this dehydration reaction is accompanied by a loss of H_2O from the system as a whole, then such H_2O would, according to the chlorite-H_2O fractionation factor of Wenner and Taylor (1971; see also Appendix D) be heavier than the residual chlorite, if the reaction occurs at temperatures above 300°C. If the breakdown reaction occurs in excess of about 350°C, which is

likely, particularly as the upper thermal stability limit of chlorite is in excess of 700°C (e.g. Evans, 1977), then the H_2O will also be heavier than the product enstatite (Friedman and O'Neil, 1977; Appendix D). Thus loss of H_2O from the high-grade ultramafic rocks because of the prograde breakdown of chlorite can only lower the whole rock $^{18}O/^{16}O$ ratio. Such a decrease would be limited to the stoichiometric H_2O content of chlorite with maximum shifts of 0.2 to 0.5‰ at temperatures of 400 to 750°C (for 15 weight% H_2O in chlorite). In conclusion the high $\delta^{18}O$ values of U10A cannot be explained by metamorphic devolatization only.

Alternative explanations for the high $\delta^{18}O$ value of this sample are that the protolith of this rock was already heavy, or that the sample exchanged oxygen with an isotopically heavy source during metamorphism. Retrograde isotopic re-equilibration is supported by the indistinguishable isotopic composition of orthopyroxene and hornblende relative to chlorite. This suggests that there is isotopic disequilibration amongst the mineral phases caused by kinetic differences in the mineral-fluid exchange, at temperatures exceeding those of retrogressive chlorite and/or serpentine stabilization (>500°C). If the anthophyllite in this sample is of retrograde origin (see section 3.2), then temperatures of retrogression were below 600°C (Evans, 1977). Using the fractionation curves from Friedman and O'Neil (1977), then a fluid in equilibrium with the pyroxene at temperatures of 500 to 730°C would have an isotopic composition for water of between 10 and 11‰. Such an ^{18}O enriched fluid is likely to be of metamorphic origin, that is, possibly derived from metasediments or high $\delta^{18}O$ gneisses.

Samples U6B and U10B were collected from the amphibolite facies greenstone sections of the Pietersburg and Rhenosterkoppies belts (Figures 1.3 and 2.1). Both samples are heavily altered and only show relict orthopyroxene and/or olivine. Assuming that these ultramafic rocks showed an initial igneous $\delta^{18}O$ signature of ~5.7‰, then their variable $^{18}O/^{16}O$ ratios as observed currently, attest to the localized control of different alteration and/or metamorphic processes.

7.3.1.1 Summary

The large range in whole rock oxygen isotopic compositions of the high-grade ultramafics may be explained by the influence of two isotopically distinct fluids: one a metamorphic fluid ($\delta^{18}O(H_2O)$ of 10 to 11‰), and the other an alteration fluid of possible seawater and/or meteoric origin. Both of these fluids affected only some but not all the ultramafic samples.

7.3.2 Mafic Rocks

7.3.2.1 Whole Rock $\delta^{18}O$ Values

Mantle derived tholeiitic rocks in general show $\delta^{18}O$ values of around 5.7‰ (Muehlenbachs and Clayton, 1972a; Kyser et al., 1982; Kyser, 1986). This limited range in values reflects a mantle of homogeneous $^{18}O/^{16}O$ ratios. However, this limited compositional range can be extended to both higher and lower values by processes of low and high temperature alteration

respectively (e.g. Muehlenbachs and Clayton, 1972a, 1972b; Spooner et al., 1974; Stakes and O'Neil, 1982; Alt et al., 1986). In the case of continental tholeiites, an extended range in isotopic compositions is commonly related to source mantle compositional variations and/or crustal contamination (Kyser et al., 1982; Kyser, 1986).

The range in oxygen isotope values shown by the mafic rocks of this study is compared in Figure 7.1 to that of the mafic granulites from Australia (McNaughton and Wilson, 1983), and to the range shown by both oceanic and continental rocks of tholeiitic affinity as given by Kyser (1986). For the mafic rocks of this study, Figure 7.1 illustrates that their stable isotope values extend from around 6.4‰ up to values of 8.6‰. From earlier discussions on the general geochemistry of the SMZ mafic rocks, it is reasonable to assume that these rocks were not extensively altered in terms of their major element geochemistry. Furthermore, although the current position of samples as shown in Figure 2.1 is certainly not the original disposition of samples, the irregular distribution of mafic rocks with high $\delta^{18}O$ and mafic rocks with low $\delta^{18}O$ values (~6.0‰) within this terrane may suggest that this shift towards ^{18}O enrichment is caused by localized variations in fluid conditions. The comparison of the mafic rocks of this study to chemically similar mafic granulites from Einasleigh, Australia (D in Fig. 7.1; McNaughton and Wilson, 1983), with the latter showing both $\delta^{18}O$ and whole rock chemistry similar to fresh oceanic tholeiites, suggests that the $\delta^{18}O$ enrichment of the SMZ mafics is not an inherent feature of progressive metamorphism. This is also reflected by the similarity in $^{18}O/^{16}O$ ratio between the greenschist facies sample

M11C and some high-grade samples (e.g. M1A, M8A, M41C). An alternative explanation for the $\delta^{18}O$ enrichment of the SMZ mafics is an open system behaviour, where the constituent minerals have exchanged oxygen with an ^{18}O-enriched fluid.

7.3.2.2 Mineral $\delta^{18}O$ Values

The mineral $\delta^{18}O$ values of the mafic rocks given in Table 7.2 generally do not show gross disequilibrium, that is, the sequence of increasing ^{18}O enrichment in the mafic samples is amphibole, pyroxene, plagioclase as would be predicted from thermodynamic calculations (e.g. Bottinga and Javoy, 1975; Kieffer, 1982). Exceptions are samples M3C and M37C, where the plagioclase is actually lighter or equivalent to the pyroxene and amphibole. Such reversals in isotopic composition are similar to those observed in hydrothermally altered rocks (e.g. Forester and Taylor, 1976; Gregory and Taylor, 1981; Gregory, 1986) and may indicate the involvement of an externally derived fluid. Secondary quartz separated from samples M37C and M52C are isotopically heavy (11.9‰, Table 7.2) implying precipitation from a metamorphic fluid of $\delta^{18}O(H_2O) > 9.2‰$ (Friedman and O'Neil, 1977; Appendix D) if such precipitation occured above temperatures of 500°C. Temperatures higher than 500°C are consistent with the absence of a greenschist facies assemblage in sample M37C (Liou et al., 1974). By analogy, isotopic reversal in sample M3C may also have been caused by infiltration of metamorphic fluids, particularly as this sample was collected from a small mafic xenolith enclosed within granitic gneisses of the Hout River Transition Zone (see also Fig. 3.2).

Other mafic samples collected from xenolith fragments within the Hout River Transition Zone include M2A, M3A and M5A, the former two also showing $\delta^{18}O$ values heavier than 8.0‰ (M5A = 6.4‰). However, none of these samples show reversals for their mineral isotopic compositions. In samples M3A and M5A the plagioclase-hornblende fractionations are very similar, even though the isotopic compositions of the minerals in M3A are about 2‰ heavier when compared to those in M5A. If this is taken to indicate that these two samples equilibrated at about the same temperature, then it would suggest that the isotopic fluid compositions with which these samples equilibrated, differed by about 2‰. As the sampled xenoliths are laterally separated by only about 100 metres, this would imply considerable fluid heterogeneity over the scale of about 100 metres. Alternatively, the degree to which an infiltrating fluid may affect such xenoliths can depend critically on the size of the xenolith and the fluid:rock ratio in the immediate vicinity, that is, a relatively large sized xenolith (such as M5A?) may remain unaffected by an infiltrating fluid. A similar dependence of mineral-mineral fractionations on the proximity of a surrounding gneiss for an iron formation xenolith has been described by Sharp et al., (1988).

In Figure 7.2 the $\delta^{18}O$(plagioclase) values are shown next to the sample positions. The relatively large compositional differences for plagioclase (range from 7.2 to 9.5‰), particularly that for the samples collected from the Hout River Transition (Fig. 2.1) argue against a pervasive oxygen exchange between different rock types via a single infiltrating fluid homogeneous in oxygen isotopic composition. It is interesting to note though, that the heaviest

$\delta^{18}O$ values for plagioclase were found close to a banded iron formation (cross in Fig. 7.2). Large-scale oxygen isotopic re-equilibration between these *mafic* rocks and the banded iron formation is, however, precluded by the preservation of high $\delta^{18}O$ values for the minerals in the banded iron formation (Table 7.4).

7.3.2.3 Summary

The mafic rocks from the SMZ show oxygen isotope values that range from about 6.4‰ up to about 8.6‰. Compared to unaltered rocks of mafic igneous composition and to mafic granulites from elsewhere, the SMZ rocks are variably enriched in $\delta^{18}O$. Such variable enrichment is best explained by the infiltration of an externally derived fluid. Existing mineral and whole rock oxygen isotopic heterogeneity suggests that this fluid was not necessarily of a terrane-wide pervasive character. Fluids calculated to be in equilibrium with veins within these rocks are enriched in ^{18}O ($\delta^{18}O(H_2O) \geq 9‰$). This could suggest the derivation of fluid from the metasediments and will be discussed further in the subsequent section.

7.3.3 Pelitic Rocks

7.3.3.1 Whole Rock $\delta^{18}O$ Values

For metasedimentary rocks a reconstruction of the pre-metamorphic isotopic signatures is complicated by the variations in the $\delta^{18}O$ of primary sediments.

Sediments generally represent a mixture of detritus obtained from eroded igneous, metamorphic and sedimentary rocks, combined with clays, authigenic quartz and some matrix carbonates formed during diagenesis of the sediment. Thus, the isotopic compositions of sediments can be expressed in terms of a clay end-member (15-30‰ ; Savin and Epstein, 1970) and an igneous rock end-member (5-10‰ ; Taylor, 1968; Longstaffe and Schwarcz, 1977). Earlier it has been established (Chapter 4) that the metasediments from the Southern Marginal Zone show geochemical features which were similar to both Archaean shales and greywackes. The SMZ metasediments are therefore compared to other greywacke-type clastic sediments as shown in Figure 7.1 (A - Margaritz and Taylor, 1976; B - Longstaffe and Schwarcz, 1977). In their study on the oxygen isotopic composition of Archaean metasediments and gneisses, Longstaffe and Schwarcz (1977) noted lower $\delta^{18}O$ values in Archaean metasediments when compared to younger metasediments (e.g. Margaritz and Taylor, 1976). These lower values were ascribed to an immaturity of the Archaean sediments as reflected by a high content of volcanic rock fragments. From Figure 7.1 it becomes apparent that this could also hold for the metapelitic members of this study. Foucarde and Javoy (1973) reported $\delta^{18}O$ values from Archaean metasedimentary granulites which were as low as 5.5 to 7.8‰ . Similarly Shieh and Schwarcz (1974) reported $\delta^{18}O$ values of 5.0 to 8.9‰ for amphibolite to granulite grade paragneisses, migmatites and granites in the Grenville province of Canada. In both cases the low $\delta^{18}O$ values are ascribed to oxygen isotope homogenization and exchange with a mafic-ultramafic reservoir. A similar explanation could also account for the low $\delta^{18}O$ values of the pelitic members. The major and trace element geochemistry of the SMZ pelitic members would, however, suggest

the first alternative, that is a sedimentary protolith low in $\delta^{18}O$ prior to metamorphism, owing to a large mafic-ultramafic volcanic input to the sediment.

Two pelitic schists of typical greenschist facies grade collected from the Pietersburg greenstone belt are also shown in Figure 7.1 (analysis of these samples are given in Table 7.4). Chemically, these two samples are considerably richer in SiO_2, Al_2O_3, but poorer in MgO, FeO, when compared to the metasediments from the Southern Marginal Zone, suggesting that these rocks may not represent low-grade equivalents to the SMZ pelites. Nevertheless, the SiO_2- and Al_2O_3-rich character of these samples (see Appendix B) indicates a clay-rich precursor, and yet their oxygen isotope compositions are not significantly heavier than those of some of the SMZ pelites. If these samples are of similar age to the protoliths for the SMZ pelitic rocks, then this may reflect an immaturity of clastic material, that is, a high content of volcanic rock input (Longstaffe and Schwarcz, 1977).

7.3.3.2 Mineral $\delta^{18}O$ Values

Thermodynamic considerations for stable isotope fractionations amongst the minerals of this study imply the following order of increasing enrichment in ^{18}O: biotite < garnet < orthoamphibole < orthopyroxene < cordierite < plagioclase < quartz (Bottinga and Javoy, 1973; 1975; Kieffer, 1982). In general, this relative order of ^{18}O enrichment among coexisting minerals in individual samples is well preserved in the pelitic members, pointing to general isotopic equilibrium (Table 7.3; Garlick and Epstein, 1967). However, isotopic

reversals do exist in some samples. In sample P45C, the garnet was found to be isotopically heavier than the plagioclase, while in samples P25C, P19C, P21C, hypersthene was found to be somewhat lighter than garnet. In view of the fact that such reversals only occur in some samples, coupled with the close similarity in terms of $\delta^{18}O$ values for phases such as garnet and hypersthene when these phases are in equilibrium at high temperatures, they are considered relatively minor. In terms of geologic implications, such reversals are important though and will be discussed in more detail in a subsequent section (8.3.2). It is interesting to note, that for samples P5C and P6C, both collected from xenolithic fragments within the Hout River Transition Zone, no isotopic reversals are observed for the minerals analyzed. These samples were collected only about 50 metres away from the mafic sample of M3C which shows gross disequilibration and mineral isotopic reversals indicative of infiltration of a fluid and a kinetically controlled oxygen exchange between the constituent minerals and the fluid (e.g. Forester and Taylor, 1976). The general order of the oxygen isotopic enrichment shown by coexisting minerals in the pelitic rocks does not support the influx of and variable equilibration with an extraneous fluid.

In Figure 7.3 the $\delta^{18}O$(quartz) values are shown next to the sample positions. $\delta^{18}O$(quartz) values for the pelitic rocks show a maximum variation of ~3.1‰. As there is no simple correlation between the whole rock $\delta^{18}O$ values and modal% quartz, this range in quartz values is unlikely to be the result of a simple change in modal abundances of the constituent minerals in these rocks. In addition Figure 7.3 indicates that there does not appear to be

any shift in $\delta^{18}O$(quartz) values with changing metamorphic grade. Of particular interest are the $\delta^{18}O$(quartz) values analyzed from the two mafic rocks M37C and M52C, as their values fall well within those for the pelitic rocks. In the previous section it was suggested that some of the mafic rocks re-equilibrated with a fluid that was derived from the metasediments. This is in agreement with the similarity in quartz isotopic compositions. Plagioclase, a common mineral to both lithologies, also provides a good opportunity to test isotopic equilibration between rocks that are thought to have had dissimilar isotopic compositions prior to metamorphism.

If the $^{18}O/^{16}O$ ratios of minerals within different rock types are controlled by the same fluid, or if there is a pervasive equilibration of oxygen isotopes between disparate rock groups, then it would be expected that minerals common to different lithologies would show similar values of $\delta^{18}O$. This is true as long as there is no difference in equilibration temperature between the different rocks. Figure 7.4 compares the $\delta^{18}O$(plagioclase) values analyzed from the mafic rocks (An 30 to 59mol%) to those analyzed from the pelitic rocks (An 21 to 42mol%). The comparison reveals that, while most of the mafic plagioclases have lower $\delta^{18}O$ values than the pelitic plagioclases, some rocks contain plagioclase of identical $\delta^{18}O$ values to the pelitic plagioclases (e.g. M3C and M3A, M2A). It could, therefore, be argued that the plagioclase in some of the mafic rocks is in isotopic equilibrium with a fluid which was also in isotopic equilibrium with plagioclase in pelitic lithologies. Such a fluid could have precipitated the secondary quartz found in some of the mafic rocks. However, this appears to be a local phenomena as it is not necessarily true for

all the mafic rocks. Similarly the banded iron formation still shows $\delta^{18}O$(quartz) values significantly higher than those observed for any other rock type analyzed.

7.3.3.3 $\delta^{18}O$ Relationships for Vein Minerals in the Pelites

For two of the rocks (P7D and P1D), concordant felsic vein material was analyzed separately, the results for each sample are given in Table 7.3 (V-P7D and V-P1D). For both analyses, the given vein-minerals were found to be identical to the rock-minerals (to within $\pm$ 0.1‰ of the mean). Hoernes and Hoffer (1979) observed changes of up to -1.4‰ between rock-quartz and vein-quartz pairs for metapelitic rocks from the Melrose formation, Namibia. This disequilibrium in rock-quartz and vein-quartz compositions has been explained by Hoernes and Hoffer (1979) as equilibration with isotopically different fluids, where the vein-quartz was in equilibrium with a mixture of deep-seated magmatic water and locally derived metamorphic fluids. The felsic veins were thus considered to represent a channelway for fluids. In contrast, the similarity in oxygen isotopic composition between rock-quartz and vein-quartz in this study is consistent with these veins representing melt segregations which were in isotopic equilibrium with the rock-quartz and hence with the whole rock.

While the above data are consistent with the occurrence of partial melting processes within these rocks, no significant correlation between MgO (or FeO, Ni, Cr, etc.) and $\delta^{18}O$ exists for the pelitic rock suite. Similarly, the various groups of pelites could not be grouped according to their $^{18}O/^{16}O$

ratios. If MgO (or any related element or oxide) is taken to represent an index of the extent of partial melting (see Chapter 4), then this lack of correlation between MgO and $\delta^{18}O$ suggests that the extraction of a felsic melt (if any?) did not significantly affect the whole rock $\delta^{18}O$ compositions. Simple modeling can be done using the equation for Rayleigh fractionation (e.g. Taylor and Sheppard, 1986):

$$R/R_i = F^{(\alpha-1)} \qquad (7.2)$$

where R and R_i refer to the final and initial isotope ratios ($^{18}O/^{16}O$) of the rock system, F corresponds to the mole-fraction of melt formed and α is the fractionation factor between melt and rock. Using PlD as an example, then assuming that at 70% partial melting the melt will have a composition similar to that of the model melt in Chapter 4 (4.4.2.2), then its $\delta^{18}O$ value will be ~10.6‰ (for approximate normative proportions similar to the model melt - plg/qtz/gar = 57/40/3). The initial rock will only be ~0.2‰ heavier than PlD. Even if the amount of partial melting was as low as 30%, then the change in bulk rock composition will only be ~0.7‰. As a change in bulk rock composition of about 0.2‰ is considerably smaller than the expected sedimentological variability in bulk rock oxygen isotopic composition of the protoliths, changes in $\delta^{18}O$ caused by ~70% partial melting will go undetected. Thus, $\delta^{18}O$ values are generally not sensitive to processes of partial melting.

7.3.3.4 Summary

The pelitic rocks show whole rock $\delta^{18}O$ values consistent with a large mafic/ultramafic input to the original protolith sediment. Infiltration of a regionally pervasive fluid low in $\delta^{18}O$ is not consistent with the general order of ^{18}O enrichment for the constituent minerals to these rocks nor with the heterogeneity shown by the $\delta^{18}O$(quartz) values for the metasediments. The similarity between the $\delta^{18}O$(plagioclase) and $\delta^{18}O$(quartz) values between some mafic rocks and pelitic rocks in general, suggests some isotopic communication across lithologic boundaries. In the case of the pelitic rocks, the veins are consistent with being internally derived by processes such as partial melt segregation.

7.3.4 Other Rocks

This "category" of rocks includes a banded iron formation sample (B4A), two charnockites (C4D, C8D), a basement gneiss (G9C), an intrusive and undeformed granodiorite (GD49C) and two pegmatitic rocks (V6D, V28C), all sampled from the high-grade terrane (see Figure 2.1). Their oxygen isotopic compositions are given in Table 7.4.

The banded iron formation B4A, was collected from a xenolith enclosed by the granitic gneisses of the Hout River Transition. This xenolith outcropped only ~20 metres away from the mafic xenoliths of M2A and M3A. When compared to the Archaean iron formations of Greenland (Perry et al., 1978) or to the early Proterozoic iron formations of the Hamersley Range (Becker and Clayton, 1976),

the quartz of B4A is found to be similar in stable isotopic composition. Magnetite, however, is somewhat heavier in composition (9.7‰ compared to values commonly less than 7‰). A combination of a high quartz/magnetite ratio and higher metamorphic grades can account for this relatively heavy signature of magnetite $\delta^{18}O$, a situation which is similar to the contact metamorphosed Biwabik/Gunflint iron formations (Perry et al., 1973). In a recent study on granulite iron formations, Sharp et al. (1988) reported $\delta^{18}O$ whole rock values for iron formation xenoliths of around 8.0 $\pm$ 0.6‰ with an identical range for the enclosing orthogneiss. The observed isotopic equilibration occuring over tens of metres was ascribed to large scale fluid exchange. As sample B4A was collected close to the xenoliths of M2A and M3A, the preservance of high $\delta^{18}O$(quartz) values in B4A suggests isotopic heterogeneity over the scale of ~20 metres.

Thin section examination and major and trace element geochemistry for sample G9C indicated that this sample could be a trondhjemitic gneiss (c.f. du Toit et al., 1983). If this is true, then its heavy $^{18}O/^{16}O$ ratio relative to Archaean orthogneisses (Barker et al., 1976; Longstaffe and Schwarcz, 1977) indicates that this sample is a paragneiss (S-type or sedimentary origin), or alternatively that this sample has exchanged oxygen with nearby metasediments (e.g. P8C). Because of the uncertain origin, this sample will not be considered further.

The charnockites (C4D and C8D) were originally considered to be a mafic phase of the Matok pluton (du Toit et al., 1983), but were subsequently classified as charnockites by van Reenen et al. (1987, 1988). For the Southern

Marginal Zone, van Reenen (1986), van Reenen and Hollister (1988) and van Reenen et al. (1988) proposed that the introduction of late metamorphic CO_2-rich fluids, derived from an underthrust greenstone succession resulted in extensive retrogression in the south of the terrane (south of the proposed orthopyroxene isograd) as well as in the formation of charnockites just north of the isograd. Such a metamorphic fluid would presumably derive its CO_2 from decarbonation of subducted carbonate sequences ($\delta^{18}O$ ~20‰ e.g. Valley and O'Neil, 1984) with only minor contributions from regionally metamorphosed lavas ($\delta^{18}O$ ~8 to 14‰ e.g. Smith, 1986). However, the value of 7.7‰ for the charnockites of this study falls into the range of $^{18}O/^{16}O$ ratios commonly quoted for Archaean granitoid plutons, which have $\delta^{18}O$ values of 7-9‰ (Barker et al., 1976; Longstaffe and Schwarcz, 1977; Baadsgaard et al., 1986). The charnockites of this study, therefore do not indicate extensive CO_2 streaming of an isotopically heavy fluid as the cause of charnockite formation as proposed by van Reenen (1988). In the Indian granulite facies terrane, Jiang et al. (1988) proposed that charnockitization occured under the influence of a mantle derived CO_2-rich fluid. A similar isotopic re-equilibration with a deep-seated magmatic fluid was proposed for the oxygen isotope compositions observed in the paragneisses of the Grenville province. However, the infiltration of a CO_2-rich fluid is not compatible with the general oxygen isotopic character observed for the other lithologies in the SMZ terrane and thus, is unlikely to have resulted in the charnockitization of samples C4D and C8D. Another possibility could be incipient charnockitization due to the formation of partial melts (e.g. Lamb and Valley, 1984).

V6D and V28C are pegmatitic rocks sampled close to the pelites of P5D and P29C respectively. Earlier (see section 4.4.2.2) it was argued that these pegmatitic rocks could represent partial melts derived from the pelitic rocks. This argument is further supported by their heavy isotopic signature (see Table 7.4). Considering that these coarse-grained granitic rocks largely consist of feldspar and quartz with minor amounts of garnet, and comparing the isotopic values to those obtained for the vein separates (V-P1D; V-P7D), then the near identical compositions suggest that these pegmatitic rocks were derived from partial melting of the metasediments. Both of these pegmatites were sampled only about 5 metres away from pelitic rocks (P29C and P5D). In the case of V28C and P29C, the pegmatite was found to be about 1.5‰ heavier, while in the case of V6D and P5D, the pegmatite is actually 1.1‰ lighter. If the simple modeling given above is appropriate, the 70% partial melting of a sediment will only result in a shift of about 0.2‰. Thus both pegmatitic rocks are out of isotopic equilibrium with the adjacent pelitic rocks, indicating that they were presumably derived by partial melting from metasediments elsewhere in the sequence. This isotopic disequilibrium, together with the absence of isotopic reversals in sample P5D, indicates isotopic heterogeneity on the scale of several metres.

7.4 Graphite $\delta^{13}C$ Analysis

Small flakes of graphite are present as trace amounts in several pelitic rocks and in the pegmatite V6D. In metasediments, the occurrence of graphite is often

regarded as syngenetic organic detritus that was converted to graphite during metamorphism (Grew, 1974; Hoefs and Frey, 1976; Weis et al., 1981). Based on textural relationships of the graphite within pelitic rocks (see Appendix A) such an interpretation is also true for the samples of this study.

The presence of graphite flakes within metamorphic rocks has an important control on the chemistry of the fluid phase present during metamorphism. French (1966) and Eugster and Skippen (1967) have demonstrated the presence of fluid species such as O_2, CO_2, CO, H_2 and CH_4 in equilibrium with both graphite and H_2O at various pressures and temperatures. The relative amounts of these species during the metamorphic history of rocks not only has important implications for the petrogenesis of granulite facies rocks (e.g. Newton et al., 1980; Lamb and Valley, 1984; Frost and Frost, 1987), but also for the stable isotope fractionations occuring in metamorphosed rocks (e.g. Stahl, 1974; Andreae, 1974; Hoefs and Frey, 1976; Vry et al., 1988; Jiang et al., 1988). In the following discussion, both of these implications will be illustrated by the graphite analysis of this study. Table 7.5 summarizes the $\delta^{13}C$ analysis for the rocks from this study. It also lists the expected $\delta^{13}C$ values of CO_2 that would be in equilibrium with graphite at the relevant peak metamorphic temperatures. For analytical procedures the reader is referred to Chapter 2.

From Table 7.5 it can be seen that the $\delta^{13}C$ values of graphite separated from the metasediments (prefixed P in Table 7.5) range from -9.1 to -15.2‰, relative to PDB. These values are much heavier than would be expected if the graphite was of biogenic origin (~-25‰; e.g. Valley, 1986). However, Barker and Friedman (1969), Andreae (1974) and Hoefs and Frey (1976) also reported

shifts towards heavier $\delta^{13}C$ values with increasing metamorphic grades of the metasediments. The study of Hoefs and Frey (1976) showed that values of $\delta^{13}C$ ranged from about -25‰ in unmetamorphosed sediments up to values of around -11‰ in pelitic rocks metamorphosed at temperatures of 500 to 550°C. These latter values are similar to those observed for the SMZ rocks (peak temperatures $\geq$ 600°C). The enrichment observed in high-grade rocks may be caused by the loss of volatile hydrocarbons (e.g. Stahl, 1974). Eugster and Skippen (1967) calculated the mole percent compositions of gas species coexisting with both graphite and H_2O at quartz-fayalite-magnetite buffering. They determined that for temperatures up to about 500°C, CH_4 is the dominant carbon species. Degassing of CH_4 during prograde metamorphism would therefore result in ^{13}C enrichments in residual graphites (see Friedman and O'Neil, 1977). The above information can be extended to explain the heavy $\delta^{13}C$ value observed for the graphite in the pegmatite, if it is accepted that the pegmatite is a partial melt derived from pelitic rocks at temperatures higher than 500°C.

An alternative explanation for isotopically heavy graphite in granulite facies rocks is the influx of mantle derived CO_2 with $\delta^{13}C$ values of around -7‰ (e.g. Katz, 1987; Jackson et al., 1988). Such pervasive flooding of CO_2 has also been proposed to cause granulite facies metamorphism (e.g. Newton et al., 1980; Jackson et al., 1988; Jiang et al., 1988). While CO_2, having $\delta^{13}C$ values of around -7‰ could be in equilibrium with the graphite in some of these sediments, a large scale influx of CO_2 is discounted as the cause of granulitization in the SMZ rocks for the following reasons. Firstly, the graphite in sample P50C, which is an orthoamphibole gneiss, has a

similar composition to the graphite in the granulites (Table 7.5). Secondly, the graphites of P-A and P-B were hand-picked in the field from a pelitic rock occuring only about 30 metres away from sample P5D, yet their graphite is 5 to 6‰ heavier than that of P5D. Such small-scale isotopic heterogeneity would not be expected for pervasive infiltration of mantle derived CO_2. Even if only small amounts of CO_2 were introduced, then these would still be expected to be in equilibrium with the graphite, as the graphite is only a trace component in most of the rocks. Lastly, values of $\delta^{13}C$ for CO_2 in equilibrium with the graphite as shown in Table 7.5 range from -7.6‰ up to 1.9‰, a range that would not be consistent with mantle $\delta^{13}C$ values for CO_2 (commonly between -5 to -10‰; Kyser, 1986)

As a corollary to the above, the presence of the isotopically heavy, syngenetic graphite may be interpreted as indicating that metamorphism of the SMZ rocks occured under conditions that were more reducing than quartz-fayalite-magnetite buffering. Similar conditions have been proposed for granulite facies terranes elsewhere (e.g. Lamb and Valley, 1984).

7.5 Conclusions

From the previous discussions on the whole rock and mineral stable isotopic compositions, the following conclusions can be made.

1. The increasing sequence in average $\delta^{18}O$ values for the different lithologies of the Southern Marginal Zone as analyzed in this study can be

given as ultramafics < mafics < pelitic rocks (Figure 7.1). This sequence is similar to that expected for unmetamorphosed ultramafic to mafic igneous rocks and sedimentary rocks.

2. While 1 above is true in general, certain samples from both the ultramafic and mafic rock groups indicate the influx, and in some cases the equilibration with, isotopically heavy fluids ($\delta^{18}O(H_2O)$ ~9-11‰). The similarity in $^{18}O/^{16}O$ ratios between plagioclase and secondary quartz in some mafic rocks and those in pelitic rocks suggests a metasedimentary origin of these fluids.

3. In contrast to the mineral $\delta^{18}O$ reversals in some mafic and ultramafic rocks, the general absence of mineral isotopic reversals in the pelitic rocks, does not support the influx of, and partial equilibration with a fluid extraneous to these rocks.

4. $\delta^{18}O$ values for concordant vein minerals separated from the pelitic rocks are consistent with these veins representing partial melts derived from the immediate surrounding sediment.

5. Pegmatitic rocks analyzed have $\delta^{18}O$ signatures consistent with those expected for partial melts derived from metasediments, but they can be out of isotopic equilibrium with the immediately adjacent metasediment.

6. Preservation of the isotopic composition of a banded iron formation, occuring only several metres from mafic lithologies, indicates isotopic heterogeneity over the scale of ~20 metres.

7. Charnockitic rocks indicate $\delta^{18}O$ signatures similar to those of plutonic igneous rocks. If charnockitization was caused by an influx of CO_2-rich fluids, then these fluids were isotopically distinct from those mentioned in 2 above, as well as to fluids derived from the decarbonation of underthrust greenstone successions (e.g. van Reenen, 1988).

8. A large scale influx of a CO_2-rich mantle derived fluid is not consistent with the $\delta^{13}C$ signatures of graphites in pelitic and pegmatitic rocks. Furthermore $\delta^{13}C$ analysis of graphites suggests isotopic heterogeneity over the scale of ~30 metres.

From points 1 to 8 above one can conclude that the SMZ rocks are not characterized by the presence of one fluid which pervasively exchanged with the various different lithologies. Instead, closed system metamorphism, where minerals, melts and possible fluid phases were in isotopic equilibrium is indicated. However, in some localized sections, mafic and ultramafic rocks may have equilibrated with a fluid of metasedimentary origin. The mechanism proposed for such localized re-equilibration is the extraction of a partial melt from the metasediments and crystallization of this melt elsewhere in the metamorphic pile. Upon crystallization, the fluids incorporated into such melts during the melting stages, will be released into immediately adjacent rocks. Isotopic re-equilibration in the infiltrated rocks will then be a function of the fluid/rock ratio, the temperature of infiltration and the isotopic difference between the initial rock and the infiltrating fluid.

An alternative possibility is that the SMZ lithologies have equilibrated with the surrounding Baviaanskloof gneisses. However, the contrasting behaviour

between the metasedimentary rocks (including the banded iron formation) and the mafic and ultramafic rocks, in addition to the localized phenomena of oxygen isotopic re-equilibration would argue against such an equilibration.

CHAPTER 8: STABLE ISOTOPE MINERAL FRACTIONATIONS AND THERMOMETRY

8.1 Introduction

The subject of stable isotope geothermometry was first introduced by Urey (1947), who realized that isotope fractionations amongst chemical phases are temperature dependant. Since then, many attempts have been made to calibrate isotopic fractionations between mineral phases relative to temperature in various experimental and/or natural systems (e.g. McCrea, 1950; Anderson et al., 1971; Matthews et al., 1983; Matsuhisia et al., 1979; Clayton et al., 1989). The great potential of oxygen isotope thermometry lies in the fact that analysis of three or more cogenetic minerals can provide two or more independent temperature estimates if their calibration curves are known. This fact, coupled with the relatively small analytical errors involved in the determination of fractionation factors (see Appendix D for definition) amongst most minerals, and the small pressure effects on oxygen isotopic fractionations (even at high pressures effects are less than analytical uncertainty - Clayton, 1981; Matthews et al., 1983; Ewald, 1985), allows for the application of oxygen isotope thermometry even in high-grade metamorphic and igneous rocks. However, considerable disagreements exist between the temperature calibrations based on experimental mineral equilibrations in hydrous systems (e.g. Matsuhisia et al., 1979; Matthews et al., 1983) and the empirical calibrations of Bottinga and Javoy (1973, 1975) where theoretical considerations were extended to

fractionation factors measured in natural assemblages. A problem with the empirical calibrations is that the mineral fractionations as measured may not reflect true isotopic equilibration at peak temperatures, but, because of some retrograde re-equilibration, may reflect temperatures lower than peak temperatures (e.g. Deines, 1977, Matthews et al., 1983). More recent experimental mineral equilibrations have been performed in anhydrous systems where calcite is used as an exchange phase (Mayeda et al., 1986; Clayton et al., 1989). The results of these experiments in the quartz-albite-anorthite-calcite system give silicate-pair fractionations which are in good agreement with those given by Bottinga and Javoy (1973; 1975), but show significant differences to the experiments performed in hydrous systems. It is suggested that this discrepancy is related to a lack of knowledge regarding the oxygen partitioning factors in water (Clayton et al., 1989). However, even though the absolute temperatures predicted by the various temperature calibrations may vary, general agreement exists in terms of relative ^{18}O enrichment in coexisting minerals, and in the inverse relationship of the magnitude of the fractionation factor to increasing temperatures (see Appendix D). Therefore, regardless of the absolute temperatures obtained from isotopic fractionations of coexisting minerals, some meaningful geological interpretations may be obtained from these mineral fractionations.

The existence of isotopic equilibrium amongst coexisting mineral and fluid phases is of critical importance to the interpretations relating to the petrogenesis of rocks. In this Chapter oxygen isotope equilibration amongst phases will be discussed in the light of both open system and closed system

isotopic exchange (see also Gregory and Criss, 1986). A closed system is here defined as a system where isotopic interactions may occur between minerals and static fluid phases, all of which occur in constant relative proportions until final isotopic closures of all phases. An open system may be defined as a system where isotopic interactions occur between coexisting minerals and an infiltrating fluid. The extent of such interactions is a complex function of the timescales of infiltration relative to kinetic diffusion rates within and amongst minerals, the temperatures involved and the fluid/rock ratios.

8.2 Oxygen Isotope Geothermometry for the SMZ Rocks

A criteria commonly used to establish whether or not a system has attained isotopic equilibrium is the temperature concordancy of at least two independent mineral pairs within a rock (e.g. Bottinga and Javoy, 1975; Deines, 1977). If such concordancy occurs, and if the resultant temperature is in agreement with both the mineral paragenesis and cation mineral geothermometers in the rocks, then the given stable isotope temperature may be geologically meaningful. In view of the disagreements between the existing oxygen isotopic calibrations, the temperatures obtained from one mineral pair may differ significantly from those calculated for another mineral pair. For the rocks under consideration, both the empirical calibrations of Bottinga and Javoy (1975) and, where possible, the experimental calibrations of Matthews et al. (1983) were used. Temperatures calculated from the recent anhydrous calibrations by Clayton et al., (1989) were found to be consistently 7-10°C lower than those calculated using Bottinga and

Javoy (1975) for the quartz-plagioclase pairs considered. As this is well within the errors quoted for the quartz-plagioclase pair by Bottinga and Javoy (1975; ± 36°C at 500°C; Appendix D), the temperatures calculated by using Clayton et al., (1989) are not discussed further. For a definition of the terminology, the equations used and the approximate analytical errors for the thermometry, the reader is referred to Appendix D. Oxygen isotope temperatures calculated are given in Tables 8.1 to 8.3.

An inspection of Tables 8.1 to 8.3 reveals that the experimental calibrations of Matthews et al. (1983) give temperatures that are consistently lower than those of Bottinga and Javoy (1975), except for the quartz-magnetite pairs where temperatures are somewhat higher. Thus, for the quartz-pyroxene pair temperatures are lower by about 110°C, for the quartz-plagioclase pairs by about 160°C, for the plagioclase-pyroxene by about 50 to 80°C, while about 35°C higher for quartz-magnetite. Similar temperature differences between the experimental and empirical methods have been reported by other workers (e.g. Clayton, 1981; Huebner et al., 1986; Sharp et al., 1988). A possible explanation is that this disagreement is caused by the different effects of water on the kinetic exchange rates and behaviour of minerals (compare "wet" and "dry" systems of Giletti et al. (1978) and Elphick et al. (1988) respectively for anorthite). Thus the hydrothermal experiments of Matthews et al. (1983) may not be applicable to essentially anhydrous, high-grade metamorphic or igneous rocks (Clayton et al., 1989; Bottinga and Javoy, 1988; Matthews, 1988). Owing to the lack of any other experimental calibration for the range of minerals constituting the rocks of this study, the empirical calibrations of Bottinga and

Javoy (1975) are used in the subsequent discussions. It is important to note though, that the temperature discordancy as shown by quartz-pyroxene relative to the quartz-plagioclase pairs is present for both the empirical calibration of Bottinga and Javoy (1975) and the experimental calibration of Matthews et al. (1983). The following interpretations on relative mineral-pair temperatures are thus not affected by the choice of calibration.

8.2.1 Oxygen Isotope Thermometry of the Pelitic Rocks

The quartz-mineral temperatures of the pelitic rocks (Table 8.1) are summarized in a temperature histogram in Figure 8.1. From Table 8.1 and Figure 8.1 it can be deduced that for most of the rocks analyzed, the quartz-plagioclase, quartz-biotite and plagioclase-biotite equilibration temperatures are concordant to within their estimated relative errors (see also Appendix D). Exceptions are P34C and P3D where the quartz-plagioclase temperatures are significantly lower than the quartz-biotite temperatures, which in turn are significantly lower than the plagioclase-biotite temperatures. Using temperature concordancy as a test of equilibration amongst the mineral species, it could be stated that quartz, plagioclase and biotite are generally in isotopic equilibrium.

The quartz-orthopyroxene, quartz-amphibole and quartz-garnet temperatures are consecutively higher than the quartz-plagioclase or quartz-biotite temperatures. In the case of the quartz-amphibole and quartz-garnet pairs the equilibration temperatures are indistinguishable for the three rocks in which quartz, amphibole and garnet were analyzed. The quartz-orthopyroxene pair,

however, is significantly different to the quartz-garnet pair in three out of the four rocks that were analyzed for coexisting quartz, garnet and orthopyroxene. Furthermore, the quartz-orthopyroxene temperatures are also significantly different to the quartz-biotite or quartz-plagioclase temperatures. Thus, for the quartz-mineral fractionations, the following sequence of increasing apparent equilibration temperatures are observed:

quartz-plagioclase $\leq$ quartz-biotite < quartz-orthopyroxene < quartz-amphibole $\simeq$ quartz-garnet.

As it is practically impossible for the quartz to be in isotopic equilibrium with garnet and orthoamphibole at high temperatures, as well as being in isotopic equilibrium with plagioclase and biotite at lower temperatures, disequilibrium of at least some of the mineral phases is indicated.

In addition to the above, it can be seen (Table 8.1) that no significant temperature differences exist between any of the different pelitic rock groups. This is illustrated in Figure 8.2 where the quartz-garnet temperatures are shown next to the sample positions. In agreement with the results from the garnet-biotite cation geothermometry (Section 6.4.2.2.1 - Fig. 6.1), no significant temperature gradient appears to be present. The same is also true for the quartz-biotite or quartz-plagioclase oxygen isotope thermometry of these rocks (Table 8.1). It is interesting to note though, that the quartz-garnet (and quartz-orthoamphibole) apparent oxygen isotope equilibration temperature shows an identical value to the peak metamorphic temperatures derived from the cation geothermometry of group 1, 2, 3 and 4 rocks (c.f. 736 $\pm$ 52°C for oxygen

isotope thermometry with 730 $\pm$ 65°C for cation geothermometry - Chapter 6). If the cation temperature is taken to represent peak metamorphic conditions, then the apparent isotope equilibration temperatures of the quartz-garnet (and quartz-orthoamphibole) pairs may represent a true metamorphic temperature. The validity of this will be discussed in more detail in a later section (Section 9.2) where the cation and anion temperatures will be compared in the light of ionic diffusion processes.

8.2.2 Oxygen Isotope Thermometry of the Mafic Rocks

Apparent isotope equilibration temperatures of the plagioclase-pyroxene and plagioclase-amphibole pairs in the mafic rocks are found to scatter more widely when compared to the quartz-mineral isotope equilibration temperatures in the pelitic rocks. In part, this scattering of temperature values could be a function of the smaller fractionation between the minerals in each pair. Thus relatively small errors in $\delta^{18}O$ ($\pm$ 0.1) lead to considerable differences in temperatures (see Appendix D). The range in oxygen isotope temperatures obtained for the plagioclase-amphibole mineral pair is found to vary considerably (526 to 832°C, Table 8.2), which is in contrast to the temperature ranges for any one of the quartz-mineral pairs in the pelitic rocks. However, the temperatures obtained for the plagioclase-pyroxene pairs in the pelitic rocks (not shown) were found to range from 628 to 914°C, which may suggest that the plagioclase in both the mafic and the pelitic rocks has changed its isotopic composition to varying degrees. Thus, in general, oxygen isotope disequilibration is indicated for the minerals in the mafic rocks.

8.2.3 Oxygen Isotope Thermometry of Various Other Rocks

By analogy to the apparent isotope equilibration temperatures in the pelitic and mafic rocks, the isotope temperatures listed for the various other rocks in Table 8.3 may reflect preferential isotopic re-equilibration of some phases relative to others. A sample of particular interest is the coarse-grained, pegmatitic rock of V6D, which yields a fairly high quartz-garnet temperature and a significantly lower quartz-plagioclase temperature. While the difference between the two mineral pairs in this rock is similar to that observed for the pelitic rocks above, the temperatures are both lower when compared to equivalent pairs in the pelitic rocks. Assuming that this sample may represent a partial melt derived from the pelites, then the low oxygen isotope temperatures in V6D may be a function of the cooling rate. Andersen et al. (1971) reported similar differences in apparent oxygen isotope equilibration temperatures between volcanic and plutonic igneous rocks.

In summary, the range of temperatures obtained for various mineral-mineral pairs in the rocks analyzed, irrespective of the temperature calibration used, suggests that at least some of the minerals are not in isotopic equilibrium. Possible causes for this will be considered below.

8.3 Factors Affecting Mineral Fractionations

The oxygen isotope disequilibrium which is implied by the low apparent isotope

temperatures could have been caused by any of the following:

1. The temperature calibrations used are incorrect and, even though the observed mineral fractionations are actually representative of peak metamorphic conditions, some lower temperatures are calculated.

2. Open system isotopic exchange where a fluid or melt phase infiltrated the rocks and exchanged isotopically with some but not all the phases. In this case, the relative oxygen diffusion rates within the minerals become important.

3. Closed system isotopic diffusion amongst the phases present and the recorded temperatures are a function of the relative isotopic closure (for a definition thereof see below) of the minerals concerned.

In view of the more recent calibration experiments (Clayton et al., 1989) point 1 above is possibly correct in the sense that the calculated temperatures may not be representative of absolute metamorphic temperatures. However, as discussed above, irrespective of the temperature calibration used (Bottinga and Javoy, 1975 or Matthews et al., 1983), the mineral-mineral fractionation factors do not appear to be in equilibrium. This is also true if the theoretical scale of Kieffer (1982) is used, where the average quartz-garnet fractionation of 2.9‰ yields temperatures in excess of ~630°C, whereas the quartz-plagioclase average fractionation of 1.9‰ yields significantly lower temperatures (~230 to 530°C for albite and anorthite respectively - Kieffer, 1982 - Figure 8 p.840). For the more recent experimental calibration Clayton et al. (1989) reported a general agreement with the theoretical calculations by

Kieffer (1982) as well as with the empirical calibrations of Bottinga and Javoy (1973, 1975), indicating that the observed disequilibrium mineral-pair fractionation differences will not be eliminated by the choice of a new set of calibrations. Furthermore, the range in temperatures indicated by one mineral-pair in the mafic rocks (e.g. plagioclase-hornblende), in combination with the isotopic reversals shown by some of the mafic rocks (see previous section) imply that some disequilibrium must be caused by factors other than incorrect calibrations. Points 2 and 3 above will be discussed below.

In the following sections, the isotopic disequilibration will be ascribed to retrogressive processes. In view of the fact that isotopic diffusion increases with increasing temperature, and that diffusion is enhanced by fluid presence (e.g. Cole and Ohmoto, 1986), all prograde isotopic changes to the rock system will tend to be equilibrated at peak metamorphic conditions. Observations such as those by Hoernes and Hoffer (1979) where biotite (or any other mineral) is considered to have isotopically closed upon its prograde crystallization, is not supported in this study. Microprobe studies of some mineral phases in these rocks (see Chapters 5, 6) indicate that chemical equilibrium has generally been attained at peak metamorphic conditions. Unless oxygen shows diffusion rates that are considerably slower than those of cations, oxygen isotope equilibrium was also attained at peak metamorphism.

8.3.1 Open System versus Closed System Isotopic Exchange

Open system exchange could involve the introduction of a fluid or melt phase

during metamorphism. In the case of the pelitic rocks, the involvement of melt and/or fluid phases is indicated by the migmatitic character of the rocks. The concordant nature of most of these small felsic bands and lenticles suggests that these melt segregations were locally derived prior to or during peak deformation (du Toit et al., 1983). However, some larger felsic bodies and veins can also be found crosscutting the general foliation and thus such bodies were presumably introduced after deformation. In the case of the mafic rocks, discordant felsic veins, and enclosing felsic material (Fig. 3.2) provide evidence for post peak-deformation introduction of melts. According to du Toit et al. (1983), the intense fabric forming deformation occured prior to or coeval with peak metamorphism. Concordant felsic segregations may therefore be expected to equilibrate with the surrounding rock. Such equilibration was reported earlier from an analysis of the isotopic composition of veins separated from P1D and P7D. The larger felsic bodies (e.g. pegmatites V6D and V28C) indicated isotopic compositions that were significantly different from those of the adjacent (~5 metres) pelites, suggesting that such pegmatites did not significantly influence the isotopic composition of the pelites over the scale of 5 metres or more. In contrast, some of the mafic rocks (e.g. M3C, M37C) showed isotopic reversals where pyroxene and hornblende were of similar isotopic composition as the plagioclase. For these rocks, the analysis of quartz from separated veins suggests the involvement of isotopically heavy fluids (>9‰). Other mafic rocks such as M2A, M3A and M5A, which are xenoliths found enclosed by felsic segregation material or grey migmatized gneisses may also suggest influence of fluids on their isotopic mineral compositions.

To test the importance of open versus closed system isotopic exchange some δ-δ plots for the rocks under consideration are shown in Figure 8.3. Also shown in these diagrams are lines of constant isotopic fractionation and hence constant temperature (see also Gregory and Criss, 1986). If rocks were subjected to identical temperature conditions, then the same mineral-pairs in different samples of these rocks should theoretically show the same isotopic fractionation (Δ) and therefore should all fall on the same isotherm. The position of mineral pairs along this line is controlled by the whole rock $\delta^{18}O$ and the modal proportions of minerals in the rock. If trends formed by the minerals in a δ-δ plot are found to deviate from the isothermal lines of slope 45°, then open system behaviour is indicated (Gregory and Criss, 1986). In such circumstances, the slope of the trend lines are a function of the mineral-fluid exchange rates, the fluid isotopic composition, fluid-rock ratios and temperature of exchange.

For the rocks of this study, the most prominent features from Figure 8.3 are as follows:

1. In the δ-δ plots for the pelitic rocks, the trends formed by the high-grade rocks (groups 3, 4 and 5; see Chapter 3) approximate 45° slopes.

2. The group 2 rocks also approximate 45° slopes in the quartz-garnet and quartz-plagioclase plots, but minor deviations can be recognized in quartz-biotite and plagioclase-biotite plots.

3. In the quartz-garnet and quartz-plagioclase plots, the trend formed by group 3, 4 and 5 rocks coincides with that for the group 2 rocks,

suggesting the same mineral fractionations (i.e. temperatures).

4. For the mafic rocks a large scatter in values occurs and no correlation exists.

For the pelitic rocks, the linearity in trends in combination with a parallelism of trends to lines of constant fractionation (isotherms), suggests closed system behaviour. The alternative explanation, that such trends indicate open system behaviour, but where the exchange rates of the minerals with a fluid are identical, can be discounted on experimental grounds. Experiments have shown that the isotope diffusion rates of various minerals in the presence of fluids differ significantly (e.g. Giletti and Anderson, 1977; Giletti et al., 1978; Freer and Dennis, 1982; Matthews et al., 1983; Farver and Giletti, 1985).

The minor deviation from parallelism as shown by group 2 rocks in quartz-biotite and plagioclase-biotite plots, could be a function of the small sample population, particularly as the orientation of the trend is largely controlled by sample P34C which shows considerably heavier $\delta^{18}O$ values compared to other group 2 rocks. This sample also shows discordancy of quartz-biotite, quartz-plagioclase and plagioclase-biotite equilibrium temperatures implying that at least one of the three mineral phases is not in equilibrium with the others. From the δ-δ plots, the most likely phase to be out of equilibrium in this sample is biotite.

The coincidence of the quartz-garnet trends and of the quartz-plagioclase trends for the group 3, 4 and 5 rocks relative to group 2 rocks is surprising, as it would suggest similar equilibrium temperatures for both rock groups.

The δ-δ plot of hornblende versus plagioclase for the mafic rocks shows a considerable scatter, even if the samples with isotopic reversals are omitted (i.e. M3C and M37C). If all the rocks were of similar isotopic composition (e.g. ~6‰) prior to metamorphism and if a fluid of homogeneous isotopic composition infiltrated these rocks, then, by analogy with the hydrothermal alteration of other natural rock systems, a nearly linear array of points would be expected (Gregory, 1986; Gregory and Criss, 1986). Such a linear array of positive slope is produced by changes in fluid/rock ratio only. The slope of the array is not 45° unless the exchange rates of the minerals plotted are identical. The wide scatter of data for the SMZ mafics may thus be related to any of the following:

a) the isotopic composition of the infiltrating fluid was not constant, b) different events of fluid-rock interactions, c) the rocks were not of the same isotopic composition prior to metamorphism, d) it is a function of the proximity of rocks to major conduits of fluid flow, that is some rocks remained unaffected while others were flooded by the fluid, e) a combination of any of the above.

Samples such as M3C and M37C suggest large fluid/rock ratios and exchange with a fluid of similar isotopic composition ($\delta^{18}O(H_2O)$ ~ 9 to 10‰). Such a fluid composition was also indicated by quartz separated from sample M52C. Therefore, if it is assumed that the isotopic composition of the infiltrating fluid is similar for all the rocks in general then a) above appears unlikely. The wide range in apparent isotopic equilibration temperatures in combination with the range in whole rock isotopic composition does not allow for any further refinement of the effects of factors b) to e) above.

In summary, while open system behaviour is indicated by at least some of the mafic rocks, pelitic rocks indicate an apparent closed system behaviour. As a corollary, the range in apparent isotopic equilibration temperatures for the mafic rocks may be explained by open system behaviour for some mafic rocks. However, this is not the case for the pelitic rocks and an alternative explanation is needed to explain the temperature discordancy in the pelitic rocks.

8.3.2 Closed-System Isotopic Re-equilibration for SMZ Rocks

The oxygen isotopic fractionations of the quartz-mineral pairs suggested the following decreasing apparent temperature sequence: quartz-garnet $\simeq$ quartz-amphibole > quartz-orthopyroxene > quartz-biotite $\geq$ quartz-plagioclase. This implies isotopic disequilibration between at least some of the minerals coexisting in these rocks. Two possible closed-system mechanisms could account for the observed isotopic disequilibration:

1. Recrystallization of some of the minerals during retrogression, where isotopic fractionations between the recrystallized minerals record the final crystallization temperature.

2. Contemporaneous crystallization of all minerals, but isotopic re-setting occurs by intercrystal diffusion of oxygen amongst the minerals during retrogression. The recorded mineral fractionation between minerals is then a function of relative oxygen isotopic closure between the phases.

In outcrop, the pelitic rocks are characterized by a coarse-grained gneissic to

migmatitic appearance (see Chapter 3). This character is defined by the presence of felsic pods, lenses and veins both of concordant and discordant nature. On thin section scale, felsic lenses are recognized by relatively large, unstrained quartz and plagioclase crystals (Appendix A), occasionally surrounding garnet. These textures support the occurrence of melting reactions as described in Chapter 3, where the breakdown of biotite, quartz and plagioclase produces garnet, orthopyroxene, cordierite and orthoamphibole together with some melt. The melt consists predominantly of quartz and feldspar components (see also Chapter 4) and upon retrogressive cooling, these phases would crystallize. The quartz-plagioclase isotopic fractionation could then, theoretically, reflect crystallization temperatures of the melts produced during prograde metamorphism, in accordance with 1 above. If the product phases of melting such as garnet, orthoamphibole and orthopyroxene are assumed to retain their isotopic compositions at the time of their formation at peak conditions, then the quartz-garnet, quartz-orthoamphibole and quartz-orthopyroxene fractionations would certainly not represent peak metamorphic temperatures. By analogy to the product phases, the $\delta^{18}O$ values of the biotite may have been fixed during the melting reaction. The quartz-biotite fractionation would then also not reflect peak metamorphic conditions.

The oxygen isotope analysis of quartz and plagioclase separated from veins occuring within the pelites P1D and P7D (see Table 7.3), revealed that they were of identical composition to the quartz and plagioclase within the host rocks. Implications of this are twofold. Firstly, it implies that the quartz and plagioclase from the rock is in isotopic equilibrium with that from the veins.

Conversely, it suggests that the melt, whose major components are quartz and plagioclase (see Chapter 4), is isotopically equivalent to the quartz and plagioclase from which it was derived. Important points emerging are that either all the quartz and plagioclase in these rocks have crystallized from a melt, or the quartz and plagioclase now forming the veins and larger felsic lenses, were derived from melts, but re-equilibrated isotopically with the rock-quartz and rock-plagioclase during retrograde cooling. Such re-equilibration may occur via intercrystal diffusion. In this regard it is interesting to note the good agreement between the quartz-biotite and the quartz-plagioclase temperatures. Texturally, there is no indication of either retrogressive biotite growth or of crystallization of biotite from a melt phase. Therefore, the above agreement in quartz-biotite and quartz-plagioclase temperatures points towards intercrystalline diffusion amongst quartz, biotite and plagioclase, possibly via fluids released from the melts during crystallization. Conversely, the disagreement between the quartz-garnet, quartz-orthoamphibole and quartz-orthopyroxene temperatures implies that the garnet, orthoamphibole and orthopyroxene did not exchange retrogressively with the quartz. This will be examined further below.

8.3.2.1 Closed System Oxygen Diffusion

8.3.2.1.1 Exchange Mechanisms in Wet and Dry Systems

Most of the experimental studies of oxygen diffusion in minerals have been

performed in the presence of water (e.g. Giletti and Anderson, 1975; Giletti et al., 1978; Freer and Dennis, 1982; Matthews et al., 1983; Dennis 1984; Giletti and Yund, 1984; Farver and Giletti, 1985; Elphick et al., 1986; Giletti and Hess, 1988; Farver, 1989). Diffusion in the hydrothermal systems is characterized by low activation energies and comparatively high diffusion rates (Freer and Dennis, 1982; Cole and Ohmoto, 1986) both of which will result in relatively fast isotopic re-equilibration. In contrast, experiments performed under essentially dry conditions, where O_2 or CO_2 are used as exchange media for oxygen (e.g. Haul and Dumbgen, 1962; Muehlenbachs and Kushiro, 1974; Elphick et al., 1988), are characterized by high activation energies and low diffusion rates (Freer and Dennis, 1982; Cole and Ohmoto, 1986), which would tend to inhibit oxygen isotope equilibration. In hydrothermal systems oxygen isotope exchange between minerals and water can essentially occur via three mechanisms: 1) by chemical reaction where an alteration assemblage is produced, 2) by solution - precipitation mechanisms where small amounts of fluids may progress along a dissolution front within the mineral and 3) by volume diffusion where the crystal remains completely solidified during oxygen exchange (Matthews et al., 1983; Cole et al., 1983; Giletti, 1985). The third alternative is the dominant process for isotopic exchange in anhydrous systems and is also the mechanism showing the slowest isotopic exchange rate (Matthews et al., 1983; Cole et al., 1983).

For the rocks of this study the first of these exchange mechanisms may be discounted as the mineral phases in the pelitic rocks are generally unaltered (Appendix A). The textural appearance of quartz and plagioclase either as small

clustered aggregates or as large unstrained grains is indicative of recrystallization processes (Hobbs, 1968). According to the results of Hobbs (1981) the presence of OH-molecules in quartz will greatly enhance both the recrystallization and the oxygen diffusivity in such crystals (see also Kerrich et al., 1977). The oxygen isotope exchange in quartz and feldspar can therefore be approximated by a mechanism similar to 2 above and, if diffusion is sufficiently fast, particularly if small amounts of fluid are present, it may explain the low quartz-plagioclase apparent equilibration temperatures. Biotite, however, still preserves pre- to synmetamorphic deformation kinks and texturally does not indicate any recrystallization. This would argue in favour of volume diffusion processes for the biotite. By analogy to the biotite, the textural appearance of the garnet, orthopyroxene and orthoamphibole suggests volume diffusion processes, if any diffusion has occured at all for these minerals.

8.3.2.1.2 Pressure Effects on Diffusion

The effect of pressure on the diffusion rates of oxygen in minerals is somewhat debatable. While Yund and Anderson (1978) observed a large increase of oxygen diffusivity in feldspar with increasing pressure, subsequent work by Freer and Dennis (1982), also on feldspar, negated any pressure effect on diffusivity. Similar inconsistencies relating to pressure effects in the quartz-water systems have been reported by Giletti and Yund (1984) and Dennis (1984). This discrepancy has subsequently been explained by Ewald (1985) and Cole and Ohmoto (1986) as being a function of reaction mechanism, that is, surface reaction or volume diffusion, which in turn critically depends on the grain size and

crystallography of the chosen mineral grains. The surface reaction mechanism can be equated to a combination of mechanisms 1 and 2 above (Cole et al., 1983). It can be concluded that while pressure effects may be important during surface reaction mechanisms, this is not the case for volume diffusion. As volume diffusion may represent the most important exchange mechanism for garnet, orthopyroxene, orthoamphibole and biotite, pressure effects are not considered important for these high-grade rocks.

8.3.2.1.3 Temperature and Crystallographic Effects on Diffusion

Temperature effects on oxygen diffusion in minerals are shown in Figure 8.4. Good experimental agreement exists for both dry and wet systems, which show that the oxygen diffusion rate of minerals is dependant on temperature according to the Arrhenius equation :

$$D = D_o \, e^{(E/RT)} \qquad (8.1)$$

where D is the diffusion coefficient (m^2/sec), D_o is the pre-exponential factor, E is the activation energy (kJ/mol of oxygen), R is the gas constant and T is the absolute temperature (e.g. Cole and Ohmoto, 1986). Thus experimental determination of E and D_o for a mineral (see references in Fig. 8.4), allows the calculation of the diffusion coefficient at a given temperature. Figure 8.4 predicts oxygen diffusion rates for hydrothermal systems in the following increasing order:

garnet < diopside < hornblende < phlogopite (~magnetite) $\leq$ quartz < feldspar.

Experiments by Farver and Giletti (1985) on the oxygen diffusion in three compositionally different amphiboles indicated that diffusion rates vary greatly for different crystallographic directions. In all cases diffusion parallel to the c-crystallographic direction was found to be an order of magnitude faster than for other crystallographic directions. However, for the same crystallographic direction in the three chemically different amphiboles, little or no significant differences in diffusion rates were noticed. Due to the similarity in the crystallographic structure between the orthorhombic and monoclinic amphiboles, particularly in the c-crystallographic direction (Deer et al., 1966), the diffusion rates of the monoclinic amphiboles are here used as an estimate to those for the orthorhombic amphiboles. Extending similar arguments to pyroxenes, then oxygen diffusion in diopside could be taken as an estimate to that for orthopyroxene. A crystallographic control on oxygen diffusion is also shown by quartz and diopside, where Giletti and Yund (1984) and Farver (1989) respectively observed diffusion rates parallel to the c-axis to be about 2 orders of magnitude faster than those normal to the c-axis (Fig. 8.4). In addition the change in log D versus T slope between alpha and beta quartz (Fig. 8.4) is also a crystallographic control. In amphibole, diopside and quartz the dominant crystallographic direction for oxygen diffusion would be parallel to the c-axis.

The diffusion rate for phlogopite by analogy to the above observations, can be used as an approximation for biotite. While the technique used to determine the oxygen diffusion rate in phlogopite was that of bulk isotopic exchange between the crystal and an ^{18}O enriched fluid, subsequent results on the

oxygen diffusion rates in several micas using both the ion microprobe and the bulk exchange techniques (Fortier and Giletti, 1987) confirmed the earlier results (Giletti and Anderson, 1975) for temperatures of around 700°C. For temperatures lower than this a divergence of activation energies between the micas is observed and, in increasing order, these are biotite, muscovite, phlogopite (Fortier and Giletti, 1987). Below 700°C the oxygen diffusion rate in biotite would thus be faster than that in phlogopite, that is, approaching the diffusional values observed for quartz parallel to the c-axis. Thus, the use of oxygen diffusion rates from phlogopite will provide a minimum diffusion rate estimate for the biotite only.

Taking the determinations of oxygen diffusion rates for monoclinic amphiboles, diopside and phlogopite as rough estimates for the orthorhombic amphiboles, orthopyroxene and biotite respectively, then the order of increasing diffusion rates for the minerals in the pelitic rocks becomes garnet, orthopyroxene, orthoamphibole, biotite, quartz, feldspar.

8.3.2.1.4 Closure to Isotopic Exchange

In theory, given enough time, all the minerals will eventually re-equilibrate with each other chemically and isotopically. In natural systems however, this is not the case as, upon cooling, the mobility of elements is greatly reduced until such time where the element becomes physically immobile. Ideally, this represents a point in time where the mineral may be considered to be closed to subsequent diffusion. Using the definition of Dodson (1973), then such an

idealized point occurs where the time constant involved for diffusion becomes infinitely large compared to the diffusion rate. As the diffusion rate of minerals is exponentially dependant on temperature, the temperature range at which minerals become closed is small and may be calculated by the following iterative equation (Dodson, 1973):

$$T_c = E/R * 1/[\ln (- ART_c^2 D_o / a^2 E\ dT/dt)] \qquad (8.2),$$

where T_c is the closure temperature; A is the diffusional anisotropy parameter (A = 55 for a sphere (feldspars, magnetite); A = 8.7 for a slab (quartz, hornblende, diopside and phlogopite); where 'sphere' indicates that oxygen diffusion rates are the same, no matter which crystallographic direction is considered while 'slab' shows diffusional anisotropy with different crystallographic directions); a is the size of the mineral grain (radius for sphere, half-thickness for a slab; in meters) and dT/dt is the cooling rate (°C/sec). E, R and D_o are as for equation 8.1 above. Thus if one can estimate the cooling rate, then the closure temperatures of minerals for which E and D_o are known can be calculated. Conversely, knowledge of the isotopic equilibration factor between minerals, together with information on grain sizes and diffusion rates in minerals may be used for determinations of cooling rates (e.g. Giletti, 1985; Sharp et al., 1988; Farver, 1989).

8.3.2.1.4.1 Cooling Rate (°C/My) and Closure Temperature (T_c) Determinations

For cooling rate determinations equation 8.2 can be rearranged:

$$dT/dt = \frac{-ART_c^2D_o}{a^2Ee^{(E/RT_c)}} \qquad (8.3)$$

Calculations on cooling rates are based on two assumptions. Firstly, over a limited range of temperature, that is, the range over which closure takes place, a linear variation of 1/T is assumed. Secondly, it is assumed that isotopic equilibrium has been attained for all minerals at peak metamorphism and that the rock, on the handspecimen scale, has remained a closed system. On the centimeter-scale, open system isotopic exchange with rapid intercrystalline (mineral to mineral) diffusion relative to intracrystalline (within a mineral) diffusion as measured for the minerals in experiments, is assumed. That is, minerals re-equilibrate rapidly with each other until their closure temperatures are reached. In a simple binary system of phases "x" and "y", once phase "x" closes to exchange, phase "y" also closes as there is no other phase left to exchange with and the oxygen isotope temperature given by "x-y" represents the closure temperature (T_c).

The relationship of cooling rate to closure temperature is illustrated in Figure 8.5 for several minerals of interest to this study. Given the appropriate information on oxygen diffusivity in minerals (see Fig. 8.4), then from equation 8.3 and Figure 8.5 it is clear that in order to constrain the cooling rate, accurate determinations of the closure temperature and grain size of minerals within the rocks are required. Rocks suited to such determinations would be those that are mineralogically simple, where each constituent mineral is of a homogeneous grain size, and those that show textural equilibrium. In addition,

the oxygen isotope mineral fractionations should be large in order to allow for an accurate determination of T_c.

The currently available data on oxygen diffusion in minerals, in combination with the above requirements, limits the choice of rocks in this study to rocks such as B4A, M41C and M11C. The data for these rocks, together with the cooling rate determinations are given in Table 8.4. By analogy to the experimental data for hornblende and pyroxene (Farver and Giletti, 1985; Farver, 1989), it is reasonable to assume that grunerite and pigeonite in B4A are closed to isotopic exchange prior to quartz and magnetite. At temperatures below the closure for grunerite and pigeonite, the quartz-magnetite system, in the absence of significant quantities of oxygen-bearing fluid, may therefore be considered as a binary system. As such, one can take the quartz-magnetite oxygen isotope equilibration temperature as T_c for this binary system. Using the calibration of Bottinga and Javoy (1975), then quartz-magnetite temperatures of 479°C correspond to cooling rates of ~24°C/My. However, if the Matthews et al. (1983) calibration is used, then temperatures of 515°C correspond to a cooling rate of ~208°C/My, illustrating the strong control of T_c on calculated cooling rates. Samples M41C and, below the diopside closure temperatures, M11C can also be considered as binary systems, consisting of plagioclase and hornblende. In these rocks the wide range in cooling rate estimates, that is ~12 and 618°C/My respectively, is not a function of different thermometry calibrations, but rather of the relative hornblende (and therefore also plagioclase) closures, as recorded by their respective plagioclase-hornblende oxygen isotope temperatures.

In other granulite terranes cooling rates have been estimated to be around 1 to 20°C/My at temperatures between 150 to 600°C (e.g. Berger and York, 1981; Cosca et al., 1987), in agreement with the estimates given by B4A and M41C at temperatures of 480 to 600°C. If the temperatures calculated by the calibration of Bottinga and Javoy (1975) are essentially correct (c.f. Clayton et al., 1989), then the most likely cause for the high plagioclase-hornblende closure temperature in M11C (see also M8A and M27C) could be lower water activities in this sample. Under essentially dry conditions oxygen diffusion rates are considerably slower than in water-rich systems such as those represented by the hydrothermal diffusion experiments (compare curves 1 and 9 in Fig. 8.4; Sharp et al., 1988). If this is indeed the case, then an interesting implication of it is the existence of a water-activity gradient during metamorphism between the mafic rocks to the north and those to the south of the orthopyroxene isograd (Fig. 2.1).

Assuming that cooling rates of ~1 to 20°C/My are applicable to the SMZ terrane, then the closure temperature for quartz and feldspar in the pelitic rocks of this study, with an average grain size corresponding to "a" $\simeq$ 1mm, are around 500°C and 220°C respectively. If the phlogopite curve is used as an approximation for biotite, then its closure temperatures would also fall around 500°C. These closure temperatures for quartz and biotite are in good agreement with the temperatures calculated from their respective oxygen isotope compositions. Values for hornblende and diopside as approximations for the coarse-grained orthoamphibole and orthopyroxene, provide closure temperatures approaching 625°C to 650°C and 800°C respectively. For the orthopyroxene

closure temperatures of around 800°C are thought to represent maximum estimates as orthopyroxene is commonly finer grained with "a" <0.5mm. While no calculations were performed for the garnet closure temperatures because of a lack in sufficient information (Freer and Dennis, 1982), from the sparse diffusion information available, it appears reasonable to assume that garnet closure temperatures are in excess of 600°C and may even approach peak temperatures for cooling rates of around 10°C/My and an average observed grainsize of larger than 2mm (Fig. 8.4). This is in good agreement with the lack of cation zonation observed for the garnet (Figure 5.5; see also Cygan and Lasaga, 1985).

8.3.2.2 Discussion

In view of the large number of uncertainties involved (e.g. the fluid contents in the natural system, crystallographic diffusional variations, phlogopite-biotite, hornblende-orthoamphibole and diopside-orthopyroxene approximations, grain size distributions, etc.) the above estimated values for closure temperatures are merely taken as rough guides for the relative sequence of closure of minerals. In spite of this, some geologically meaningful information can be summarized as follows:

1. A more or less simultaneous closure of quartz and biotite is suggested from the above information (see also Fortier and Giletti, 1987). The preservation of quartz-plagioclase, quartz-biotite and plagioclase-biotite fractionations, all corresponding to temperatures of ~550°C, would suggest that the fluid

component present in the pelitic rocks during retrogression was very small or absent. Therefore, once the quartz and biotite were closed to oxygen diffusion, no oxygen bearing phase was left for the plagioclase to exchange with and the plagioclase is effectively closed. On the other hand, it could be argued that if the closed system isotopic re-equilibration occured in the absence of fluids, then the experimental data for the dry diffusion systems should be used. If the experimental results for quartz from Haul and Dumbgen (1962) and that of Elphick et al. (1988) for anorthite are used to calculate closure temperatures, then the values obtained will be considerably higher than peak metamorphic temperatures (see Fig. 8.4). In such a case no oxygen diffusion and retrograde re-equilibration is allowed for the rocks of this study. The quartz-plagioclase mineral fractionation could then be taken as representing crystallization temperatures, where these two phases crystallized from a melt that was produced from the pelites during prograde metamorphism (see above). This would not explain the quartz-biotite fractionation though, necessitating some volume diffusion, which may have been enhanced by small amounts of fluids released from the melts.

2. It was suggested above that the high closure temperatures recorded for hornblende in mafic rocks found north of the orthopyroxene isograd (Fig. 2.1) relative to those found south of it, is caused by decreasing water activities ($a(H_2O)$) from south to north. A decrease in $a(H_2O)$ is also consistent with the mineralogic changes observed both in the mafic and the pelitic rocks (Chapter 3). However, no such differences in mineral closure temperatures appear to exist in the pelitic rocks as suggested by the similarity in all

mineral-mineral oxygen isotope temperatures. A likely explanation for this is that the $a(H_2O)$ in the pelitic rocks is buffered by the presence of partial melts within these rocks. Upon crystallization of these melts, the previously adsorbed H_2O will be released and, as melt crystallization occurs at temperatures above the closure temperatures for biotite, residual quartz and plagioclase, these minerals will re-equilibrate with these fluids.

3. The sequence of quartz-mineral temperatures observed for the pelitic rocks may best be explained by closed system diffusion of oxygen amongst coexisting minerals, where the minerals show a successive closure sequence of garnet, $\pm$ orthoamphibole, $\pm$ orthopyroxene, biotite, $\pm$ quartz, plagioclase with decreasing temperature in a system with a low fluid/rock ratio. The closure sequence is schematically represented in Figure 8.6 where the relative mineral isotopic values are illustrated as a function of time (and temperature) during retrogression. In this simplistic representation, garnet and orthoamphibole are considered to close at peak metamorphic conditions (closure indicated by solid lines). Orthopyroxene is considered to exchange down to somewhat lower temperatures ('Mid T' in Fig. 8.6) than garnet or orthoamphibole, possibly because of its smaller grain size. During the time interval between 'Peak T' and 'Mid T', the exchanging phases left are quartz, plagioclase (-cordierite), orthopyroxene and biotite. In terms of modal abundance, quartz and plagioclase make up the bulk of the oxygen reservoir with which orthopyroxene and biotite (+cordierite?) may exchange. It is therefore expected that small increases in $\delta^{18}O$ of quartz and plagioclase will be balanced by somewhat larger decreases in $\delta^{18}O$ of orthopyroxene and

biotite. This may result in orthopyroxene becoming lighter in oxygen isotope composition relative to garnet as is observed for P25C, P19C and P21C. In sample P25C, the high quartz-garnet temperature but average quartz-biotite and quartz-plagioclase temperatures relative to these temperatures in other pelitic rocks, may be explained by a low biotite/(quartz+plagioclase) modal ratio during 'Mid T' to 'Close T' isotopic exchange (see also Table 3.3). That is, in sample P25C the oxygen reservoir available for quartz is smaller compared to the other pelitic rocks because of the low biotite abundance. Similar arguments may be used to explain the cordierite-plagioclase relationship. Theoretical considerations would predict that plagioclase is somewhat heavier than cordierite. However, in one rock out of the four in which both cordierite and plagioclase were analysed, the cordierite is actually heavier than the plagioclase (P1D). Thus cordierite closure to oxygen diffusion prior to that of plagioclase may account for the reversed isotopic fractionation between these two phases.

The only other oxygen isotope reversal amongst the minerals of the pelitic rocks is found in sample P45C. For this sample garnet was actually observed to be richer in ^{18}O than plagioclase. This sample also shows a large quartz-plagioclase fractionation, significantly larger than that for any other quartz-plagioclase pair in the pelitic rocks. The quartz-garnet fractionation though compares well with that for the other pelites, suggesting that the plagioclase isotopic composition may have been altered. The possibility that plagioclase is a minor phase compared to quartz is discounted by the modal proportions given in Table 3.3. An alternative closed

system explanation could be that the fluid/rock ratio in this sample was high enough so that the fluid phase provided an oxygen exchanging reservoir for the plagioclase, subsequent to quartz closure. In contrast, the high quartz-biotite temperatures relative to the quartz-plagioclase temperatures in samples P34C and P1D may be explained by relatively low fluid/rock ratios where the biotite, in the absence of sufficient fluid as a catalyst for oxygen exchange, closed prior to quartz and plagioclase.

4. An interesting corollary to the above is that while quartz has retrogressively exchanged with plagioclase and biotite, the relatively high modal abundance of quartz suggests that ^{18}O enrichment in quartz was relatively minor. As such, the quartz-garnet temperatures may represent minimum estimates of peak metamorphic temperatures.

5. The discussion on closed system behaviour so far largely concentrated on quartz-mineral and plagioclase-biotite isotopic fractionations. It remains to be seen whether the above-mentioned closed system interpretation is also internally consistent with other mineral-pair fractionations. Temperatures (using Bottinga and Javoy, 1975) derived from plagioclase-orthopyroxene oxygen isotope fractionations average around 773°C (Range 628 to 914°C), those for plagioclase-garnet average 1053°C (Range 725-1635°C) while those for garnet-biotite average 304°C (Range 235-403°C). Examination of Figure 8.6 reveals that the closed system behaviour outlined above is also consistent with the temperatures obtained for the plagioclase-orthopyroxene, plagioclase-garnet, and garnet-biotite oxygen isotope fractionations.

8.4 Conclusions

From the foregoing discussions, the following points arise:

1. Temperatures calculated from the oxygen isotope mineral fractionations using the experimentally derived calibrations of Matthews et al. (1983) are significantly lower in absolute value than those determined from the empirical calibrations of Bottinga and Javoy (1975) or the calibration of Clayton et al. (1989).

2. The quartz-mineral fractionations in the pelitic rocks imply the following order of decreasing temperatures:

   quartz-garnet ~ quartz-orthoamphibole > quartz-orthopyroxene > quartz-biotite ~ quartz-plagioclase.

   This sequence appears to be true irrespective of whether the empirical (Bottinga and Javoy, 1975), the experimental (Matthews et al., 1983) or even the theoretical (Kieffer, 1982) temperature calibrations are used.

3. In δ-δ plots for the minerals from the pelitic rocks, linear trends with 45° slopes are indicative of closed system behaviour. For the mafic rocks such linearity is not observed and may suggest open system behaviour for at least some of the mafic rocks and minerals.

4. No significant difference in oxygen isotope temperatures is evident, for any mineral-mineral pair, between the various pelitic rock groups.

5. Mineral oxygen isotope fractionations for the mafic rocks are difficult to

interpret (see above). For some mafic rocks considered to have remained closed systems since peak metamorphism, differences in the plagioclase-hornblende temperatures between rocks sampled from both sides of the orthopyroxene isograd are observed. Such differences are interpreted to be the result of differences in $a(H_2O)$ between these rocks, with lower $a(H_2O)$ suggested for the rocks north of the isograd.

6. If the oxygen diffusion experiments performed in hydrothermal systems are appropriate for the SMZ rocks, then cooling rates can be estimated at ~12 to 25°C/My over a temperature range of 480 to 600°C.

The involvement of a partial melt phase produced during the prograde metamorphism of the pelitic rocks, in combination with intercrystalline diffusion of oxygen amongst cogenetic minerals is the mechanism that can best account for the above observations. Implications of this mechanism can be summarized as follows:

Prograde partial melting may effectively dehydrate the surrounding rock as water is partitioned into the melt phase. Removal of water will reduce the oxygen diffusion rates considerably and therefore allow for the preservation of oxygen isotope compositions of the product phases to the partial melting processes (e.g. garnet and orthopyroxene). Retrograde cooling will eventually result in the crystallization of partial melts consisting predominantly of quartz and plagioclase. If the fluid/rock ratios are small enough so that the fluids are not a significant oxygen reservoir relative to the mineral phases, then the quartz-plagioclase fractionation may reflect crystallization temperatures. The fluids expelled from the crystallizing melts may serve as catalysts for

intercrystalline diffusion amongst mineral phases. The oxygen isotope effects of such diffusion amongst minerals in the vicinity of crystallizing melts will be a function of their respective oxygen diffusion rates, their modal abundances and fluid/rock ratios. Thus a mineral such as biotite, allowing for relatively fast diffusion rates, may be easily affected as is shown by the agreement in quartz-feldspar, quartz-biotite and plagioclase-biotite isotope equlibration temperatures. These temperatures indicate final closure temperatures to oxygen isotope exchange and thus could represent minimum estimates to crystallization temperatures. As quartz is generally the most abundant oxygen-bearing phase, the ^{18}O enrichment in quartz may only be small. The quartz-garnet temperatures, therefore, represent minimum estimates to peak-temperature conditions. The agreement in temperatures for the quartz, plagioclase, biotite mineral triplet also points to small fluid/rock ratios during retrogression. Large fluid/rock ratios, where the fluid becomes an oxygen exchanging reservoir, would tend to isotopically exchange with the feldspar down to temperatures below the quartz and biotite closures, resulting in isotopic disequilibration in the quartz, plagioclase and biotite mineral triplet.

Removal of some of the partial melts and crystallization of such melts in the vicinity of mafic rocks elsewhere in the metamorphic pile may cause isotopic disequilibration in the immediately adjacent mafic rocks. Isotopic disequilibration in these rocks is a function of the fluid/rock ratio, the temperature of fluid infiltration and the isotopic composition of the infiltrating fluid.

CHAPTER 9: TOWARDS A METAMORPHIC MODEL

9.1 Amphibolite - Granulite Facies Metamorphism

The ultramafic, mafic and pelitic rocks of this study were largely collected from a crustal section of the northern Kaapvaal Craton that is characterized by a transition from amphibolite to granulite facies metamorphic conditions. This transition is represented by the orthopyroxene isograd (Fig.'s 1.3 and 2.1) and is defined by the first appearance of orthopyroxene in pelitic rocks (van Reenen, 1983). In contrast to the studies of van Reenen (1978, 1983, 1986), the orthopyroxene isograd is here interpreted to be of a prograde nature (see Section 3.5, Section 5.5 and 6.5). According to van Reenen (1978, 1986), and van Reenen et al. (1987, 1988) the high-grade granulite terrane was thrust southwards onto adjacent lower grade rocks along E-W trending shear zones. Subsequently, the southern portion of the granulite terrane was subjected to a CO_2-H_2O fluid streaming (van Reenen, 1986; van Reenen et al., 1988) which resulted in the retrogression of granulites to form the orthoamphibole gneisses found south of the orthopyroxene isograd. In the light of the results from this study, this retrogression by fluid streaming is considered incorrect as explained below (see also Chapter 3).

Upon progressive metamorphism, the fluid release is accompanied by a reduction in both the porosity and permeability of rocks due to the recrystallization of the constituent minerals in a rock (e.g. Fyfe et al., 1978;

Walther and Orville, 1982). Such porosity decreases will, therefore, largely inhibit retrograde reactions unless fluid access is continuous and voluminous as is commonly the case along fractures and shear zones. If the orthoamphibole gneisses were formed by an influx of retrograde CO_2-rich fluids into precursor granulite rocks, then the complete absence of orthopyroxene from the orthoamphibole gneisses would suggest large fluid-rock ratios and pervasive fluid flow. However, the stable isotope heterogeneity over the scale of 5 to 20 metres, even for samples collected from "large scale crustal shear zones" (see Fig.'s 1.3 and 2.1; also van Reenen et al., 1987) negates large fluid/rock ratios and pervasive fluid flow. Besides the oxygen and carbon isotope evidence for fluid heterogeneity, large fluid/rock ratios are also discounted on the basis of fluorine contents in biotite (section 5.4.2).

In a recent study on fluid inclusions of the pelitic rocks across the isograd, van Reenen and Hollister (1988) observed that both north and south of the orthopyroxene isograd, carbonic and aqueous fluid inclusions of similar composition and densities are found. From this observation they concluded that the rocks north and south of the isograd were infiltrated by the same fluids, but only the rocks in the south were rehydrated by the CO_2-rich fluids as they were cooler compared to the rocks in the north. The cooling of the southern rocks is believed to be conductive cooling as these rocks were thrust over cold greenstone material. Differential thermal contraction of coexisting mineral grains in these rocks allowed for the influx of retrograde fluids. However, the high-density CO_2 inclusions, the fluids of which are considered to have caused the retrogression, were found to be more abundant in the rocks north of the

isograd. This suggests that the rocks north of the isograd must have experienced a similar or even higher degree of thermal contraction and therefore cooling. In addition, the entrapment of the postulated retrogressive fluid as fluid inclusions within quartz grains would suggest that quartz isotopically re-equilibrated with this fluid, particularly as the P-T conditions implied by the fluid inclusion data (~640°C; 6kbars; van Reenen and Hollister, 1988) fall well above the closure temperatures for quartz (c.f. Fig. 8.5). Oxygen diffusion data for feldspars indicates that the feldspar should also have equilibrated with the retrogressive fluid. For the rocks north and south of the isograd, however, no significant difference in quartz-feldspar fractionation was observed, implying that no significant temperature gradient existed between the rocks on either side of the isograd. This similarity in temperature is also consistent with the similarity in fluid densities of the fluid inclusions both north and south of the isograd (van Reenen and Hollister, 1988).

9.1.1 Cation Versus Anion Thermometry

At this stage it is interesting to note that the cation geothermometry (see Chapter 6) does appear to record a temperature gradient between rocks to the north (peak temperatures of ~730 $\pm$ 65°C) and the rocks to the south (620 $\pm$ 50°C) of the orthopyroxene isograd, if the garnet-biotite thermometer of Perchuk and Lavrenteva (1983) is used. This is in direct contrast to the similarity in oxygen isotope fractionation factors and hence also in apparent isotopic equilibration temperatures, for the same mineral pairs in rocks both north and south of the orthopyroxene isograd. Some possible explanations that

could account for the discrepancy are the following:

1. The temperature calibrations used for the cation and/or anion thermometry are either incorrect, or not applicable to the rocks of this study due to retrograde exchange effects, or variations in factors such as water activity.

2. The discrepancy is solely a function of the relative diffusion rates of cations relative to anions.

3. The temperature difference between the peak temperatures for the rocks to the north and the rocks to the south of the isograd is less than the average error for the oxygen isotope thermometry.

These will be considered in more detail below.

It is well known that oxygen isotope fractionation amongst coexisting minerals is a direct function of temperature and even at high pressures, the equilibrium fractionation is largely independent of pressure (e.g. Javoy, 1977; Clayton, 1981; Ewald, 1985). Furthermore, the isotope fractionation factor of a given mineral pair is generally independent of the bulk rock chemistry and on the mineralogic constituents in a rock (e.g. Deines, 1977; Clayton, 1981). In addition, while the oxygen diffusion rates are critically dependent on the presence or absence of water, the actual equilibrium mineral-pair fractionation factor at a given temperature is not dependent on the water content (e.g. Matthews et al., 1983). These observations apply irrespective of the temperature calibration used. Thus, while different calibrations may provide different absolute temperatures, the fact remains that both north and south of

the isograd, fractionation factors for a given mineral pair are the same (Section 8.2.1).

In contrast, accurate cation geothermometry is critically dependant on a detailed knowledge of elements that could interfere with the ideal exchange of cations amongst coexisting phases (e.g. Wood and Fraser, 1977; Essene, 1982). This is exemplified by a comparison of the different garnet-biotite thermometers used in this study. Inaccuracies in this thermometer are largely caused by Al and Ti substitutions for Fe/Mg in biotite and by Ca, Mn substitutions for Fe/Mg in garnet (Ferry and Spear 1978; Indares and Martignole, 1985). While the Ca and Mn contents of garnet in this study are low, the higher Al^{VI} and lower Ti contents of biotite from the orthoamphibole gneisses may certainly contribute towards lower garnet-biotite temperatures in these rocks relative to the granulites (Section 5.4.2 and 6.4.2.2.1). Thus for the garnet-biotite thermometer of Indares and Martignole (1985b), which corrects for Al and Ti interference on Fe/Mg exchange in biotite, no significant temperature difference was observed between the orthoamphibole gneisses and the granulites (Section 6.5). In addition, as described in Section 6.4.2, retrograde Fe/Mg exchange between biotite and cordierite (or biotite + cordierite and orthopyroxene) with an observed Mg-enrichment sequence of cordierite > biotite > orthopyroxene (~orthoamphibole) > garnet, may cause retrogressive Fe-enrichment of biotite in cordierite-bearing rock samples, resulting in higher apparent garnet-biotite equilibration temperatures in the cordierite-bearing rocks.

A more critical evaluation of retrogressive exchange of Fe/Mg requires knowledge on diffusivities of cation species. The scarce experimental information available on cation diffusion in the phases relevant to this study is illustrated relative to temperature in Figure 9.1. For both cation and anion diffusion, the diffusion rates were found to be significantly faster in hydrous systems. In general, Figure 9.1 suggests that the relative diffusion rates of different ions in the same mineral are a function of their ionic radii. Thus, faster diffusion rates for relatively small ions such as Na^{+}, Mg^{2+} and Fe^{2+} are commonly observed relative to diffusion rates for O^{2-}, K^{+} and Rb^{+} ions. By analogy to the relative diffusion rates shown in Figure 9.1, Fe/Mg exchange during retrogression amongst ferromagnesian phases such as biotite and cordierite can then be expected to be faster than the O^{2-} exchange amongst biotite, quartz and/or feldspar. For garnet, while Fe/Mg diffusion is observed to be faster than that of oxygen diffusion (Cygan and Lasaga, 1985; Freer and Dennis, 1982), in both cases the garnet crystallization temperature is probably lower than its closure temperatures. This is in agreement with the absence of retrograde chemical profiles for the garnets of this study (Fig. 5.5b). The large compositional variations shown by both biotite and cordierite in the rocks of this study (Sections 5.4.2 and 5.4.6) can be explained by crystallization temperatures of these minerals falling above their diffusional closure temperatures and retrograde centimeter-scale diffusion of cations.

The above diffusion data has some important implications to the geothermometry of the SMZ rocks:

1. From the presently available diffusion data for both cations and anions, it would appear that the quartz-garnet temperatures derived from the oxygen isotope thermometry may represent the closest estimate of peak metamorphic temperatures. As it has been shown that quartz has retrogressively exchanged oxygen with phases such as plagioclase and biotite, the average quartz-garnet temperature (~736 $\pm$ 52°C) will represent a minimum estimate only. However, as quartz is the dominant oxygen-bearing species in the pelitic rocks in general, retrograde ^{18}O enrichment in quartz is expected to be relatively small. Thus peak metamorphic temperatures would not be expected to be significantly higher than ~736 $\pm$ 52°C.

2. A combination of Al and Ti substitution for Fe/Mg in biotite and the ease of retrograde Fe/Mg exchange amongst ferromagnesian phases such as biotite and cordierite, could account for the lower garnet-biotite temperatures in the orthoamphibole gneisses relative to the granulitic rocks. Thus if peak temperature differences did exist between these gneisses and the granulites, then such differences were probably less than the average error on the oxygen isotope thermometry.

9.2 A Proposed Metamorphic Model

The proposed metamorphic model for the rocks of the Southern Marginal Zone is shown in simplified form in Figure 9.2. Little is known about the low grade history of the terrane now represented by the SMZ rocks. However, from the general geochemistry of the various members, it is likely that the SMZ-terrane may have formed a sequence of deep-water argillaceous sediments and/or greywackes, overlying an ophio;itic-type mafic-ultramafic crust, similar to that proposed for other Archaean greenstone belts (Chapter 4; e.g. Hoffman et al., 1986; de Wit et al., 1987). If this is the case, then prograde metamorphic conditions could have been fluid-rich. The high-grade data from the SMZ rocks support a model where the transition from amphibolite facies rocks, as represented by the orthoamphibole gneisses, to the granulite facies rocks was formed in response to lower water activities at similar peak temperature conditions (~736 $\pm$ 52°C at 6.1 $\pm$ 1.5kbars; temperatures at least within error of the oxygen isotope thermometry). Such a lowering is considered to reflect buffering of H_2O by partial melting processes similar to those described by Touret (1971), Phillips (1980), Corbett and Phillips (1981) and Waters and Whales (1984). In melting experiments performed on starting assemblages of quartz-plagioclase-biotite, Knabe (1970a, b) and Hoschek (1976) observed the formation of product phases such as garnet, orthopyroxene, orthoamphibole and cordierite. The formation of each particular product mineral phase, or mineral assemblage, was ascribed to being a critical function of the biotite chemistry, the oxygen fugacity and small variations in the partial pressures of H_2O. High-grade metamorphism, and therefore the initial melting in the pelitic rocks,

presumably occured under fluid-present conditions as suggested above. Fluid-present melting is also consistent with the complete absence of free K-feldspar from the pelitic rocks. Under such conditions the experiments of Knabe (1970a, b) at $P(H_2O)$ = 2kbars, predict that initial melts may be as high as 50% by weight. As H_2O is preferentially partitioned into the granitic melts formed (e.g. Kadik and Eggler, 1975; Mysen, 1976), the fluid phase in equilibrium with the melt will get enriched in CO_2 (van Reenen and Hollister, 1988). In addition, subsequent melting may best be described as fluid-absent melting (e.g. Thompson, 1982; Grant, 1985; Clemens and Vielzeuf, 1987; Waters, 1988). Such melting may explain the small amounts of K-feldspar occuring as antiperthite in the cordierite-bearing, high MgO rocks. Partial extraction of the melts formed will result in the occurrence of some disequilibrium textures and incomplete mineral reactions (Chapter 3), as well as in the formation of a residual rock enriched in FeO+MgO (Chapter 4). Accumulation of a number of extracted melt pockets can then result in the formation of pegmatitic bodies with $\delta^{18}O$ signatures similar to those of the pelitic rocks (Chapters 4 and 7).

Upon retrograde crystallization of melts, the previously adsorbed fluids will be released. Minimum temperatures of 550 $\pm$ 50°C for the crystallization are given by the quartz-plagioclase oxygen isotope temperatures. On the handspecimen scale, crystallization of small, residual melt pockets within the pelitic rocks can account for the incipient hydration of cordierite, the retrogressive growth of an Al_2SiO_5 polymorph and, in the high-Mg rocks, the resultant $P(H_2O)$ increase may cause the replacement of garnet by orthopyroxene

and cordierite (van Reenen, 1983). In addition, the presence of such small amounts of fluids will greatly enhance the diffusivity of ions, resulting in cation and oxygen isotopic re-equilibration amongst coexisting minerals that have not yet reached their closure temperatures (Chapters 6 and 7). The small retrograde aluminosilicate crystals were identified by van Reenen (1978) as kyanite which, together with the position of the granite solidus (Fig. 9.2), may suggest nearly isobaric cooling. If the garnet breakdown reaction to form orthopyroxene and cordierite is also related to retrogressive fluid release by the melts, then the similarity in calculated pressures between the cordierite-garnet granulites and the garnet granulite is also consistent with isobaric retrogression (Chapter 6).

Removal of some larger-sized melt pockets and crystallization of the melts in the vicinity of mafic lithologies may then account for the isotopic disequilibration amongst mafic mineral phases. Terrane-wide, penetrative retrogression is, however, inhibited as the bulk of the melts formed were presumably removed to higher crustal levels before crystallization. The large "shear zones" found cross-cutting the high-grade terrane may thus represent zones of partial melt accumulation and migration (e.g. Thompson, 1983).

The above proposed P-T-time path for the SMZ rocks is common to many granulite facies terranes and is suggestive of an underplating by large volumes of magma (e.g. Bohlen, 1987). Proposed melts for other granulite terranes vary in composition from being tonalitic-trondhjemitic (e.g. Tarney and Windley, 1977; Waters, 1986), to mafic-ultramafic (e.g. Frost and Frost, 1987; Cohen et al., 1988). However, unlike the model proposed by Frost and Frost (1987), no

extensive CO_2 infiltration is implied by the stable isotope data for the SMZ rocks. Indeed, the contrasting behaviour observed between the pelitic and the mafic/ultramafic rocks of this study (Chapters 7 and 8) suggests that there was no extraneous fluid-infiltration during the high-grade metamorphism of the SMZ rocks. This implies that the sequence of rocks represented by the Bandelierkop Formation was deposited on, or intruded into essentially dry "basement rocks", now represented by the Baviaanskloof gneisses. These gneisses could have experienced an earlier event of dehydration metamorphism prior to the deposition of the Bandelierkop Formation.

CHAPTER 10: HIGH-GRADE METAMORPHISM AND GOLD MINERALIZATION PROCESSES

10.1 Introduction

Currently two models for the origin of Archaean lode gold deposits exist. The magmatic model (e.g. Burrows et al., 1986; Burrows and Spooner, 1987) is based upon the close spatial association between plutonic igneous rocks and gold depositional environments. In this model both gold and the fluids are derived from the magmatic intrusive as evidenced by mineralogic, fluid inclusion and stable isotope information. The metamorphic model (e.g. Kerrich and Fyfe, 1981; Groves et al., 1985) postulates that metamorphically degassed fluids leach a sufficient amount of gold from source rocks and precipitate it by reaction with suitable country rocks. The ore fluid and ore components are derived by devolatization of a metamorphic pile with no significant partial melting taking place. For the latter model, the fluids are commonly considered to be derived from greenschist-amphibolite facies devolatization. Recent work in the Superior Province of Canada, has led to a third model which largely combines magmatic and high-grade metamorphic processes (Colvine et al., 1988; Fyon et al., 1988). In the latter model it is suggested that the introduction of gold , CO_2, H_2O and other incompatible elements (K, S - e.g. Phillips et al., 1987) into specific structural sites was part of a complex sequence of events involving mantle diapirism coupled with crustal melting, granulitization and tectonism. While no constraints are placed on the mode of transport for the gold and associated incompatibles and volatiles, it is suggested in this latter model

that gold is partitioned into anatectic magmas derived from crustal and/or mantle material. Crystallization of these magmas in the mantle and in the crust will release the magmatic fluid in which gold and the accompanying elements are dissolved. This fluid, in turn, gets focussed into large scale structures. It is also suggested that the lower crust, particularly the zone of granulitization, presents a large enough source reservoir to satisfy the gold budget (Fyon et al., 1988). Studies by Sighinolfi and Santos (1976) and Cameron (1989) showed that granulite facies rocks are significantly depleted in gold with respect to lower metamorphic grade equivalents and other crustal rocks (Crocket, 1974).

The granulitization model for the SMZ rocks as represented in this study would be in good agreement with the above proposed "lower crustal maturation processes" (Fyon et al., 1988; Colvine et al., 1988). The relevance of the metamorphic model proposed for the SMZ rocks to gold mineralization processes, is therefore worth examining further, particularly as various gold mineralization occurrences exist both in the high-grade area (e.g. on the farm Borkum 143 LS and the Harlequin Mine on farm Goedgenoeg 185 LS - Hammerbeck, 1976) and in the adjacent granite-greenstone terranes (e.g. goldmines of the Pietersburg, Murchison and Sutherland greenstone belts - Hammerbeck, 1976).

10.2 Composition of Hypothetical High-Grade Mineralizing Fluids

10.2.1 Fluid Species and CO_2/H_2O Ratios

The metamorphic model proposed for the SMZ rocks in Chapter 9 suggests the internal derivation of fluids under conditions of low fluid/rock ratios. This imposes constraints on the isotopic composition of the fluids. Furthermore, in section 7.4 it was argued that the presence of graphite flakes within the pelitic rocks has important controls on the chemistry of the fluid phase present. Thus while CH_4 is commonly described to be the predominant carbon-bearing phase for temperatures up to 500°C, for temperatures exceeding 500°C, CO_2 predominates. At temperatures of around 700°C to 800°C (i.e. approximate peak metamorphic temperatures), the CH_4 content is negligible compared to CO_2 and, in addition, the mole-fraction of H_2O may be as small as 0.25 at fluid pressures of 2kbars and quartz-fayalite-magnetite buffering (Eugster and Skippen, 1967; Ohmoto and Kerrick, 1977). At the onset of granite minimum melting, and therefore migmatization, Ohmoto and Kerrick (1977) calculated minimum $X(H_2O)$ values of 0.1 to 0.2 for a fluid phase coexisting with the melt.

It is well known that anatectic melts, or granitic melts in general, dissolve more H_2O than CO_2 as the solubility of CO_2 is less than H_2O in such melts (Kadik and Eggler, 1975; Mysen, 1976). Mysen (1976), for example, estimates maximum $X(CO_2)$ values of 0.48 in silicate melts (i.e. CO_2/H_2O ratio ~ 1.0). Because of the lower CO_2 solubility in granitic melts, such

melts also become more easily saturated in CO_2 relative to H_2O (e.g. Cameron and Hattori, 1987). Therefore, upon crystallization, the first fluid released from the melt can be highly enriched in CO_2 while fluids released during subsequent crystallization become more H_2O-rich. The CO_2/H_2O ratios of the fluids released from melts may therefore be variable, but on average are estimated at around 1.0 or less. The implications of variable CO_2/H_2O ratios will be discussed below.

10.2.2 Oxygen Isotope Compositions of Fluids

In Figure 10.1, the approximate average range for $\delta^{18}O$ values compositions of carbonate and quartz are given as analyzed from mineralized Archaean lode gold deposits in the Murchison and Pietersburg greenstone belts (Smith, 1986; 1987), and from various Canadian gold deposits (Kerrich, 1986 a, b). Temperatures of deposition are commonly estimated to be in the range of 250°C to about 400°C (e.g. Pretorius et al., 1986; Kerrich and Fyfe, 1981; Smith et al., 1984; Ho et al., 1985). The shaded curves in the diagram represent the oxygen isotope values of carbonate and quartz precipitated from CO_2 and H_2O respectively, where these fluids were in isotopic equilibrium with the high-grade minerals. The H_2O oxygen isotope value was calculated from the quartz-water fractionation curves given in Friedman and O'Neil (1977) resulting in an average $\delta^{18}O$ value of 9.7‰ and a standard deviation of 0.9‰ (range 8.5 to 11.7‰) at 560°. The CO_2 oxygen isotope value was calculated by combining the CO_2-calcite and calcite-H_2O fractionation curves given in Friedman and O'Neil (1977) at temperatures of 560°C to obtain both a CO_2-H_2O fractionation

curve and a CO_2-quartz fractionation curve at high temperatures (see Appendix D). The average $\delta^{18}O$ for CO_2 in equilibrium with the pelitic quartz is 18.1‰ (s.d. = 0.9‰ and range 17.0 to 20.1‰). The temperature of 560°C represents the approximate quartz-plagioclase-biotite closure temperature after crystallization and therefore the final equilibration of the fluids with the anatectic melts in the high-grade terrane. Fluid isotopic compositions were considered to remain constant during the precipitation of quartz and carbonate as depositional environments are characterized by high fluid/rock ratios (e.g. Kerrich and Fyfe, 1981; Phillips et al., 1987).

From Figure 10.1 it can clearly be recognized that neither H_2O nor CO_2 have the appropriate isotope characteristic to be able to precipitate quartz or carbonate with the isotope values that are observed for these minerals in the mineralized greenschist facies shear zones. However, fluid inclusion evidence from Archaean lode gold deposits indicate mineralizing fluids of varying CO_2/H_2O ratios, low salinities (<4wt% equivalent NaCl) and only in some special cases the presence of minor CH_4 (e.g. Kerrich and Fyfe, 1981; Smith et al., 1984; Ho et al., 1985; Pretorius et al., 1986). While some fluid inclusion work suggests nearly pure CO_2 fluids (e.g. Burrows and Spooner, 1987; Brown, 1986), more commonly CO_2/H_2O mole ratios of 0.03 to 0.5 are quoted (Kerrich and Fyfe, 1981; Smith et al., 1984; Ho et al., 1985; Pretorius et al., 1986). From the ubiquitous presence of CO_2 in mineralizing fluids, it seems reasonable to suggest that the minerals precipitating from the ore fluids (i.e. quartz and carbonate) may derive their oxygen both from the CO_2- and the

H_2O-component in the fluid. In Table 10.1 the fluid $\delta^{18}O$ compositions have been calculated for various CO_2/H_2O mole ratios using the average high-grade (560°C) $\delta^{18}O$ values of 9.7‰ for H_2O and 18.1‰ for CO_2. Given the CO_2/H_2O mole ratio and the corresponding bulk fluid $\delta^{18}O$ value, then the relevant $\delta^{18}O(H_2O)$ and $\delta^{18}O(CO_2)$ values at temperatures lower than 560°C can be calculated from CO_2-H_2O fractionation curves (see Appendix D for derivation of a high temperature CO_2-H_2O fractionation curve). The values of $\delta^{18}O$(quartz) and $\delta^{18}O$(carbonate) precipitating from such mixed CO_2-H_2O fluids can then be computed, and as CO_2 and H_2O were calculated to be in equilibrium with each other, the quartz and carbonate will be in equilibrium with both the H_2O and the CO_2 in the mineralizing fluid. The recent oxygen isotope calibration of Clayton et al. (1989) for the quartz-calcite fractionation predicts Δ(quartz-carbonate) values of about 1.1‰ at 350°C. This is in reasonable agreement with the 1.5‰ fractionation obtained via the above described method (Table 10.1). For the purpose of the following discussion, the derivation of $\delta^{18}O$ values for quartz and carbonate in mineralized zones as outlined above, is therefore considered to be acceptable.

The results given in Table 10.1 for 350°C are summarized in Figure 10.2. In this Figure, the observed $\delta^{18}O$ values for quartz and carbonate, as also shown in Figure 10.1, are represented by the horizontal lines, whereas the $\delta^{18}O$(quartz) and $\delta^{18}O$(carbonate) values, calculated for varying values of CO_2/H_2O at 350°C, are given by the lines shown at an angle to the horizontal lines. A temperature of 350°C was chosen as representing an

estimated average temperature of mineralization (Kerrich and Fyfe, 1981; Smith et al., 1984; Ho et al., 1985; Pretorius et al., 1986). For decreasing temperatures the quartz and carbonate precipitation curves will rotate towards steeper slopes in a clockwise fashion. The results of these calculations can be summarized as follows:

1. At precipitation temperatures of 350°C the minimum CO_2/H_2O mole ratios that can precipitate carbonate and quartz of equivalent isotopic compositions to those found for these minerals in lode gold deposits can be estimated to be 0.1 and 0.3 respectively. Maximum CO_2/H_2O mole ratios for carbonate and quartz are 3.5 and 8.5 respectively.

2. At correspondingly lower temperatures of precipitation, the minimum values will be increased, while the maximum values will be decreased.

3. Average CO_2/H_2O ratios expected from fluids in equilibrium with the high-grade pelitic rocks can range from very low values up to maximum values of about 10 (section 10.2) and would therefore appear to be in good agreement with the ranges indicated by Figure 10.2 (see 1 above).

4. If anatectic melts are involved during fluid transfers, then the average maximum range of CO_2/H_2O of 1 (section 10.2) would also appear to be in reasonable agreement with the ranges indicated by 1 above.

5. The range in CO_2/H_2O ratios from ~0.1 to 10 is also in agreement with CO_2/H_2O mole ratios of up to about 0.5 as deduced from fluid inclusion studies elsewhere.

10.2.3 Carbon Isotope Compositions of Fluids

It was suggested earlier that, if the mineralizing fluids are derived from the high-grade terrane at temperatures of 560°C, then CO_2 will be the major carbon-bearing phase. This is most certainly the case if the release of fluid is related to the crystallization of anatectic melts formed close to peak metamorphic temperature conditions (~730°C; Eugster and Skippen, 1967; Ohmoto and Kerrick, 1977). The CO_2-rich character of the high-grade fluid is also evidenced by fluid inclusion work on the SMZ high-grade terrane and granulite facies terranes in general (e.g. Touret, 1971; van Reenen and Hollister, 1988). CO_2 in equilibrium with graphite both within the metasediments and the pegmatites shows a range in $\delta^{13}C$ values at 560°C of -5.9 to +3.0‰ (Friedman and O'Neil, 1977). This range in calculated $\delta^{13}C$ values for fluid CO_2 is in excellent agreement with those calculated for carbonates from the Murchison greenstone belt, as well as those calculated from carbonates in other Archaean lode gold deposits, which commonly show $\delta^{13}C(CO_2)$ values ranging from +4 to -6‰ (Smith, 1986; Golding and Wilson, 1983; Burrows et al., 1986; Burrows and Spooner, 1987; Groves et al., 1988).

10.3 Discussion and Conclusions

In view of the large number of uncertainties involved, such as source-rock CO_2/H_2O estimates, temperatures of ore deposition, molar CO_2/H_2O variations during deposition of quartz and carbonate, late stage alteration of mineral compositions during secondary fluid infiltrations, etc., the above

agreement is promising and may be taken to indicate that CO_2/H_2O mixed fluids derived from the high-grade terrane are possible candidates for Archaean lode gold deposits. Furthermore, the importance of considering both CO_2 and H_2O when calculating "mineralization fluid" isotopic compositions is clearly emphasized.

During the prograde metamorphism of a sequence of rocks such as may be represented by a greenstone belt sequence, most of the fluid release will occur during the greenschist to amphibolite facies transition (e.g. Winkler, 1976). It is therefore commonly argued, that gold-mineralization fluids are predominantly derived from metamorphic devolatization at greenschist to amphibolite facies transitions (e.g. Kerrich and Fyfe, 1981; Phillips et al., 1987). However, there are several advantages of fluid derivation from a high-grade source, particularly if hydrous melting is involved. In a recent study on fluid flow in metamorphic rocks, Ferry (1987) concluded that, with increasing metamorphic grade, the fluid flow becomes less channelized and more pervasive. If this is the case, then the partial melts formed at high-grade metamorphism effectively absorb large amounts of fluid from the adjacent high-grade lithologies, thereby dehydrating the terrane (e.g. Lamb and Valley, 1984). In addition, such anatectic melts could incorporate potassium and sulphur provided by the breakdown of phases such as biotite and sulphide. Extraction of these melts from the high-grade terrane and emplacement into upper-crustal zones of structural weakness (e.g. shear zones), could then provide an optimal transporting medium for the fluids, gold and associated elements. Crystallization of these melts will then release the fluids and associated elements more effectively, that is

in a more concentrated manner, than greenschist to amphibolite transition dehydration. The level of crystallization of the melts within the crust will be a function of their composition, in particular their H_2O contents.

To conclude, a "lower crustal maturation" model similar to that proposed by Colvine et al. (1988), presents a viable model for the interpretation of gold deposits in greenstone belts adjacent to the SMZ, and also for the small scale gold occurrences within the high-grade terrane (i.e. residual melt crystallization). Future work should focus on geochemical, stable isotopic and fluid inclusion studies both on the high-grade deposit and on several deposits immediately adjacent to the high-grade terrane.

CHAPTER 11: SUGGESTED FUTURE WORK

Although this study is certainly not intended to represent a comprehensive account of the metamorphism in the Southern Marginal Zone of the Limpopo belt, the conclusions presented point towards some new ideas regarding the high-grade metamorphism of the Bandelierkop Formation rocks. Future work may aid in refining the proposed metamorphic model. Such a model can then provide a good background for future studies on mineralizations occuring within the high grade terrane and also adjacent to this terrane. The following are some points which are considered to be important guidelines for future work:

1. The importance of partial melting processes both on a small scale (e.g. mineralogic scale) and on a large scale (e.g. shear zones or terrane scale). Not only may the crystallization of small melt pockets left within the pelites result in the breakdown of garnet to cordierite and orthopyroxene, but the removal of larger amounts of melts may cause bulk compositional shifts paralleling the shifts observed for the Fe/Mg relationships in constituent mineral phases (see van Reenen, 1983). On a larger scale the "shear zones" as given by van Reenen et al. (1987) may represent zones of partial melt accumulation and migration (e.g. Thompson, 1983). Further geochemical and stable isotope work on the migmatites, pegmatites and the shear zone components (melts, xenoliths, etc.) may help to establish the importance of melting processes (e.g. Sawyer, 1987).

2. Detailed work on the structural, metamorphic and geochemical relationships

of the Baviaanskloof gneisses (basement gneisses?) to the members of the Bandelierkop Formation is important before any large metamorphic model can be established (e.g. Watkeys, 1986). In addition, detailed geochemical studies on the mafic, ultramafic and pelitic rock suites are needed in order to test whether the former two rock suites were of originally intrusive or extrusive origin and whether the Bandelierkop Formation as a whole may represent an ophiolitic-type sequence.

3. Independent determinations on water activities ($a(H_2O)$) across the amphibolite-granulite transition may help in establishing whether this transition is related to initial $a(H_2O)$ differences only (e.g. Glassley, 1980; Valley and O'Neil, 1984; Waters and Whales, 1984), or is temperature related only, or both temperature and $a(H_2O)$ related (e.g. Phillips, 1980). A promising method could involve mineral solid solutions (e.g. Rumble, 1976; Bhattacharya and Sen, 1986; Lamb and Valley, 1988).

4. With the aid of more qualitative information on diffusion for cations and anions in various mineral phases, retrograde ion or element exchange in various systems can be re-evaluated. This not only has important consequences on interpretations of pressure-temperature conditions, or on oxygen isotope exchange, but may also prove useful for geochronological work (e.g. Hopgood et al., 1983; Cliff, 1985). In this regard the garnet-biotite gneisses, garnet granulites and pegmatites could be of particular interest as these rocks have a relatively simple mineralogy and are not complicated by retrograde garnet breakdown. Rb/Sr techniques on pelitic biotites and plagioclases may provide retrograde crystallization/closure

ages whereas Sm/Nd techniques on garnet, orthopyroxene and orthoamphibole may provide peak metamorphic formation ages. These rocks may also prove important for peak pressure-temperature determinations.

5. Further precise graphite and possibly ultramafic, metamorphic carbonate $\delta^{13}C$ determinations in addition to D/H stable isotope work should prove useful for discussions on the importance of carbon-bearing and hydrogen-bearing fluid species during metamorphism. In addition such work, combined with detailed geochemical studies in mineralized lode deposits both within and adjacent to the high grade terrane (e.g. stable isotope work on fluid inclusions and their host minerals) could contribute towards resolving the controversies regarding metamorphic versus igneous gold mineralization models (e.g. Groves et al., 1985; Burrows et al., 1986; Colvine et al., 1988). Implicit to such a resolution are detailed geochronological studies (e.g. Marmont and Corfu, 1988).

In summary, the Southern Marginal Zone provides a good terrane for a number of detailed studies that are of current interest to the larger scientific and industrial communities.

REFERENCES

Alt J C, Muehlenbachs K and Honorez J, 1986. An oxygen isotopic profile through the upper kilometer of the oceanic crust, DSDP Hole 504B. Earth Planet. Sci. Let. 80: 217-299.

Anderson A T, Clayton R N and Mayeda T K, 1971. Oxygen isotope thermometry of mafic igneous rocks. Jour. Geology 79: 715-729.

Andreae M O, 1974. Chemical and stable isotope composition of the high grade metamorphic rocks from the Arendal area, S. Norway. Contrib. Mineral. Petrol. 47: 300-316.

Anhaeusser C R, 1979. Rodingite occurrences in some Archaean ultramafic complexes in the Barberton Mountain Land, South Africa. Precamb. Res. 8: 49-76.

Armbruster T H and Bloss F D, 1980. Channel CO_2 in cordierites. Nature 286: 140-141.

Argast S and Donnelly T W, 1986. Compositions and sources of metasediments in the upper Dharwar Supergroup, south India. Jour. Geology 94: 215-231.

Arndt N T, Naldrett A J and Pyke D R, 1977. Komatiitic and iron-rich tholeiitic lavas of Munro Township, NE Ontario. Jour. Petrol. 18: 319

Arndt N T, Francis D and Hynes A J, 1979. The field characteristics and petrology of Archaean and Proterozoic komatiites. Can. Mineral. 17: 147-163.

Ashworth J R and Chinner G A, 1978. Coexisting garnet and cordierite in migmatites from the Scottish Caledonides. Contrib. Mineral. Petrol. 65: 379-394.

Baadsgaard H, Nutman A P, Rosing M, Bridgwater D and Longstaffe F J, 1986. Alteration and metamorphism of Amitsoq gneisses from the Isukasia area, West Greenland: recommendations for isotope studies of the early crust. Geochim. Cosmochim. Acta 50: 2165-2172.

Barbey P and Cuney M, 1982. K, Rb, Sr, Ba, U and Th geochemistry of the Lapland granulites (Fennoscandia): LILE controlling factors. Contrib. Mineral. Petrol. 81: 304-316.

Barker F and Friedman I, 1969. Carbon isotopes in pelites of the Precambrian Uncompahyne Formation, Needle Mountains, Colorado. Geol. Soc. Am. Bull. 80: 1403-1408.

Barker F, Friedman I, Hunter D R and Gleason J D, 1976b. Oxygen isotopes of some gneisses and associated mafic rocks. Precam. Res. 3: 547-557.

Barton J M Jr, Du Toit M C, van Reenen D D and Ryan B, 1983b. Geochronologic studies in the Southern Marginal Zone of the Limpopo Belt, Southern Africa. In: Van Biljon W J, Legg J H, (Eds), The Limpopo Belt: Spec. Publ., Geol. Soc. South Africa 8: 55-64.

Barton J M and Key R M, 1983. Rb-Sr ages and geologic setting of certain rock units from the central zone of the Limpopo Mobile Belt, near Zanzibar, Eastern Botswana. In: Van Biljoen W J and Legg J H, (Eds), The Limpopo Belt. Spec. Publ. Geol. Soc. S. Afr., 8: 19-25.

Beaty D W and Taylor HP, 1982. The oxygen isotope geochemistry of komatiites - evidence for water-rock interaction. In: Komatiites, N T Arndt, E G Nisbet (Eds), George, Allen + Unwin Publishers : 267-280.

Becker R H and Clayton R N, 1976. Oxygen isotope study of a Precambrian banded iron-formation. Hamersley Range W. Australia. Geochim. Cosmochim. Acta 40: 1153-1165.

Berger G W and York D, 1981. Geothermometry from $^{40}Ar/^{39}Ar$ dating experiments. Geochim. Cosmochim. Acta: 795-881.

Beswick A E, 1982. Some geochemical aspects of alteration and genetic relations in komatiitic suites. In: Komatiites, Arndt N T and Nisbet E G, (Eds), Allen + Unwin publishers. : 283-308.

Battacharya A and Sen S K, 1986. Granulite metamorphism, fluid buffering, and dehydration melting in the Madras charnockites and metapelites. Jour. Petrol. 27: 1119-1141.

Battacharya A, Mazumdar A L and Sen S K, 1988. Fe - Mg mixing in cordierite: Constraints from natural data and implications for cordierite-garnet geothermometry in granulites. Am. Mineral. 73: 338-344.

Black P M, 1974. Oxygen isotope study of metamorphic rocks from the Onegon District New Caledonia. Contrib. Mineral. Petrol. 47: 197-206.

Bohlen S R, 1987. Pressure - temperature - time paths and a tectonic model for the evolution of granulites. Jour. Geology 95: 617-632.

Bohlen S R and Essene E J, 1989. A critical evaluation of two-pyroxene thermometry in Adirondack granulites. Lithos 12: 335-345.

Bohlen S R, Valley J W and Essene E J, 1985. Metamorphism in the Adirondacks. I Petrology, pressure and temperature. Jour. Petrol. 26: 971-992.

Borthwick J and Harmon R S, 1982. A note regarding ClF_3 as an alternative

to BrF_5 for oxygen isotope analysis. Geochim. Cosmochim. Acta 46: 1665-1668.

Bottinga Y and Javoy M, 1973. Comments on oxygen isotopic geothermometry. Earth Planet. Sci. Let. 20: 250-265.

Bottinga Y and Javoy M, 1975. Oxygen isotope partitioning among the minerals in igneous and metamorphic rocks. Reviews Geophys. Space Geophys. 13: 401-408.

Brown P E, 1986. Fluid inclusions, fluids and lode gold ores Wabigoon Subprovince, NW Ontario, Canada. In: Geocongress 86, Extended Abstracts Geol. Soc. S. Africa: 279-282.

Bryan W, Finger L W and Chayes F, 1969. Estimating proportions in petrogenetic mixing equations by least squares approximation. Science 163: 926-927.

Burger A J and Walraven F, 1976. Summary of age determinations carried out during the period: April 1975 - March 1976. Ann. geol. Surv. S. Africa 11: 323-329.

Burger A J and Walraven F, 1979. Summary of age determinations carried out during the period: April 1976 - March 1977, April 1977 - March 1978. Ann. geol. Surv. S. Africa 12: 199-207.

Burrows D R and Spooner E T C, 1987. Generation of a magmatic H_2O - CO_2 fluid enriched in Mo, Au and W within an Archaean sodic grandiorite stock, Mink Lake, NW Ontario. Econ. Geol. 82: 1931-1957.

Burrows D R, Wood P C and Spooner E T C, 1986. Carbon isotopic evidence for a magmatic origin for Archaean gold-quartz vein ore deposits. Nature 321: 851-854

Cameron E M, 1989. Scouring of gold from the lower crust. Geology 17: 26-29.

Cameron E M and Baumann A, 1972. Carbonate sedimentation during the Archaean. Chem. Geol. 10: 17-30.

Cameron E M and Garrels R M, 1980. Geochemical compositions of some Precambrian shales from the Canadian shield. Chem. Geol. 28: 181-197.

Cameron E M and Hattori K, 1987. Archaean gold mineralization and oxidized hydrothermal fluids. Econ. Geol. 82: 1177-1191.

Carmichael D M, 1969. On the mechanism of prograde metamorphic reactions in quartz bearing pelitic rocks. Contrib. Mineral. Petrol. 20: 244-267.

Chamberlain C P and Rumble D, 1988. Thermal anomalies in a regional metamorphic terrane: an isotopic study of the role of fluids. Jour. Petrol. 29: 1215-1232.

Chernosky J V, 1974. The upper stability of clinochlore at low pressures and the free energy of formation of Mg-cordierite. Am. Mineral. 59: 496-507.

Chernosky J V, 1976. The stability of anthophyllite - A reevaluation based on new experimental data. Am. Mineral. 61: 1145-1155.

Chipera S J and Perkins D, 1988. Evaluation of biotite-garnet geothermometers: application to the English River subprovince, Ontario. Contrib. Mineral. Petrol. 98: 40-48.

Clayton R N, 1981. Isotopic thermometry. In: Newton R C, Navrotsky A and Wood B J eds. Thermodynamics of minerals and melts: New York, Springer Verlag: 85-109.

Clayton R N and Mayeda T D, 1963. The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. Geochim. Cosmochim. Acta 27: 43-52.

Clayton R N, Goldsmith J R and Mayeda T, 1989. Oxygen isotope fractionation in quartz, albite, anorthite and calcite. Geochim. Cosmochim. Acta 53: 725-733.

Clemens J D and Vielzeuf D, 1987. Constraints on melting and magma production in the crust. Earth Planet. Sci. Let. 86: 287-306.

Clemens J D and Wall V J, 1981. Origin and crystallization of some peraluminous (S-type) granitic magmas. Can. Mineral. 19: 111-131.

Cohen A S, O'Nions R K and O'Hara M J, 1988. Melting, depletion and textural equilibration of Lewisian granulites. Chem. Geol. 70:

Cole D R and Ohmoto H, 1986. Kinetics of isotopic exchange at elevated temperatures and pressures. Reviews Mineral. 16: 41-90.

Cole D R, Ohmoto H and Lasaga A C, 1983. Isotopic exchange in mineral fluid systems, I. Theoretical evaluation of oxygen isotopic exchange accompanying surface reactions and diffusion. Geochim. Cosmochim. Acta 47: 1681-1693.

Colvine A L, Fyon J A, Heather K B, Marmont S, Smith P M and Troop D G, 1988. Archaean lode gold deposits in Ontario. Ontario Geol. Surv. Miscel. Paper 139: 136pp.

Condie K C, Macke J E and Reimer T O, 1970. Petrology and geochemistry of

early Precambrian graywackes from the Fig Tree group, South Africa. Geol. Soc. Am. Bull. 81: 2759-2776.

Condie K C, Viljoen M J, Kable E J D, 1977. Effects of alteration on element distributions in Archaean tholeiites, from Barberton greenstone belt, South Africa. Contrib. Mineral. Petrol. 64: 75.

Corbett G J and Phillips G N, 1981. Regional retrograde metamorphism of a high grade terrain: the Willyama Complex, Broken Hill, Australia. Lithos 14: 59-73.

Cosca M A, Essene E J and Sutter J F, 1987. Denudation rates of Grenville basement near Parry Sound, Ontario: constraints from $^{40}Ar/^{39}Ar$ thermochronology. Trans. Am. Geophys. Union 68: 432.

Coward M P, James P R and Wright L, 1976. Northern margin of the Limpopo Mobile Belt. Geol. Soc. Am. Bull. 87: 601-611.

Cox K G, Bell J D and Pankhurst J, 1979. The Interpretation of Igneous Rocks. George Allen + Unwin, Great Britain, 450pp.

Cox K G, Gurney J J and Harte B, 1973. Xenoliths from the Matsoka Pipe. In: Lesotho Kimberlites, P H Nixon (Ed). Lesotho Nat. Dev. Corp.

Craig H, 1957. Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide. Geochim. Cosmochim. Acta 12: 133-149.

Craig H, 1961. Standard for reporting concentrations of deuterium and oxygen-18 in natural waters: Science 133: 1833-1834.

Crocket J H, 1974. Gold. In: Wedepohl K H (Ed), Handbook of Geochemistry II, Springer Verlag, Berlin, Ch.79 B-D.

Crowley J C and Giletti B J, 1983. Patterns of oxygen isotope depletion, multiple hydrothermal circulation systems and the cooling history of the Stony Mountain intrusive complex, Colorado. Earth Planet. Sci. Let. 64: 231-243.

Currie K L, 1971. The reaction 3 cordierite = 2 garnet + 4 sillimanite + 5 quartz as a geological thermometer in the Opinicon Lake Region, Ontario. Contrib. Mineral. Petrol. 33: 215-226.

Currie K L, 1974. A note on the calibration of the garnet-cordierite geothermometer and geobarometer. Contrib. Mineral. Petrol. 44: 35-44.

Cygan R T and Lasaga A C, 1985. Selfdiffusion of Mg in garnet at 750°C to 900°C. Am. Jour. Sci. 285: 328-350.

Dallmeyer R D, 1974. Metamorphic history of the north-eastern Reading Prong, New York and northern New Jersey. Jour. Petrol. 15: 325-359.

Danchin R V, 1970. Aspects of the geochemistry of some related South African fine grained sediments. Unpubl. Ph. D. thesis. University of Cape Town.

Danckwerth P A and Newton R C, 1978. Experimental determination of the spinel peridotite to garnet peridotite reaction in the system $MgO-Al_2O_3-SiO_2$ in the range 900°C-1100°C and Al_2O_3 isopleths in the spinel field. Contrib. Mineral. Petrol. 66: 189-202.

De Beer J H, Stettler E H, Barton J M, van Reenen D D and Vearncombe J R, 1986 Crustal structure of the Archaean granite-greenstone terrane in the northern Kaapvaal craton. Lunar and Planetary Institute, Technical Report, Houston.

Deer W A, Howie R A and Zussman J, 1966. An Introduction to the Rock Forming Minerals. Longman Group Ltd. England 528pp.

Deines P, 1970. Mass spectrometer correction factors for the determination of small isotopic composition variations of carbon and oxygen. Int. J. Mass Spectrom. Ion Phys., 4: 283-295.

Deines P, 1977. On the oxygen isotope distribution among mineral triplets in igneous and metamorphic rocks. Geochim. Cosmo. Acta 41: 1709-1730.

de la Roche H, 1966. Sur l'existence de plusieurs facies geochimique dans les schistes Paleozoiques des Pyrenees luchonnaises. Geol. Rundschau 55: 274-301.

Dennis P F, 1984. Oxygen selfdiffusion in quartz under hydrothermal conditions. Jour. Geophys. Res. 89: 4047-4057.

de Waard D, 1965. A proposed subdivision of the granulite facies. Am. Jour. Sci. 163: 455-461

Dodson M H, 1973. Closure temperature in cooling geochronological and petrological systems. Contrib. Mineral. Petrol. 40 :259-274.

Donnelly T W, Thompson G and Salisbury M H, 1980. Chemistry of altered basalts at site 417 DSDP Leg 51 Initial Reports 51/53: 1319-1330.

Du Toit M C, 1979. Die geologie en struktuur van die gebiede Levubu en Bandelierkop in Noord-Transvaal. Unpubl. Ph.D thesis, Rand Afrikaanse University, Johannesburg, 243pp.

Du Toit M C and van Reenen D D, 1977. The southern margin of the Limpopo Belt, northern Transvaal, with special reference to metamorphism and structure. In: Ermanovics I F, Key R M, McEwan G (Eds) The proceedings

of a seminar pertaining to the Limpopo Mobile Belt. Bull. Geol. Surv. Botswana 12: 248pp.

Du Toit M C, van Reenen D D and Roering C, 1983. Some aspects of the geology, structure and metamorphism of the southern marginal zone of the Limpopo Metamorphic Complex. In: van Biljon W J and Legg J H (Eds), The Limpopo Belt. Spec. Publ. Geol. Soc. S. Africa 8: 121-142.

Edwards A B, 1957. Amphibolites from the Broken Hill district. Jour. Geol. Soc. Austral. 5: 1-32.

Edwards R L and Essene E J, 1988. Pressure, temperature and C-O-H fluid fugacities across the amphibolite-granulite transition, northwest Adirondack Mountains, New York. Jour. Petrol. 29: 39-72.

Ellis D J, 1982. Garnet-liquid Fe^{2+}-Mg equilibria and implications for the beginning of melting in the crust and subduction zones. Am. Jour. Sci. 286: 765-791.

Elphick S C, Dennis P F and Graham C M, 1986. An experimental study of the diffusion of oxygen in quartz and albite using an overgrowth technique. Contrib. Mineral. Petrol. 92: 322-330.

Elphick S C, Graham C M and Dennis P F, 1988. An ion microprobe study of anhydrous oxygen diffusion in anorthite: a comparison with hydrothermal data and some geological implications. Contrib. Mineral. Petrol. 100: 490-495.

Engel A E J and Engel C G, 1962. Progressive metamorphism of amphibolites, northwest Adirondack Mountains, New York. In: Petrologic studies: A volume to honour A F Buddington, Engel, James and Leonard (Eds). Geol. Soc. Am. 37-82.

Essene E J, 1982. Geologic thermometry and barometry. In: Reviews in Mineralogy, Min. Soc. Am. 10: 153-206.

Eugster H P and Skippen G B, 1967. Igneous and metamorphic reactions involving gas equilibria. In: P H Abelson (Ed). Researches in Geochemistry Vol. 2. John Wiley and Sons, New York.

Evans B W, 1977. Metamorphism of alpine peridotite and serpentinite. Ann. Rev. Earth Planet. Sci. 5: 397-447.

Ewald A H, 1985. The effect of pressure on oxygen isotope exchange in silicates. Chem. Geol. 49: 179-185.

Farver J R, 1989. Oxygen self-diffusion in diopside with application to cooling rate determinations. Earth Planet. Sci. Let. 92: 386-396.

Farver J R and Giletti B J, 1985. Oxygen diffusion in amphiboles. Geochim. Cosmo. Acta 49 : 1403-1411.

Fawcett J J and Yoder H S, 1966. Phase relationships of chlorites in the system $MgO-Al_2O_3-SiO_2-H_2O$. Am. Mineral. 51: 353-380.

Fediukova E and Suk M, 1979. An example of migmatite origin by dehydrating metamorphism. Bull. Geol. Soc. Finland 51: 1-9.

Ferry J M, 1987. Metamorphic hydrology at 13-km depth and 400-550°C. Am. Mineral. 72: 39-58.

Ferry J M and Spear F S, 1978. Experimental calibration of partitioning of Fe and Mg between biotite and garnet. Contrib. Mineral. Petrol. 66: 113-117

Foland K A, 1974a. Ar^{40} diffusion in homogeneous orthoclase and an interpretation of Ar diffusion in K-feldspar. Geochim. Cosmo. Acta 38: 151-166.

Foland K A, 1974b. Alkali diffusion in orthoclase. In: A W Hofmann, B J Giletti, H S Yoder and R A Yund (Eds), Geochemical Transport and Kinetics. Carnegie Inst. Wash. Publ. 634: 77-98.

Forester H and Taylor H P, 1976. ^{18}O, D/H and $^{13}C/^{12}C$ studies of the tertiary igneous complex of Skye, Scotland. Am. Jour. Sci. 277: 136-177.

Foucarde S and Javoy M, 1973. Rapports $^{18}O/^{16}O$ dans les roches du vieux socle catazonal d'In Ouzzal (Sahara Algerien). Contrib. Mineral. Petrol. 42: 235-244.

Fortier S M and Giletti B J, 1987. Oxygen self-diffusion in biotite, muscovite and phlogopite micas. Trans. Geophys. Un. Am. 68: 417.

Freer R, 1979. An experimental measurement of cation diffusion in garnet. Nature 280: 220-222.

Freer R, Carpenter M A, Long J V P and Reed S J B, 1982. "Null-results" diffusion experiments with diopside: implications for pyroxene equilibria. Earth Planet. Sci. Let. 58: 285-292.

Freer R and Dennis P F, 1982. Oxygen diffusion studies 1. A preliminary microprobe investigation of oxygen diffusion in some rock forming minerals. Mineral. Mag. 45: 147-179.

French B M, 1966. Some geological implications of equilibrium between graphite and C-O-H gas at high temperatures and pressures. Rev. Geophys. 4: 223-253.

Friedman I and O'Neil J R, 1977. Data of geochemistry: Sixth edition; Chapter kk. Compilation of stable isotope fractionation factors of geochemical interest, United States Geological Survey, Professional Paper 440-kk, M Fleisher (ed).

Frost B R, 1975. Contact metamorphism of serpentinite, chloritic blackwall and rodingite at Paddy-Go-Easy Pass, Central Cascades, Washington. Jour. Petrol. 16: 272-313.

Frost B R and Frost C D, 1987. CO_2 melts and granulite metamorphism. Nature 327: 503-506.

Fyfe W S, Price N J and Thompson A B. Fluids in the Earths Crust. Developments in Geochemistry _ 1, Elsevier, Amsterdam 383pp.

Fyon J A, Macdonald A J, Marmont S and Troop G, 1988. Shield wide introduction of gold into Archaean crust, Superior Province, Ontario: coupling between mantle initiated magmatism and lower crustal maturation. Bicentennial Gold 88, Extended Abstracts, Geol. Soc. Austral.: 313-318.

Garlick G D and Epstein S, 1967. Oxygen Isotope ratios in coexisting minerals from regionally metamorphosed rocks. Geochim. Cosmo. Acta 31: 181-214.

Ghent E D, Knitter C C, Raeside R P and Stout M Z, 1982. Geothermometry of and geobarometry of pelitic rocks, upper kyanite and sillimanite zones, Mica Creek area, British Columbia. Can. Mineral. 20: 295-305.

Ghent E D Robbins D B and Stout M Z, 1979. Geothermometry, geobarometry and fluid compositions of metamorphosed calc-silicates and pelites, Mica Creek, British Columbia. Am. Mineral. 64: 874-885.

Giletti B J, 1974. Studies in diffusion I: Argon in phlogopite mica. In: Geochemical Transport and Kinetics, A W Hofmann, B J Giletti, H S Yoder and R A Yund (Eds), Carnegie Inst. Washington D.C. Publ. 634: 107-116.

Giletti B J, 1985. The nature of oxygen transport within minerals in the presence of hydrothermal water and the role of diffusion. Chem. Geol. 53: 197-206.

Giletti B J and Anderson T F, 1977. Studies in diffusion II. Oxygen in phlogopite mica. Earth Planet. Sci. Let. 28: 225-233.

Giletti B J and Hess K C, 1988. Oxygen diffusion in magnetite. Earth Planet. Sci. Let. 89: 115-122.

Giletti B J, Semet M P and Yund R A, 1978. Studies in diffusion III. Oxygen in feldspars. An ion microprobe determination. Geochim. Cosmo. Acta 42: 45-57.

Giletti B J and Yund R A, 1984. Oxygen diffusion in quartz. Jour. Geophys. Res. 89: 4039-4046.

Glassley W E and Sorenson K, 1980. Constant P_s-T amphibolite to granulite facies transition in Agto (West-Greenland) metadolerites: implications and applications. Jour. Petrol. 21: 69-105.

Golding S D and Wilson A F, 1983. Geochemical and stable isotope studies of the No. 4 lode, Kalgoorlie, Western Australia. Econ. Geol. 78: 438-450.

Gonfiantini R, 1978. Standards for stable isotope measurements in natural compounds. Nature 271: 534-536.

Graham C M, 1981. Experimental hydrogen isotope studies III. Diffusion of H in hydrous minerals and stable isotope exchange in metamorphic rocks. Contrib. Mineral. Petrol. 76: 216-228.

Grant J A, 1973. Phase equilibria in high grade metamorphism and partial melting of pelitic rocks. Am. Jour. Sci. 273: 289-317.

Grant J A, 1981. Orthoamphibole and orthopyroxene relations in high grade metamorphism of pelitic rocks. Am. Jour. Sci. 281: 1127-1143.

Grant J A, 1985. Phase equilibria in partial melting of pelitic rocks. In: Migmatites, J R Ashworth (Ed), Blackie, Glasgow: 86-144.

Greenwood H J, 1963. Synthesis and stability of anthophyllite. Jour. Petrol. 4: 317-351.

Gregory R T, 1986. Oxygen isotope systematics of quartz-magnetite pairs from Precambrian iron formations: evidence for fluid-rock interaction during diagenesis and metamorphism. In: Fluid-Rock Interactions during Metamorphism. Advances in Phys. Chem. 5: 132-153.

Gregory R T and Criss R E, 1986. Isotopic exchange in open and closed systems. In: Reviews in Mineralogy, Stable Isotopes in High Temperature Geologic Processes. Am. Mineral. Soc. 16: 91-128.

Gregory R T, Criss R E and Taylor H P, 1981. Analytical models of ^{18}O systematics of coexisting minerals in hydrothermally altered plutonic rocks. Trans. Am. Geophys. Un. 62: 1064.

Grew E S, 1974. Carbonaceous material in some metamorphic rocks of New England and other areas. Jour. Geol. 82: 50-73.

Groves D I, Phillips G N, Ho S E and Houstoun S M, 1985. The nature of gold mineralization in Archaean greenstone belts of the Western Australian Shield: a brief review. Trans. Geol. Soc. S. Africa 88: 149-159.

Guidotti C V, 1984. Micas in metamorphic rocks. Reviews in Mineralogy, Min. Soc. Am. 13: 357-456.

Hallberg J A and Williams D A C, 1972. Archaean mafic and ultramafic rock associations in the Eastern Goldfields Region, Western Australia. Earth Planet. Sci. Let. 15: 191-200.

Hammerbeck E C I, 1976. Gold outside the Witwatersrand Triad. In: Mineral Resources of the Republic of South Africa. Handbook 7, Geol. Survey: 75-92.

Hanson G N, 1978. The application of trace elements to the petrogenesis of igneous rocks of granitic composition. Earth Planet. Sci. Let. 38: 26-43.

Harley S L and Green D H, 1982. Garnet-orthopyroxene barometry for granulites and peridotites. Nature 300, 697-701.

Harris N B W and Holland T J B, 1984. The significance of cordierite - hypersthene assemblages from Beitbridge region of central Limpopo Belt; evidence for rapid decompression in the Archaean. Am. Mineral. 69: 1036-1049.

Haul R and Dumbgen G, 1962. Untersuchung der Sauerstoffbeweglichkeit in Titandioxyd, Quarz und Quarzglas mit Hilfe des heterogenen Isotopenaustausches. Zeit. Elektrochem. 66: 636-641.

Hensen B J and Green D H, 1972. Experimental study of the stability of cordierite and garnet in pelitic compositions at high pressures and temperatures II. Compositions without excess aluminosilicate. Contrib. Mineral. Petrol. 35: 331-354.

Hensen B J and Green D H, 1973. Experimental study of the stability of cordierite and garnet in pelitic compositions at high P and T III. Synthesis of experimental data and geological applications. Contrib. Mineral. Petrol. 38: 151-166.

Ho S E, Groves D I and Phillips G N, 1985. Fluid Inclusions as indicators of the nature and source of ore fluids and ore depositional conditions for Archaean gold deposits of the Yilgarn Block, W-Australia. Trans. Geol. Soc. S. Africa 88: 149-158.

Hobbs B E, 1968. Recrystallization of single crystals of quartz. Tectonophysics 6: 353-401.

Hobbs B E, 1981. The influence of metamorphic environment upon deformation of minerals. Tectonophysics 78: 335-383.

Hodges K V and Spear F S, 1982. Geothermometry, geobarometry and the

Al_2SiO_5 triple point at Mt. Moosilauke, New Hampshire. Am. Mineral. 67: 1118-1134.

Hoefs J and Frey M, 1976. The isotopic composition of carbonaceous matter in a metamorphic profile from the Swiss Alps. Geochim. Cosmo. Acta 40: 945-951.

Hoernes S and Hoffer E, 1979. Equilibrium relations of prograde metamorphic mineral assemblages: a stable isotope study of rocks of the Damara Orogen from Namibia. Contrib. Mineral. Petrol. 68: 377-389.

Holdaway M J, 1971. Stability of andalusite and the aluminium silicate phase diagram. Am. Jour. Sci. 271: 97-131.

Holdaway M J and Lee S M, 1977. Fe-Mg cordierite stability in high grade pelitic rocks based on experimental, theoretical and natural observations. Contrib. Mineral. Petrol. 63: 175-198.

Hoffer E, 1978. Melting reactions in aluminous metapelites: stability limits of biotite, sillimanite and quartz in the presence of albite. Neu. Jahrb. Mineral. Monatsh. 9: 396-407.

Hoffer E and Grant J A, 1980. Experimental investigation of the formation of cordierite-orthopyroxene paragenesis in pelitic rocks. Contrib. Mineral. Petrol. 73: 15-22.

Hoffman S E, Wilson M and Stakes D S, 1986. Inferred oxygen isotope profile of Archaean oceanic crust, Onverwacht Group, South Africa. Nature 321: 55-58.

Hofmann A W, Giletti B J, Hinthorne J R, Anderson C A and Comaford D, 1974. Ion microprobe analysis of a potassium self-diffusion experiment in biotite. Earth Planet. Sci. Let. 24: 48-52.

Hopgood A M, Bowes D R and Halliday A N, 1983. U-Pb and Rb-Sr Isotopic study of polyphase deformed migmatites in the Svecokarelides, Southern Finland. In: Migmatites, Melting and Metamorphism, M P Atherton and C D Gribble (Eds), Shiva, Nantwich : 80-91.

Hoschek G, 1976. Melting relations of biotite + plagioclase + quartz. Neu. Jahrb. Mineral. Monatsh. 2: 79-83.

Huebner M, Kyser T K and Nisbet E G, 1986. Stable Isotope geochemistry of high grade metapelites from the central zone of the Limpopo Belt. Am. Mineral. 71: 1343-1353.

Hynes A, 1980. Carbonitization and mobility of Ti, Y and Zr in Ascot Formation Metabasalts, Quebec. Contrib. Mineral. Petrol. 75: 79-87.

Indares A and Martignole J, 1985a. Biotite - garnet geothermometry in granulite facies rocks: evaluation of equilibrium criteria. Can. Mineral. 23: 187-193.

Indares A and Martignole J, 1985b. Biotite - garnet geothermometry in the granulite facies: the influence of Ti and Al in biotite. Am. Mineral. 70: 272-278.

Jackson D H, Mattey D P and Harris N B W, 1988. Carbon isotope composition of fluid inclusions in charnockites from southern India. Nature 333: 167-170.

Jahn B-M and Zhang Z, 1984. Archaean granulite gneisses from eastern Hebei Province, China: rare earth geochemistry and tectonic implications. Contrib. Mineral. Petrol. 85: 224-243.

Javoy M, 1977. Stable isotopes and geothermometry. Jour. Geol. Soc. Lond. 133: 609-636.

Jiang J, Clayton R N and Newton R C, 1988. Fluids in granulite facies metamorphism: A comparative oxygen isotope study on the south India and Adirondack high grade terrains. Jour. Geol. 96: 517-533.

Jolly W T, 1980. Development and dehydration of Archaean lavas, Abitibi area, Canada, in the light of major element geochemistry. Jour. Petrol. 21: 323-351.

Jolly W T, 1982. Progressive metamorphism of komatiites and related Archaean lavas of the Abitibi area, Canada. In: Komatiites, N T Arndt and E G Nisbet (Eds). George, Allen and Unwin publishers, London: 247-266.

Kadik A A and Eggler D H, 1975. Melt-vapour relations on the join $NaAlSi_3O_8$-H_2O-CO_2. Yearb. Carnegie Inst. Wash. 74: 479-484.

Katz M b, 1987. Graphite deposits of Sri Lanka: a consequence of granulite facies metamorphism. Mineral. Deposita 22:18-25.

Kerrich R, 1986a,b. Archaean lode gold deposits of Canada: Part I, a synthesis of geochemical data from selected mining camps with emphasis on pattern of alteration. Part II, characteristics of the hydrothermal systems and models of origin. Economic Geology Research Unit Infor. Circ. No's 182 and 183, University of the Witwatersrand, Johannesburg.

Kerrich R, Beckinsale R D and Durham J J, 1977. The transition between deformation regimes dominated by intercrystalline diffusion and intercrystalline creep evaluated by oxygen isotope thermometry. Tectonophysics 38: 241-257.

Kerrich R and Fyfe W S, 1981. The gold-carbonate association: Source of

CO_2 and CO_2 fixation reactions in Archaean lode deposits. Chem. Geol. 33: 265-294.

Kerrich R, La Tour T E and Willmore L, 1984. Fluid participation in deep fault zones: evidence from geological, geochemical and $^{18}O/^{16}O$ relations. Jour. Geophys. Res. 89 B6: 4331-4343.

Kieffer S W, 1982. Thermodynamics and lattice vibrations of minerals: 5. Applications to phase equilibria, isotopic fractionation and high pressure thermodynamic properties. Rev. Geophys. Space Phys. 20: 827-849.

Klein C, 1983. Diagenesis and metamorphism of Precambrian bandad iron formations. In: Iron-Formation: Facts and Problems, A F Trendall and R C Morris (Eds). Developments in Precambrian Geology 6, Elsevier: 417-469.

Knabe W, 1970a. Reaktion des Biotits bei der Anatexis. Geol. Jahrb. 88: 355-372.

Knabe W, 1970b. Anatexis von Quarz-Plagioklas-Biotit Metamorphiten. Geol. Jahrb. 89: 1-32.

Kyser T K, 1986. Stable Isotope variations in the mantle. In: Stable Isotopes in high Temperature Geologic Processes. Reviews in Mineralogy. Am. Mineral. Soc. 16: 141-164.

Kyser T K, O'Neil J R and Carmichael I S E, 1982. Genetic relations among basic lavas and ultramafic nodules: evidence for oxygen isotope compositions. Contrib. Mineral. Petrol. 81: 88-102.

Lamb W M and Valley J W, 1988. Granulite facies amphibole and biotite equilibria, and calculated peak-metamorphic water activities. Contrib. Mineral. Petrol. 100: 349-360.

Lamb W M and Valley J W, 1984. Metamorphism of reduced granulites in low CO_2 vapour-free environments. Nature 312: 56-58.

Leake B E, 1978. Nomenclature of amphiboles. Can. Mineral. 16: 501-520.

Lee H Y and Ganguly J, 1988. Equilibrium Compositions of coexisting garnet and orthopyroxene: experimental determinations in the system FeO-MgO-Al_2O_3-SiO_2 and applications. Jour. Petrol. 29: 93-113.

Lindsley D H, 1983. Pyroxene thermometry. Am. Mineral. 68: 477-493.

Liou J G, Kuniyoshi S and Ito K, 1974. Experimental studies of the phase relations between greenschist and amphibolite in a basaltic system. Am. Jour. Sci. 274: 613-632.

Longstaffe F J and Schwarcz H P, 1977. $^{18}O/^{16}O$ of Archaean clastic metasediments: A petrogenetic indicator for Archaean gneisses. Geochim. Cosmo. Acta 41: 1303-1312.

Loomis T P, 1975. Reaction zoning of garnet. Contrib. Mineral. Petrol. 52: 285-305.

Lowe D R, 1980. Archaean Sedimentation. Ann. Rev. Earth Planet. Sci. 8: 145-167.

Luth W C, Jahns R H and Tuttle O F, 1964. The granite system at pressures of 4 to 10 Kilobars. Jour. Geophys. Res. 69: 759-773.

MacRae N D and Nesbitt H W, 1980. Partial melting of common metasedimentary rocks: a mass balance approach. Contrib. Mineral. Petrol. 75: 21-26.

Magaritz M and Taylor H P, 1976. Oxygen, hydrogen and carbon isotopic studies of the Franciscan Formation, Coast Ranges, California. Geochim. Cosmo. Acta. 40: 215-234.

Marmont S and Corfu F, 1988. Timing of gold introduction in the late Archaean tectonic framework of the Canadian Shield: evidence for U-Pb zircon geochronology of the Abitibi Belt. Bicentennial Gold 88, Extended Abstracts, Geol. Soc. Austral.: 45-50.

Martignole J and Nantel N, 1982. Geothermobarometry of cordierite-bearing metapelites near the Morin Anorthosite Complex, Grenville Province, Quebec. Can. Mineral. 20: 307-318.

Martignole J and Sisi J C, 1981. Cordierite-garnet-H_2O equilibrium: a geological thermometer, barometer and H_2O fugacity indicator. Contrib. Mineral. Petrol. 77: 38-46.

Mason B and Moore C B, 1982. Principles of Geochemistry. 4th Ed. John Wiley and Sons, New York, 344pp.

Mason R,1973. The Limpopo Mobile Belt - southern Africa. Roy. Soc. Lond. Phil. Trans. A273: 464-485.

Matsuhisia Y, Goldsmith J R and Clayton R N, 1979. Oxygen isotope fractionation in the system quartz-albite-anorthite-water. Geochim. Cosmo. Acta 43: 1131-1140.

Matthews A, 1988. Oxygen isotope thermometry in regional metamorphism. Chem. Geol. 70: 185.

Matthews A, Goldsmith J R and Clayton R N, 1983a. On the mechanisms and kinetics of oxygen isotope exchange in quartz and feldspar at elevated temperatures and pressures. Bull. Geol. Soc. Am. 94: 396-412.

Matthews A, Goldsmith J R and Clayton R N, 1983b. Oxygen isotope fractionation involving pyroxenes: the calibration of mineral-pair geothermometers. Geochim. Cosmo. Acta 47: 631-644.

Mayeda T K, Goldsmith J R and Clayton R N, 1986. Oxygen isotope fractionation at high temperature. Terra Cognita 6: 261.

McCourt S and Vearncombe J R, 1986. West-directed emplacement of the central zone of the Limpopo Mobile Belt. Geocongress 86, Extended Abstracts, Geol. Soc. S. Africa: 841-844.

McCrea J M, 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. Jour. Chem. Phys. 18: 849-857.

McLennan S M, 1982. On the geochemical evolution of sedimentary rocks. Chem. Geol. 37: 335-350.

McLennan S M and Taylor S R, 1984. Archaean sedimentary rocks and their relation to the composition of the Archaean continental crust. In: Archaean Geochemistry, A Kroner, G N Hanson, A M Goodwin (Eds), Springer Verlag: 47-72.

McNaughton N J and Wilson A F, 1980. Problems in oxygen isotope geothermometry in mafic granulite facies rocks from Einasleigh, northern Queensland. Precam. Res. 13: 77-86.

McNaughton N J and Wilson A F, 1983. The geochemical and oxygen isotope affinities of Proterozoic mafic granulites from the Einasleigh metamorphics, northern Queensland. Precam. Res. 21: 21-37.

Moecher D P, Essene E J and Anovitz L M, 1988. Calculation and application of clinopyroxene-garnet-plagioclase-quartz geobarometers. Contrib. Mineral. Petrol. 100: 92-106.

Morimoto N, Fabries J, Fergusen A K, Ginzburg I V, Ross M, Seifert F A, Zussman J, Aoki K and Gottardi G, 1988. Nomenclature of pyroxenes. Am. Mineral. 73: 1123-1133.

Muehlenbachs K and Clayton R N, 1972. Oxygen isotope studies of fresh and weathered submarine basalts. Can. Jour. Earth Sci. 9: 172-184.

Muehlenbachs K and Kushiro I, 1974. Oxygen isotope exchange and equilibration of silicates with CO_2 and O_2. Carn. Inst. Wash. Yearbook 73: 232-236.

Munoz J L, 1984. F-OH and Cl-OH exchange in micas with application to hydrothermal ore deposits. Reviews in Mineralogy. Mineral. Soc. Am. 13: 469-493.

Mysen B O, 1976. The role of volatiles in silicate melts: solubility of

carbon dioxide and water in feldspar, pyroxene and feldspathoid melts to 30 kb and 1625°C. Am. Jour. Sci. 276: 969-996.

Naqvi S M, Sawkar R H, Subba Rao D V, Govil P K, Guaneswar Rao T, 1988. Geology, geochemistry and tectonic setting of Archaean greywackes from Karnataka nucleus, India. Precam. Res. 39: 193-216.

Newton R C, 1972. An experimental determination of the high pressure stability limits of magnesian cordierite under wet and dry conditions. Jour. Geol. 80: 398-420.

Newton R C, 1983. Geobarometry of high grade metamorphic rocks. Am. Jour. Sci. 283A: 1-28.

Newton R C and Haselton H T, 1981. Thermodynamics of the garnet-plagioclase-Al_2SiO_5-quartz geobarometer. In: Thermodynamics of Minerals and Melts, R C Newton, A Navrotsky and B J Wood (Eds), Springer Verlag, New York, 129-145.

Newton R C and Perkins D(III), 1982. Thermodynamic calibration of geobarometers based on the assemblages garnet-plagioclase-orthopyroxene (clinopyroxene)-quartz. Am. Mineral. 67: 203-222.

Newton R C, Smith J V and Windley B F, 1980. Carbonic metamorphism, granulites and crustal growth. Nature 286: 45-50.

Newton R C and Wood B J, 1979. Thermodynamics of water in cordierite and some petrologic consequences of cordierite as a hydrous phase. Contrib. Mineral. Petrol. 68: 391-405.

Nisbet E G, Bickle M J and Martin A, 1977. Mafic and ultramafic lavas of the Belingwe greenstone belt, Rhodesia. Jour. Petrol. 18: 521-548.

Norrish K and Hutton J T, 1969. An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. Geochim. Cosmo. Acta 33: 431-453.

Ohmoto H and Kerrick D M, 1977. Devolatization equilibria in graphitic systems. Am. Jour. Sci. 277: 1013-1044.

O'Neil J R and Ghent E D, 1975. Stable isotope study of coexisting metamorphic minerals from the Esplanade Range, British Columbia. Bull. Geol. Soc. Am. 86: 1708-1712.

Papike J J, Cameron K L and Baldwin K, 1974. Amphiboles and pyroxenes: characterization of other than quadrilateral components and estimates of ferric iron from microprobe data. Geol. Soc. Am. Abstracts with Programs 6: 1053-1054.

Pearton T N, 1982. Gold and antimony mineralization in altered komatiites of the Murchison greenstone belt, South Africa. In: Komatiites, N T Arndt and E G Nisbet (Eds), George Allen and Unwin publishers, London: 459-475.

Perchuk L L and Lavrenteva I V, 1983. Experimental Investigation of exchange equilibria in the system cordierite-garnet-biotite. In: Kinetics and equilibrium in mineral reactions, S K Saxena (Ed), Springer, Berlin, 199-239.

Perchuk L L, Podlesskii K K and Aranovich L Y, 1981. Calculation of thermodynamic properties of endmember minerals from natural paragenesis. In: Thermodynamics of Minerals and Melts, Adv. Phys. Geochem. 1: 111-130.

Perry E C, Ahmed S N and Swulius T M, 1978. The oxygen isotope composition of 3800 My old metamorphosed chert and iron formation from Isukasia, west Greenland. Jour. Geol. 86: 223-229.

Perry E C, Tan F C and Morey G B, 1973. Geology and stable isotope geochemistry of the Biwabik Iron Formation, northern Minnesota. Econ. Geol. 68: 1110-1125.

Phillips G N, 1980. Water activity changes across an amphibolite - granulite facies transition, Broken Hill, Australia. Contrib. Mineral. Petrol. 75: 377-386.

Phillips G N, Groves D I, and Brown I J, 1987. Source requirements for the Golden Mile, Kalgoorlie: significance to the metamorphic replacement model for Archaean gold deposits. Can. Jour. Earth Sci. 24: 1643-1651.

Podpora C and Lindsley D H, 1979. Fe-rich pigeonites: minimum temperatures of stability in the Ca-Mg-Fe quadrilateral. Trans. Am. Geophys. Un. 60: 420-421.

Powell R, 1978. The thermodynamics of pyroxene geotherms. Phil. Trans. R. Soc. Lond. A288: 457-469.

Powell R, 1983. Fluids and melting under upper amphibolite facies conditions. Jour. Geol. Soc. Lond. 140: 629-633.

Pretorius A I, van Reenen D D and Barton J M, 1986. Fluid-inclusion studies of gold mineralization at the Fumani gold mine, Sutherland greenstone belt. Geocongress 86, Geol. Soc. S. Africa: 383-386.

Raase P, 1974. Al and Ti contents of hornblende, indicators of pressures and temperatures of regional metamorphism. Contrib. Mineral. Petrol. 45: 231-236.

Raase P, Raith M, Ackermand D and Lal R K, 1986. Progressive metamorphism of mafic rocks from greenschist to granulite facies in the Dharwar craton

of south India. Jour. Geol. 94: 261-282.

Richardson S W, Bell P M and Gilbert M C, 1969. Experimental determination of the kyanite-andalusite and andalusite-sillimanite equilibria; the aluminium silicate triple point. Am. Jour. Sci. 267: 259-272.

Reinhardt E W, 1968. Phase relations in cordierite-bearing gneisses from the Gananoque area, Ontario. Can. Jour. Earth Sci. 5: 455-482.

Robinson P T, Flower M F J, Schmincke H U and Ohnmacht W, 1980. Low temperature alteration of oceanic basalts. DSDP Leg 37, Initial reports 37: 775-794.

Rollinson H R and Windley B F, 1980. Selective element depletion during metamorphism of Archaean granulites, Scourie, NW Scotland. Contrib. Mineral. Petrol. 72: 257-263.

Rumble D(III), 1976. The use of mineral solid solutions to measure chemical potential gradients in rocks. Am. Mineral. 61: 1167-1174.

Rumble D(III) and Spear F S, 1983. Oxygen-isotope equilibration and permeability enhancement during regional metamorphism. Jour. Geol. Soc. Lond. 140: 619-628.

Rye D M and Bradbury H J, 1988. Fluid-flow in the crust: An example from a Pyrenean thrust ramp. Am. Jour. Sci. 288: 197-235.

Savin S and Epstein S, 1970. The oxygen and hydrogen isotope geochemistry of clay minerals. Geochim. Cosmo. Acta 34: 25-42.

Sawyer E W, 1987. The role of partial melting and fractional crystallization in determining discordant migmatite leucosome compositions. Jour. Petrol. 28: 445-473.

Scarfe C M and Wyllie P J, 1967. Experimental redetermination of the upper stability limit of serpentine up to 3 kbars. Trans. Am. Geophys. Un. 48: 225.

Schreyer W and Abrahams K, 1978. Symplectitic cordierite-orthopyroxene-garnet assemblages as products of contact metamorphism of pre-existing basement granulites in the Vredefort structure, South Africa and their relations to pseudotachylite. Contrib. Mineral. Petrol. 68: 53-62.

Sen S K and Bhattacharya A, 1984. An orthopyroxene-garnet thermometer and its application to the Madras charnockites. Contrib. Mineral. Petrol. 88: 64-71.

Sen S K and Ray S, 1971. Breakdown reactions for natural hornblendes in granulite facies. Neu. Jahrb. Mineral. Abh. 114: 301-319.

Seyfried W E, Mottl M J and Bischoff J L, 1978. Seawater/basalt ratio effect on chemistry and mineralogy of spelites from the ocean floor. Nature 275: 211-213.

Sharp Z D, O'Neil J R and Essene E J, 1988. Oxygen isotope variations in granulite grade iron formations: constraints on oxygen diffusion and retrograde isotopic exchange. Contrib. Mineral. Petrol. 98: 490-501.

Sheppard S M F, 1986. Characterization and isotopic variation in natural waters. Reviews in Mineralogy. Min. Soc. Am. 16: 165-184.

Shieh Y N and Schwarcz H P, 1974. Oxygen isotopic studies of granite and migmatite, Grenville province of Ontario, Canada. Geochim. Cosmo. Acta 38: 21-45.

Sighinolfi G P and Santos A M, 1976. Geochemistry of gold in Archaean granulite facies terrains. Chem. Geol. 17: 113-123.

Simmons E C, Lindsley D H and Papike J J, 1974. Phase relations and crystallization sequence in a contact-metamorphosed rock from the Gunflint iron formation, Minnesota. Jour. Petrol. 15: 539-65.

Smith D, 1972. Stability of iron-rich pyroxene in the system $CaSiO_3$-$FeSiO_3$-$MgSiO_3$. Am. Mineral. 57: 1413-1428.

Smith H S, 1986. Evidence from ^{13}C and ^{18}O isotopes in carbonate minerals for the origin of fluids in Archaean greenstone belt metamorphic and mineralization processes. Geocongress 86, Geol. Soc. S. Africa: 341-344.

Smith H S, 1987. Metamorphic fluids and their significance in gold mineralization processes. In: National Geoscience Programme, Progress Reports: 126-140.

Smith H S and Erlank A J, 1982. Geochemistry and petrogenesis of komatiites from the Barberton greenstone belt, South Africa. In: Komatiites, N T Arndt and E G Nisbet (Eds), George, Allen and Unwin publishers, London: 347-398.

Smith H S, O'Neil J R, and Erlank A J, 1984. Oxygen isotope compositions of minerals and rocks, and chemical alteration patterns in pillow lavas from the Barberton greenstone belt, South Africa. In: Archaean Geochemistry, A Kroner, G N Hanson and A M Goodwin (Eds), Springer Verlag: 115-137.

Smith T J, Cloke P L and Kesler S E, 1984. Geochemistry of fluid inclusions from the McIntyre-Hollinger gold deposits, Ontario, Canada. Econ. Geol. 79: 1265-1285.

Spear F S, 1980. The gedrite-anthophyllite solvus and the composition limits of orthoamphibole from the Post Pond volcanics, Vermont. Am. Mineral. 65: 1103-1118.

Spear F S, 1981. An experimental study of hornblende stability and compositional variability in amphibole. Am. Jour. Sci. 281: 697-734.

Spooner E T C, Beckinsale R D, Fyfe W S and Smewing J D, 1974. ^{18}O enriched ophiolitic metabasic rocks from E. Liguria (Italy), Pindos (Greece) and Troodos (Cyprus). Contrib. Mineral. Petrol. 47: 41-62.

Srikantappa C, Hormann P K and Raith M, 1984. Petrology and geochemistry of layered ultramafic to mafic complexes from the Archaean craton of Karnataka, southern India. In: Archaean Geochemistry, A Kroner, G N Hanson and A M Goodwin (Eds), Springer, Berlin: 138-160.

Srikantappa C, Raith M and Ackermand D, 1985. High grade regional metamorphism of ultramafic and mafic rocks from the Archaean Sargur terrane, Karnataka, south India. Precam. Res. 30: 189-219.

Stahl W, 1974. Carbon isotope fractionations in natural gases. Nature 251: 134.

Stakes D S and O'Neil J R, 1982. Mineralogy and stable isotope geochemistry of hydrothermally altered oceanic rocks. Earth Planet. Sci. Let. 57: 285-301.

Stephenson N C N, 1979. Coexisting garnets and biotites from Precambrian gneisses of the south coast of Western Australia. Lithos 12: 73-87.

Stoddard E F, 1976. Granulite facies metamorphism in the Colton-Rainbow Falls area, N. W. Adirondacks, New York. Unpubl. Ph.D. thesis, University of California, 289 pp.

Tarney J and Windley B F, 1977. Chemistry, thermal gradients and evolution of the lower continental crust. Jour. Geol. Soc. Lond. 134: 153-172.

Taylor H P Jr, 1968. The oxygen isotope geochemistry of igneous rocks. Contrib. Mineral. Petrol. 19: 1-74.

Taylor H P Jr, 1977. Water/rock interactions and the origin of H_2O in granitic batholiths. Jour. Geol. Soc. Lond. 133: 509-558.

Taylor H P and Sheppard S M F, 1986. Igneous Rocks: I. Processes of isotope fractionation and isotope systematics. In: Reviews in Mineralogy, Mineral. Soc. Am. 16: 227-271.

Thompson A B, 1976. Mineral reactions in pelitic rocks II. Calculation of some P-T-X (Fe-Mg) phase relations. Am. Jour. Sci. 276: 425-454.

Thompson A B, 1982. Dehydration melting of pelitic rocks and the generation of H_2O undersaturated granitic liquids. Am. Jour. Sci. 282: 1567-1595.

Thompson A B, 1983. Fluid absent metamorphism. Jour. Geol. Soc. Lond. 140: 533-547.

Thompson J B, 1957. The graphical analysis of mineral assemblages in pelitic schists. Am. Mineral. 42: 842-858.

Touret J, 1974a. Le facies granulite en Norvege Meridionale I. Les association mineralogiques. Lithos 4: 239-249.

Touret J, 1974b. Le facies granulite en Norvege Mreidionale II. Les inclusions fluides, Lithos 4: 423-436.

Tracy R J and Robinson P, 1983. Acadian Migmatite Types in Pelitic Rocks of central Massachusetts. In: Migmatites, Melting and Metamorphism, M P Atherton and C D Gribble (Eds), Shiva, Nantwich: 163-173.

Tracy R J, Robinson P and Thompson A B, 1976. Garnet composition and zoning in the determination of temperature and pressure of metamorphism, central Massachusetts. Am. Mineral. 61: 762-775.

Trommsdorff V and Evans B W, 1969. The stable association enstatite-forsterite -chlorite in amphibolite facies ultramafics of the Lepontine Alps. Schweiz. Mineral. Petrogr. Mitteil. B49: 325-332.

Turner F J, 1981. Metamorphic Petrology. McGraw-Hill, New York, 2nd Ed. 520pp.

Urey H C, 1947. The thermodynamics of isotopic substances. Jour. Chem. Soc. Lond. 2: 562-581.

Valley J W, 1986. Stable Isotope geochemistry of metamorphic rocks. Reviews in Mineralogy, Mineral. Soc. Am. 16: 445-490.

Valley J W and O'Neil J R, 1984. Fluid heterogeneity during granulite facies metamorphism in the Adirondacks: stable isotope evidence. Contrib. Mineral. Petrol. 85: 158-173.

van der Plas, 1966. The identification of detrital feldspars. Elsevier publishers, Amsterdam, 227pp.

Vaniman D T, Papike J J and Labotka T, 1980. Contact-metamorphic effects of the Stillwater complex, Montana: the concordant iron formation.

van Reenen D D, 1978. Metamorfe studies van granoliete en verwante hoe-graadse gesteentes in die suidelike grenssone van die Limpopo Metamorfe Kompleks in Suid Afrika. Unpubl. Ph.D. thesis, Rand Afrikaans University, Johannesburg. 478 pp.

van Reenen D D, 1983. Cordierite + garnet + hypersthene + biotite bearing assemblages as a function of changing metamorphic conditions in the southern marginal zone of the Limpopo Metamorphic Complex, South Africa. In: The Limpopo Belt, W J van Biljon and L H Legg (Eds), Spec. Publ. Geol. Soc. S. Africa 8: 143-167.

van Reenen D D, 1986. Hydration of cordierite and hypersthene and a description of the retrograde orthoamphibole isograd in the Limpopo Belt, South Africa. Am. Mineral. 71: 900-915.

van Reenen D D, Barton J M Jr, Roering C, Smit C A and van Schalkwyk J F, 1986. Himalayan tectonics in the Limpopo Belt. Geocongress 86, Geol. Soc. S. Africa: 893-898.

van Reenen D D, Barton J M Jr, Roering C, Smit C A and van Schalkwyk J F, 1987. Deep crustal response to continental collision: The Limpopo Belt of southern Africa. Geology 15: 11-14.

van Reenen D D and Hollister L S, 1988. Fluid inclusions in hydrated granulite facies rocks, southern marginal zone of the Limpopo Belt, South Africa. Geochim. Cosmo. Acta 52: 1057-1064.

van Reenen D D, Roering C, Smit C A, van Schalkwyk J F and Barton J M Jr, 1988. Evolution of the northern high grade margin of the Kaapvaal craton, South Africa. Jour. Geol. 96: 549-560.

Vernon R H and Flood R H, 1977. Interpretation of metamorphic assemblages containing fibrolitic sillimanite. Contrib. Mineral. Petrol. 59: 227-235.

Vennemann T W, 1985. The geochemistry of some mafic and ultramafic volcanic rocks from the Kromberg Formation of the Barberton greenstone belt. Unpubl. Honours thesis, University of Cape Town, 180pp.

Viljoen M J and Viljoen R P, 1969. The geology and geochemistry of the ultramafic unit of the Onverwacht group and a proposed new class of igneous rocks. Spec. Publ. Geol. Soc. S. Africa 2: 55-112.

Viljoen M J, Viljoen R P and Pearton T N, 1982. The nature and distribution of Archaean Komatiite volcanics in South Africa. In: Komatiites, N T Arndt and E G Nisbet (Eds), George Allen and Unwin publishers, London: 53-79.

Viljoen R P and Viljoen M J, 1970. The geology and geochemistry of the layered ultramafic bodies of the Kaapmuiden area, Barberton Mountain Land. In: Symposium on the Bushveld Igneous Complex and other layered intrusions. Geol. Soc. S. Africa Spec. Publ.: 601-686.

Vry J, Brown P E, Valley J W and Morrison J, 1988. Constraints on granulite

genesis from carbon isotope compositions of cordierite and graphite. Nature 332: 66-68.

Walther J V and Orville P M, 1982. Volatile production and transport in regional metamorphism. Contrib. Mineral. Petrol. 79: 252-257.

Warren R G, 1983. Metamorphic and tectonic evolution of granulites, Arunta block, central Australia. Nature 305: 300-303.

Waters D J, 1986. Metamorphic zonation and thermal history of pelitic gneisses from western Namaqualand, South africa. Trans. Geol. Soc. S. Africa 89: 97-102.

Waters D J, 1988. Partial melting and the formation of granulite facies assemblages in Namaqualand, South Africa. Jour. Metam. Geol. 6: 387-404.

Waters D J and Whales C J, 1984. Dehydration melting and the granulite transition in metapelites from southern Namaqualand, South Africa. Contrib. Mineral. Petrol. 88: 269-275.

Watkeys M K, 1983. Brief explanatory notes on the provisional geologic map of the Limpopo belt and environs. In: The Limpopo Belt, W J van Biljon and J H Legg (Eds), Geol. Soc. S. Africa Spec. Publ. 8: 5-8.

Watkeys M K, 1986. The Achab Gneiss: a "floor" in Bushmanland or a flaw in Namaqualand? Trans. Geol. Soc. S. Africa. 89: 103-116.

Watkeys M K, Light M P R and Broderick T J, 1983. A retrospective view of the central zone of the Limpopo belt, Zimbabwe. In: The Limpopo Belt, W J van Biljon and J H legg (Eds), Spec. Publ. Geol. Soc. S. Africa 8: 65-80.

Watkeys M K, Vennemann T W and Armstrong R A, 1988. The Limpopo belt: Natural consequence of a PTt loop. Geocongress 88, Geol. Soc. S. Africa: 721-724.

Weis P L, Friedman I and Gleason J P, 1981. The origin of epigenetic graphite: evidence from isotopes. Geochim. Cosmo. Acta. 45: 2325-2332.

Wells P R A, 1977. Pyroxene thermometry in simple and complex systems. Contrib. Mineral. Petrol. 62: 129-139.

Wells P R A, 1979. Chemical and thermal evolution of Archaean sialic crust, southern West Greenland. Jour. Petrol. 20: 187-226.

Wenk E and Keller F, 1969. Isograde in Amphibolitserien der Zentralalpen. Schweiz. Mineral. Petrogr. Mitteil. B49: 157-199.

Wenner D B and Taylor H P, 1971. Temperature of serpentinization of ultramafic rocks based on $^{18}O/^{16}O$ fractionation between coexisting serpentine and magnetite. Contrib. Mineral. Petrol. 32: 165-182.

Willis J P, Ahrens L H, Danchin R V, Erlank A J, Gurney J J, Hofmeyer P K, McCarthy T S and Orren M J, 1971. Some interelement relationships between lunar rocks and fines and stony meteorites. In: E D Levinson (Ed), Proceedings of the second lunar science conference 2, MIT Press, Cambridge Mass.: 1123.

Willis J P, Erlank A J, Gurney J J, Theil R H and Ahrens L H, 1972. Major, minor and trace element data for some Apollo 11, 12, 14 and 15 samples. In: L D Heymann (Ed), Proceedings of the third lunar science conference, 2, MIT Press, Cambridge, Mass. : 1269.

Winkler H G F, 1976. Petrogenesis of Metamorphic Rocks. Springer Verlag, 4th Edition, 334pp.

White A J R and Chappell B W, 1977. Ultrametamorphism and granitoid genesis. Tectonophysics 43: 4-22.

Woodsworth G J, 1977. Homogenization of zoned garnets from pelitic schists. Can. Mineral. 15: 230-242.

Wood B J, 1974. The solubility of alumina in orthopyroxene coexisting with garnet. Contrib. Mineral. Petrol. 46: 1-15.

Wood B J and Banno S, 1973. Garnet-orthopyroxene and orthopyroxene-clinopyroxene relationships in simple and complex systems. Contrib. Mineral. Petrol. 42: 109-124.

Wood B J and Fraser D G, 1977. Elementary Thermodynamics for Geologists. Oxford University Press, 303pp.

Wood B J and Walther J V, 1983. Rates of hydrothermal reactions. Science 122: 413-415.

Wood B J and Wather J V, 1986. Fluid flow during metamorphism and its implications for fluid-rock ratios. In: Fluid-Rock Interactions, Dev. Phys. Geochem. 5: 89-108.

Yardley B W D, 1983. Quartz veins and devolatization during metamorphism. Jour. Geol. Soc. Lond. 140: 657-663.