

Genesis of Metasomatic Sapphirine-Corundum-Spinel-bearing

Granulites in Sri Lanka

An Integrated Field, Petrological and Geochemical Study

Dissertation

Zur Erlangung des Grades

‘Doktor der Naturwissenschaften’

am Fachbereich Geowissenschaften

der Johannes Gutenberg-Universität Mainz

G.W.A. Rohan Fernando

aus Matale, Sri Lanka

Mainz 2001

Ich versichere, daß ich die Arbeit selbständig und nur unter Verwendung der angegebenen Quellen und Hilfsmittel verfaßt habe.

Mainz, den 16 .01.2001

ACKNOWLEDGMENTS

It is a great pleasure to think of all those who have contributed to my research work from various aspects. Foremost, I wish to state my deepest appreciation and gratitude to my chief advisor, who is also the head of the petrology research group, for accepting me as his PhD student. He stimulated my work with great interest and taught me the basic fundamentals of phase petrology, fluid- rock interactions and computer modeling. He nurtured me how to resolve research problems independently, especially the problems in high-grade metamorphism and metasomatism. Working with him is a great privilege and I wish to extend my very special thanks to him for his patience, guidance and especially for having the unpleasant task of correcting each version of my manuscript. I am indebted to my co-advisor, without whose help guidance and constant encouragements, this presentation may not have become a success. His advices are invaluable in mineralogical and gemmological aspects of this research work. He generously provided financial support for chemical analyses for the entire project from the Institute of Gemstone Research and also for participating international conferences, which enabled me to strengthen international contacts.

This work was benefited from the scholarship from the German Academic Exchange Service (DAAD) of the Federal Republic of Germany. I would like to thank DAAD for generous financial help during the entire stay in Germany. Travelling and fieldwork were also supported by grants from the DAAD.

Throughout the course of this project I have benefited from fruitful discussions with members of 'petrology research group'. Thanks to all of them for their encouragement and all enjoyable discussions, which I benefited so much. Many thanks to all of technical staff of the institut für Geowissenschaften, especially the incharge of the electron microprobe and XRF. This presentation greatly benefited from the advanced geological software of 'Programm Gibbs' and 'PerpleX'. Thanks for the providers of the softwares and their lively discussions and written communications through out the study.

In Sri Lanka, I wish to thank the co-ordinator of this academic exchange program and for his comments and English corrections of the first manuscript. Special thanks to the Geological Survey and Mines Bureau (GSMB) and the National Building Research Organization (NBRO) in Sri Lanka for providing me with a preliminary geological report

of the area around Rupaha and to the for allowing me to use their unpublished geological maps.

My mother and all the family members always encouraged me to continue my studies during my entire life. And last but not least, my beloved wife had a tremendous patient, when I was away from her in Germany for more than 3 years or when I had long nights in the University while she accompanied me in Mainz. She also helped me during the field works. She was able to teach me that life does exist outside of geology. It is to all of you I dedicate this thesis.

ZUSAMMENFASSUNG

Ziel der vorliegenden Arbeit war es, die Mechanismen des Massentransfers, die Zusammensetzung und Rolle der Fluide während der krustalen Metasomatose in hochtemperierten metamorphen Gebieten zu verstehen. Für diese Untersuchung bietet sich die Region Rupaha an, ein Gebiet im Hochland-Komplex von Sri Lanka. Es repräsentiert einen Teil des Superkontinentes Gondwana. An 10 Lokalitäten wurden Aufschlüsse ultramafischer Gesteine, eingebettet in Granuliten, beprobt. Die Grenze zwischen Ultramafiten und Granuliten läßt sich mit Hilfe einer ca. 50cm breiten Reaktionszone kartieren. Ausgehend von den Ultramafiten folgen in Richtung der Granulite drei Zonen mit den folgenden, charakteristischen Mineralvergesellschaftungen: (1). Phlogopit + Spinell + Sapphirin, (2). Spinell + Sapphirin + Korund sowie (3). Korund + Biotit + Plagioklas.

Um den Verlauf des P-T-t-Pfades, den Höhepunkt der Metamorphose und die Exhumierungsgeschichte festzustellen, wurden verschiedene Thermobarometer ebenso wie ein Diffusionsmodell für die Zonierung von Granat angewendet. Dabei ergab sich eine maximale Temperatur von $875 \pm 20^\circ\text{C}$ (Opx-Cpx-Thermometer) und ein maximaler Druck von $9.0 \pm 0.1\text{kbar}$ (Grt-Cpx-Plag-Qz) für die sauren Granulite. Für die Ultramafite ergeben sich für den Höhepunkt Temperaturen von $840 \pm 70^\circ\text{C}$ (Opx-Cpx-Thermometer) und ein Druck von 9kbar. Aus koexistierendem Spinell und Sapphirin in der Reaktionszone ergibt sich eine Temperatur von $820 \pm 40^\circ\text{C}$. Dies stimmt mit den Maximaltemperaturen überein, die von den benachbarten Granuliten und Ultramafiten berichtet werden. Die strukturelle Konkordanz der Ultramafite und der sauren, granulitischen Wirtsgesteine stützt die These, daß alle untersuchten Einheiten die gleiche Peakmetamorphose erfahren haben. Die Modellierung der Diffusion in den zonierten Granaten der mafischen Ultramafite führt zu einer dreistufigen Abkühlungsgeschichte. Im initialen Abkühlungsstadium wird die maximale Abkühlrate auf $1^\circ\text{C}/\text{Ma}$ geschätzt, gefolgt von einer zweiten Abkühlphase mit einer Rate von $30^\circ\text{C}/\text{Ma}$. Die äußeren Granatränder weisen auf eine etwas langsamere Abkühlung mit einer Rate von $10 - 15^\circ\text{C}/\text{Ma}$ hin.

Die Abfolge der Mineralzonen, die in den Reaktionszonen, die die Ultramafite von den Si-reichen Gesteinen trennen, verschiedene Al-reiche, Si-untersättigte Minerale enthalten, können mit Hilfe des Diffusionsmodells erklärt werden. Dies bezieht auch die Diffusion von Mg von den Ultramafiten über die verschiedenen Lagen ein, sowie die Diffusion von K und Si in entgegengesetzter Richtung. Die chemischen Potentiale von Mg und Si erzeugten einen kontinuierlichen, monotonen Gradienten, der einen diffusionalen Transport im stabilen Zustand über das Profil ermöglichte. Die starke Al-Anreicherung und der bemerkenswerte Verlust von Si während der Ausbildung der Reaktionsbänder können aus Isoconendiagrammen verdeutlicht werden. Der Si-Verlust und die Al-Zunahme sind sehr wahrscheinlich auf Fluide zurückzuführen, die parallel zu den Grenzbereichen der Gesteineinheiten zirkulierten.

Diese Studie hat nun gezeigt, daß der Massentransport bei verschiedenen geologischen Verhältnissen nicht nur von Druck- und Temperaturbedingungen, sondern ganz besonders auch vom P_{H_2O} und der Konzentration von Chlor und Fluor in wässrigen Lösungen kontrolliert wird.

ABSTRACT

The goal of the present study is to understand the mechanism of mass transfer, the composition and the role of fluids during crustal metasomatism in high-temperature metamorphic terranes. A well constrained case study, a locality at Rupaha, Sri Lanka was selected. It is located in the Highland Complex of Sri Lanka, which represents a small, but important fragment of the super-continent Gondwana. Excellent exposures of ultramafic rocks, which are embedded in granulites, were found at 10 localities. These provide a unique background for understanding the metasomatic processes. The boundary between the ultramafic and the granulite rocks are lined with metasomatic reaction zones up to 50cm in width. Progressing from the ultramafics to the granulite host rock, three distinct zones with the following mineral assemblages can be distinguished: (1). phlogopite + spinel + sapphirine, (2). spinel + sapphirine + corundum and (3). corundum + biotite + plagioclase.

In order to assess the P-T-t path, the peak metamorphism and the exhumation history were constrained using different thermobarometers, as well as a diffusion model of garnet zoning. A maximum temperature of $875 \pm 20^\circ\text{C}$ (Opx-Cpx thermometer) and at the peak pressure of 9.0 ± 0.1 kbar (Grt-Cpx-Pl-Qtz) was calculated for the silicic granulite. The ultramafic rocks recorded a peak temperature of $840 \pm 70^\circ\text{C}$ (Opx-Cpx thermometer) at 9 kbar. Coexisting spinel and sapphirine from the reaction zone yield a temperature of $820 \pm 40^\circ\text{C}$. This is in agreement with the peak-temperatures recorded in the adjacent granulites and ultramafics rocks. The structural concordance of the ultramafic rocks with the siliceous granulite host rock further support the suggestion, that all units have experienced the same peak metamorphism. Diffusion modeling of retrograde zoning in garnets from mafic granulites suggests a three-step cooling history. A maximum cooling rate of $1^\circ\text{C}/\text{Ma}$ is estimated during the initial stage of cooling, followed by a cooling rate of $\sim 30^\circ\text{C}/\text{Ma}$. The outermost rims of garnet indicate a slightly slower cooling rate at about $10\text{-}15^\circ\text{C}/\text{Ma}$.

The sequences of mineral zones, containing a variety of Al-rich, silica undersaturated minerals in the reaction zones separating the ultramafic rocks from the silica-rich rocks can be explained by a diffusion model. This involves the diffusion of Mg from ultramafic rocks across the layers, and K and Si diffuse in opposite direction. Chemical potential of Mg and Si generated continuous monotonic gradient, allowing steady state diffusional

transport across the profile. The strong enrichment in Al, and the considerable loss of Si, during the formation of reaction bands can be inferred from isocon diagrams. Some Al was probably added to the reaction zones, while Si was lost. This is most likely due to fluids percolating parallel to the zones at the boundary of the rock units.

This study has shown that not only pressure and temperature conditions but most importantly P_{H_2O} and the concentration of the chlorine and fluorine in aqueous fluids also control the mass transport in different geological environments.

TABLE OF CONTENTS

Acknowledgments	i
Abstract (German summary).	iii
Abstract	v
Chapter 1 Introduction	1
Chapter 2 Retrograde diffusion zoning in garnet: Implications for three-stage cooling history of mafic granulites in the Highland Complex of Sri Lanka	25
Chapter 3 High-temperature metasomatism and retrogression of granulite facies..... ultramafics from the Highland complex of Sri Lanka: Field relationships, phase equilibria and fluid fluxes	57
Chapter 4 Genesis of silica-undersaturated sapphirine-corundum-spinel-bearing- Reaction zones from Rupaha, Sri Lanka	92
Appendix A List of Abbreviations	143
Appendix B Analytical procedures 1 – X-Ray Fluorescence Spectroscopy.....	145
Analytical procedures 2 – Electron Probe Microanalyser	151
Appendix C Tables of Chemical analysis	154
Appendix D Sample List.....	173

Chapter 1

Introduction

GENERAL INTRODUCTION

Crustal fluids have long been recognized as an important driving force in metamorphic systems. Fluids play a potentially major role in the transfer of thermal energy in the crust (Braddy 1988), as a catalyst of metamorphic reactions (Rubie 1986), a driving force for reactions (Ferry 1984) and as a medium for mass transfer (Fyfe et al. 1978). Fluids are required for large-scale metasomatism because they transport solutes by diffusion, and more importantly by infiltration. In such systems, the dissolution and precipitation of minerals by crustal fluids control the location and the size of ore deposits and other metasomatic rocks. The role of fluids, their composition, source and amount during the deep-crustal granulite grade metamorphism and metasomatism remains the subject of lively discussions (e.g. Valley and O'Neil 1984; Newton 1986; Valley et al. 1990; Touret and Hartl 1990).

The theoretical studies in understanding the fundamental physical and chemical parameters that governs the fluid flow and mass transport have advanced significantly (e.g. Frantz and Weisbrod 1974; Frantz and Mao 1976, 1979; Helgeson and Lichtner 1987). Nevertheless, applications are limited to simple idealized systems. A few studies have attempted to quantify diffusion-advection processes in deep crustal environments using, detailed stable isotopic analyses across intact, well-exposed lithological contacts (e.g. Cartwright and Valley 1991).

This study provides constraints on the mechanism of mass transfer, the composition, and the role of fluids in the deep crust, by means of, a well-constrained case study in a previously poorly known terrane of Sri Lanka. I have conducted an integrated field, petrologic and geochemical study of the siliceous granulite-ultramafic rock suite in the Rupaha area. This suite in the Proterozoic basement Sri Lanka contains is one of the best-preserved examples of metasomatic alteration. Metasomatic reaction zones separate the silica-saturated granulites from meta-ultramafic rocks. The most spectacular occurrence in the reaction zone is the presence of colourless sapphirine within the reaction zones. It is the fourth reported occurrence of sapphirine in the Sri Lankan Proterozoic basement (Osanaï et al. 1989, 1996; Kriegsman 1991a, Kriegsman and Schumacher 2000). Formation of sapphirine in metasomatic zones has so far been reported only in a few instances (Schumacher and Robinson 1987; Dunkley et al. 1999; Hokada et al. 1999).

The latter part of this chapter contains a short summary of the geology of Sri Lanka: recently published data on basement units, lithology, geochronology, large-scale structural trends and its metamorphic history. It also includes a detailed account of the geology of Rupaha, which including a new geological map by the PhD candidate. Chapters 2 to 4 have been written in the form of papers. Hence, there may be some overlapping of the text, especially during the interpretation of geology of Sri Lanka. Mineral abbreviations follow Kretz (1983) throughout the thesis.

Chapter 2 documents the P-T-t path of the granulites at Rupaha. The P-T-t paths characterized by isobaric cooling at deep crustal levels suggest a more prolonged residence in the lower crust. The rocks have experienced slow cooling during this episode and much or all the information needed to construct P-T paths associated with these rocks have erased much of the prograde history. We estimated the cooling history of the area using diffusion modeling of retrograde zoning in garnets from the mafic granulites. A three stage cooling history is proposed.

Chapter 3 gives a detailed account of peak and post-peak metamorphic conditions of the ultramafic rocks at Rupaha. The peak metamorphic assemblages enstatite, diopside, forsterite, spinel and phlogopite are overprinted by retrograde assemblages containing tremolite, talc, dolomite and serpentine. P-T-Phase equilibria, activity-activity diagrams, and temperature-activity diagrams for these assemblages are used to decipher the intricate history of these rocks. They have undergone granulite facies metamorphism, followed by a protracted history of fluid-rock interactions on cooling and exhumation.

The complete petrography, textures, and phase petrology of the metasomatic zones are discussed in **Chapter 4**. The sequence of mineral zones that formed between ultramafic and pelitic units are composed of corundum, sapphirine, spinel, biotite and plagioclase. The P-T conditions of the metasomatic zones were evaluated to ascertain this indicates that: these bands formed during granulite facies conditions. This was achieved through spinel-sapphirine thermometry and T- μ diagrams. The final part of this chapter discusses the mechanism of the mass transport between the ultramafic rocks and the siliceous granulites. Here, chemical potential diagrams, mass balance calculations, biotite chemistry

are used. Mass balance calculations between two rock units show high amounts of mass changes for Si, Mg and some trace elements. Major element chemistry and halogen content of biotite across the rock unit provide insight into the fluid composition.

INTRODUCTION TO THE GEOLOGY OF SRI LANKA

Sri Lanka was a part of East Gondwana, together with fragments of Antarctica, Australia, India, Madagascar, Mozambique and Tanzania (e.g. Powell et al., 1988; Kröner, 1991; Yoshida et al., 1992; Jacobs et al., 1998; Dissanayake and Chandrajith 1999). Sri Lanka acted as a bridge through which Antarctica and East Africa can be correlated. It is thus not surprising that Sri Lanka reveals remarkable geological, geochronological and geotectonic similarities with its neighbouring Gondwana fragments.

Sri Lankan geology has received increasing attention in the last two decades. As a result of this, the nomenclature of rock units, definition of geological boundaries and the timing of major metamorphic and tectonic events have changed substantially. The nomenclature of the basement units, as described in the special issue of the *Journal of Precambrian Research* - volume 66 on 'Tectonic, metamorphic and isotopic evolution of deep crustal rocks, with special emphasis on Sri Lanka', is used throughout this thesis.

The Proterozoic basement of Sri Lanka exposes substantial parts of the lower continental crust. Four different units were distinguished on the basis of isotopical, geochronological, geochemical and petrological constraints (e.g. Kröner et al., 1991; Cooray 1994; Milisenda et al., 1994)(Fig.1.1).

- (1). the Highland Complex (HC);
- (2). the Vijayan Complex (VC);
- (3). the Wannai Complex (WC) and
- (4). the Kadugannawa Complex (KC)

The HC consists mainly of interbedded metapelites, quartzites, marbles, metabasites and charnockites. Calc-silicate gneisses, sapphirine-bearing granulites, cordierite-bearing gneisses and corundum-bearing gneisses are exposed in minor quantities. The VC exposed in eastern Sri Lanka consists of meta-igneous gneisses of tonalitic to leucogranitic

composition. Rocks of the KC are seen in the cores of the six doubly plunging synforms, which were named as '*Arenas*' by Vithanage (1972). The dominant rocks of the KC and WC are hornblende-biotite gneisses, granitic, granodioritic and tonalitic associations. Some granulites are exposed in the southern part of VC near Buttala and Kataragama. They comprise rocks similar to those of HC and are interpreted as tectonic nappes namely: Buttala klippe, Kuda Oya klippe and Kataragama klippe (Fig 1.1).

Isotopic and tectonic history

Isotopic data from HC shows prolonged crustal history. Supracrustal rocks of the central high-grade belt of HC were derived from early Proterozoic to late Archaean source terranes (3.2 - 2.4 Ga) and were probably deposited some ~2 - 2.4 Ga ago in a Proterozoic basement, which is now believed to be the host for the present day stratigraphic succession (Table 1.1, see also Crowford 1969; Crowford and Oliver 1969; Hölzl et al. 1994; Kröner et al. 1987; Milisenda et al. 1988). The rocks from VC, WC and KC, which are predominantly of granitoids, yield relatively younger deposition ages at ~1.1Ga ago (Milisenda et al. 1988). This implies that igneous activity had occurred after the deposition of supracrustal rocks of HC, but prior to fabric-forming events since their tectonic layering is parallel to that of supracrustal rocks (Table 1.1. see also Hölzl et al. 1991, 1994; Kröner and Jaeckel 1994).

The HC and WC were separated from each other until at least 750 Ma ago. They must have come together, perhaps during WC thrusting over HC, prior to peak granulite facies metamorphism (Kröner and Jaeckel 1994). The boundary between HC and WC is an isotopic boundary based on large-scale sample grids and, as such, not recognizable in the field (Milisenda et al. 1988; Milisenda 1991). The absence of field evidence at the boundary of WC and HC provided that high-grade fabric-forming events may have been destroyed the possible pre-peak metamorphic tectonism (Kröner et al. 1991). The source terrane for the Wannu supracrustal association remains controversial and is unlikely to be present in Sri Lanka.

Although HC and WC are characterized by different primary sedimentary and magmatic ages, it appears that both segments have been affected by a common peak metamorphism of Pan-African age. The timing of peak metamorphism was estimated to be ~610-~550 Ma

old. No significant Pb loss occurred in the time record between 1900 Ma (the end of the deposition of supracrustal rocks of HC) and 600 Ma ago (Bauer, et al., 1991; Hölzl et al., 1991, 1994; Kröner et al., 1991; Kröner and Williams, 1993). Taking into account similarities in geology, geotectonics and geochronology in the other Gondwana fragments, the rocks of the HC show a link to the Pan-African Mozambique belt (Kriegsman 1991b; Kröner et al. 1991; Powell et al. 1998; Dissanayake and Chandrajith 1999). The HC and WC were together thrust over the VC with a top to the eastward vergence at about 580-550 Ma under upper amphibolite facies conditions (Kleinschrodt 1994). The rocks of WC have been subjected to upper amphibolite to granulite facies metamorphism. Further exhumation of the lower crustal rocks was not accompanied by tectonic events as all deformation fabrics were preserved during subsequent slow cooling.

During the Jurassic time, the Sri Lankan basement experienced crustal extension (Table 1.1 see also Powell et al., 1988). The Jurassic sediments on the top of the crystalline basement are preserved at three isolated occurrences (Tabbowa, Andigama and Pallama) in northwestern Sri Lanka (Cooray, 1984; Vithanage, 1985) (Fig 1.1.). After the initial break-up of Gondwana, Sri Lanka has moved together with India. In the Miocene period, the Cauvery basin, which separates India and Sri Lanka, was created. It was filled by a thick cover of limestone, which is now resting on the northwestern coastal strip of Sri Lanka and the southeastern India (Vithanage, 1985). Table.1.1 summarizes the geochronological and tectonic events identified so far in the basement of Sri Lanka.

Structural history

The structural evolution presented here is based on the detailed studies of Berger and Jayasinghe (1976), Voll and Kleinschrodt (1991), Kriegsman (1993) and Kehelpannala (1997). At least three major phases of structural events (D_1 , D_2 and D_3) have been recognized. Some workers have identified locally up to 6 deformation events (e.g. Kehelpannala, 1997). Nevertheless, they can be broadly categorised into three major phases (Fig 1.2).

D_{1a} – Early extension and low P/high T metamorphism

The growth of fibrolitic sillimanite suggest the low P/high T metamorphism prior to crustal thickening occurred at the earliest deformation.

D_{1b} – Crustal thickening

The crustal thickening is demarcated by crenulated sillimanite inclusions in garnet and the formation of granitic layering, which now appear as parallel to the early foliation planes (S_1). Crustal thickening was followed by peak granulite metamorphism at 9kbar at the deepest levels of Highland Complex (Schumacher et al. 1990; Kriegsman 1993).

D₂ – Extensional collapse

D_2 deformation event is dominant in many places. The large-scale isoclinal and recumbent folds, boudinage of metabasite and calc-silicate rocks in the metapelites matrix and the nappe tectonics are ascribed to the D_2 events. D_2 affected close to the peak metamorphic conditions as evidenced from L-S tectonic fabric with N-S stretching lineation, present in many rock types.

D₃ – Late folding and thrusting

The last major deformation (D_3) took place with the development of N-S trending upright folds within HC, thrusting of HC over VC, local development of biotite lineation with E-W azimuth, E-verging asymmetric inclined folds near HC/VC contact cut by eastward direct thrusts, N-S trending upright folds and steep shear zones.

Metamorphic history

Peak P-T conditions of crystalline rocks of Sri Lanka have been estimated using numerous thermobarometers and different mineral paragenesis. Schumacher and Faulhaber (1994) estimated the P-T condition of the Eastern, North-Eastern and South-Eastern parts of the HC at 760-830°C (Grt-Opx thermometer of Harley, 1984) and 9-10kbar (Grt-Cpx-Pl-Qtz barometer of Newton and Perkins, 1982). Sandiford et al. (1988), using Grt-Cpx and Grt-Opx thermometry, estimated that the minimum temperature of peak metamorphism was 670-730°C. Kriegsman (1993) obtained the peak equilibrium temperatures of sapphirine-bearing granulites in HC at 830°C and 9 kbar with a petrogenetic grid. Schenk et al. (1988) (two-pyroxene thermometry) obtained a maximum temperature of 900°C for the HC. Voll et al. (1994) derived peak temperatures of metamorphism at 850-900°C using two-feldspar thermometry.

It is now evident that the ion-exchange thermometries, all of which assemblages include garnet, show peak temperatures and pressures at lower values relative to two-pyroxene and two-feldspar thermometries. It can be speculated that all thermometries, which have garnet as an exchange mineral, show lower values due to retrograde resetting of garnet during slow cooling. Therefore, it seems that most of the granulites in HC experienced a maximum temperature of around 850-900°C as revealed by two-pyroxene and two-feldspar thermometries.

A field pressure gradient in the HC has been proposed from the central and eastern part to the southwestern regions. The maximum pressures at 9-10 kbar in the central and eastern parts of HC decrease to about 5-6 kbar in the western part of HC (Hapuarachchi, 1975; Newton and Hansen, 1986; Schenk et al, 1991; Schumacher et al., 1990; Faulhaber and Raith, 1991; Schumacher and Faulhaber, 1994), though this was questioned by Perera (1984) and Mathavan and Fernando (1991).

The retrograde path of the HC is controversial. The cooling and decompression paths obtained from meta-igneous rocks are different from those obtained from metasedimentary rocks, although they are part of the same supracrustal succession. Sandiford et al. (1988) obtained an early decompression path for the orthogneisses followed by an isobaric cooling path. An early isobaric cooling path prior to the decompression event was recognised in the metabasite and Fe-rich charnockites (Schumacher et al. 1990; Prame 1991). The isobaric cooling subsequent to the decompression event was previously thought to confine only to the meta-igneous rocks of the HC. These events are now also reported in metasediments in the Buttala klippe (Mathavan and Fernando, *in press*).

A clockwise P-T path of the whole HC is indicated by the presence of early kyanite inclusions in garnets, following peak metamorphic sillimanite and the retrograde andalusite in metapelitic rocks (Hiroi et al. 1987; Raase and Schenk 1994). Kriegsman (1993) reviewed the available P-T and structural data, and, combined with his own data from sapphirine-bearing granulites, proposed a clockwise P-T-t path for the Sri Lankan lower crust. This would imply a crustal thickening event, which was followed by heating and unroofing (Fig. 1.2).

The temperatures in the WC, VC and KC are identical to each other. They record considerably lower temperatures than the rocks from HC. Hornblende-plagioclase thermometry of amphibolites yields a temperature of 700 ± 75 °C. The overall pressure was estimated at 6.9 kbar (Burton and O’Nions 1990; Schumacher et al. 1990).

GEOLOGY OF THE RUPAHA AREA

The area around Rupaha is part of a hilly to mountainous terrain that also forms the majority of the central highlands of Sri Lanka. The whole area is crossed by a northeasterly flowing trellis drainage system. Much of the drainage follows fractures, joints and distinct shear zones. In general terms, it seems that there is a close match between topography and the geological framework of the area. The rocks with a high percentage of quartz (e.g. quartzite, charnockite) are responsible for most of the ridges of the area, while easily weathered carbonate-bearing rocks and biotite-feldspar-rich rocks form valleys. A noteworthy feature is that numerous peaks protrude as high as 2,000 metres above sea level.

The geological and structural framework of this area is largely based on a provisional geological map (1:100 000) of the Geological survey and Mines Bureau of Sri Lanka (GSMB). A detailed mapping on 1:10,000 scale was needed for very thin bands of different rock units, which could not be identified in large-scale maps (Fig. 1.3). The rocks strike generally N-S, a dip of 25-40° towards the west. Apart from this, the northwestern part of the area is characterized by a doubly plunging synform with an axial trace of NNW-SSE.

Two principal rock units were identified and are broadly categorized as orthogneisses and paragneisses. Orthogneisses are largely composed of charnockites, charnockite gneisses and biotite gneisses. The latter are grey gneisses, but usually lack orthopyroxene. The orthogneisses in the area are of granodioritic to quartz monzonitic composition. They contain mafic minerals of orthopyroxene, clinopyroxene, hornblende and a few biotites. Some quartz grains are up to few centimetres long and mark an intensely flattened and stretched texture.

Granulite grade, multiply deformed metasediments are exposed within a synform in the NW, as well as in thin bands in the rest of the mapping area. These paragneisses consist mainly of quartzites, quartzofeldspathic gneisses, a few scattered occurrences of marbles and semi pelitic gneisses, including garnet-biotite gneisses, corundum-biotite gneisses and garnet-sillimanite-graphite gneisses, with large porphyroblastic garnets formerly termed as '*khondalites*'. Streaky, banded khondalite layers act as stratigraphic markers in the area. The pelitic paragneisses are extensively weathered, probably due to the presence of high feldspar content. A few outcrops of marbles occur throughout. Accessory minerals include apatite, zircon, ilmenite and rutile. Outcrops of garnet-biotite gneisses have been partly migmatized. The migmatized patches are essentially leucocratic, distinctly layered medium-grained quartzo-feldspathic gneisses, intercalated at places with charnockitic gneisses.

Ultramafic complexes have been found to the west of the Rupaha village. They were interpreted earlier as intrusive bodies, which cut through older basement rocks. Coomaraswamy (1904) provided the first report of a serpentinite deposit from Rupaha and termed it a 'serpentine marble' mainly due to its pale green colour and the differences in mineralogy from those of other marbles. Soyza (1986) has provided an account of the economic importance of the body. Siriwardena (1988) has carried out a preliminary study of this 'serpentine marble' deposit. He described two corundum-bearing locations near the ultramafic body. Corundum-bearing rocks described here are from one of 11 reported *in-situ* occurrences in Sri Lanka referred by Coomaraswamy (1903), Cooray and Kumarapeli (1960), Coates (1935), Wells (1956), Silva and Siriwardena (1988) and Rupasinghe and Dissanayake (1987). Recent work by Fernando et al. (1995) interpreted the ultramafic body as a part of the supracrustal succession, which has been subjected to intense high-grade metamorphism and deformation events.

Despite the fact that there is a considerable wealth of information on the economic importance of the serpentinite body, no attempts were made to present a mechanism for the formation of silica-undersaturated corundum bearing rocks at the contact of this serpentinite body. The present study focuses on the serpentinite body and its contact rock units, which are well exposed along the tributary of the main river Halgran Oya, named '*Garandu Kandura*' (Fig. 1.4).

GEOLOGY OF THE STUDY AREA

The geology around the deposit was described by Siriwardena (1988). The exposure around serpentinite body contains three mineralogically and the petrologically different rock units; (1). granulite zone; (2). ultramafic zone; (3). reaction zone. The granulite zone preserves the original metamorphic textures and minerals typical of granulites in the area. The reaction zone has been recognized in between these two rock units. This succession is roughly repeated in at least ten locations within 300m distances before the rocks are covered by thick soil overburden (Fig. 1.4).

Granulite zone

The rocks from the Granulite zone are described in the preceding section as garnet-biotite gneisses and charnockites. But in particular, Garnet-biotite gneisses and charnockites display thin compositional banding with development of lineated quartz and mica flakes. The thin bands of impure marble (calc-silicate gneisses) and sillimanite-biotite gneisses are intercalated with charnockites and garnet-biotite gneisses in the vicinity of the ultramafic rocks (Fig. 1.4).

Ultramafic zone

Ultramafic rocks form as several lens shaped bodies with a maximum width of 100 metres and extensions along strikes of 50 metres or more. The Rupaha exposure consists predominantly of medium-grained, dark brown and greenish-grey serpentinites, with carbonate veins and are intensely sheared. At places, the serpentinites contain white coloured, fresh, medium-grained orthopyroxenes. Pale green ultramafic rock is characterized by numerous cross cutting veinlets in irregular fashion. The dark green ultramafic variety is less altered; nevertheless some purplish coloured clusters of spinel are embedded at places. The textural features demonstrated that the ultramafic body has been subjected to high-grade metamorphism with other regional granulitic rocks. The phlogopite is found at the interface of ultramafic-siliceous granulite.

Reaction zone

The reaction zone is composed of four distinct mineral assemblages. The zone adjacent to siliceous gneisses consists of syenitic-looking Crn(5%)-Bt-Pl-bearing gneisses. This zone is generally up to 3m thick at places. The randomly arranged porphyroblastic corundum

crystals are embedded in this feldspar matrix in the quartz undersaturated rock. The rest of the zone consists of thin bands of Crn(30%) + Pl + Bt-bearing gneisses, Crn + Spr + Spinel-bearing gneisses and Phl + Spr + Spl-bearing gneisses. The zone boundaries are very sharp, which are roughly aligned parallel to the regional foliation.

REFERENCES

- Bauer N, Kröner A, Todt W, Liew TC, Hofmann AW* (1991). U-Pb isotopic systematics of zircons from prograde and retrograde transition zones in high-grade orthogneisses, Sri Lanka. *J. Geol.* 99: 527-545
- Berger AR, Jayasinghe NR* (1976). Precambrian structure and chronology in the Highland Series of Sri Lanka. *Precam. Res.* 3: 559-576
- Braddy JB* (1988) The role of volatiles in the thermal history of metamorphic terranes. *J. Petrol.* 29: 1187-1213
- Burton KW, O'Nions RK* (1990). The timescale and mechanism of granulite formation at Kurunegala, Sri Lanka. *Contrib. Mineral. Petrol.* 106: 66-89
- Cartwright I, Valley JW* (1991). Steep oxygen-isotope gradients at marble-metagranite contacts in the northwest Adirondack Mountains. New York USA: products of fluid hosted diffusion. *Earth Planet. Sci. Lett.* 107: 148-163
- Coates JS* (1935). The Geology of Ceylon, *Cey. J. Sci.* 19: 101-191
- Coomaraswamy AK* (1903). Occurrences of corundum insitu near Kandy, Ceylon. *Geol. Mag.* 21: 348-350
- Coomaraswamy AK* (1904) Administrative report. *Mineral. Surv. Ceylon.*
- Cooray PG, Kumarapeli PS* (1960). Corundum in biotite-sillimanite gneiss from near Polgahawela, Ceylon. *Geol. Mag.* 47: 480-487
- Cooray PG* (1984). An introduction to the geology of Sri Lanka. National Museums of Sri Lanka, (second ed), pp340
- Cooray PG* (1994) The Precambrian of Sri Lanka: a historic review. *Precam. Res.* 66: 3-18
- Crowford AR* (1969). India, Ceylon and Pakistan: near age data and comparisons with Australia. *Nature* 223: 380-384
- Crowford AR, Oliver RL* (1969). Precambrian chronology of Ceylon. *Geol. Soc. Australia Sp. Publ* 2: 283-316
- Dissanayake CB, Chandrajith R* (1999). Sri Lanka-Madagascar Gondwana Linkage: evidence for a Pan-African Mineral belt. *J. Geol.* 107: 223-235
- Dunkley DJ, Clarke GL, Harley SL* (1999). Diffusion metasomatism in silica-undersaturated sapphirine-bearing granulite from Rumdoole Peak, Framnes Mountains, east Antarctica. *Contrib. Mineral. Petrol.* 134: 264-276
- Faulhaber S, Raith M* (1991). Geothermometry of high-grade rocks: a case study on garnet-pyroxene granulites in southern Sri Lanka. *Mineral Mag.* 55: 33-56

- Fernando GVAR, Dissanayake CB, Rupasinghe MS* (1995). Corundum mineralization of Sri Lanka and its relationships to Gondwana tectonics, (abs), Proceed. Intern. Symp. On "India and Antarctica during the Precambrian and granulite and crustal processes in East Antarctica", Vishakapatnam, India, 18
- Ferry JM* (1984). A biotite isograd in south central Maine, USA: mineral reactions, fluid transfer and heat transfer. *J. Petrol.* 25: 871-893
- Frantz JD, Mao HK* (1976). Bimetasomatism resulting from intergranular diffusion: I. A theoretical model for monomineralic reaction zone sequences. *Am. J. Sci.* 276: 817-840
- Frantz JD, Mao HK* (1976). Bimetasomatism resulting from intergranular diffusion: II. Prediction of multimineraleic zone sequences *Am. J. Sci.* 279: 302-323
- Frantz JD, and Weisbraod A* (1974). Infiltration metasomatism in the system $K_2O-SiO_2-Al_2O_3-H_2O-HCl$. In: *Geochemical transport and kinetics* (*Hofmann AW; Giletti BJ; Yoder HSJ; Yund RA* eds). Carnegie Institute Washington DC, 261-271
- Fyfe WS, Price NJ, Thompson AB* (1978). *Fluids in the earth's crust*: Elsevier Publ., Amsterdam, pp583
- Geological Survey and Mines Bureau* (1996). Geological Map of Kandy and Hanguranketha, provisional map series, Sheet 14
- Hapuarachchi DJAC* (1975). The granulite facies in Sri Lanka. *Geol. Surv. Dept. Sri Lanka, Prof. Pap. 4*: pp29
- Harley SL* (1984). An Experimental study of the partitioning of Fe and Mg between garnet and orthopyroxene. *Contrib. Mineral. Petrol.* 86: 359-373
- Helgeson HC, Lichtner PC* (1987). Fluid flow and mineral reactions at high temperatures and pressures. *J. Geol. Soc. London* 144: 313-326
- Hiroi Y, Yoshida Y, Vithanage PW* (1987). Relict kyanite in the Highland and Southwest gneisses in Sri Lanka: evidence of prograde metamorphism and a characteristic in common with the Lützom-Holm Complex in East Antarctica. *Geol. Soc. Sri Lanka Sp. Publ. 3*: pp28
- Hokada T, Osanai Y, Toyoshima T, Owada M, Tsunogae T, Crowe WA* (1999). Petrology and metamorphism of sapphirine-bearing aluminous gneisses from Tonagh Island in the Napier Complex, East Antarctica, *Polar Geosci.* 12: 49-70
- Hözl S, Hofmann AW, Todt W, Köhler H* (1994). U-Pb geochronology of the Sri Lanka basement. *Precam. Res.* 66: 123-149

- Hözl S, Köhler H, Kröner A, Jaeckel P, Liew TC (1991). Geochronology of Sri Lankan basement. In: The crystalline crust of Sri Lanka, Part 1, Summary of the research of the German-Sri Lankan Consortium (Kröner A ed). Geol. Surv. Dept. Sri Lanka Prof. Pap. 5: 237-257
- Jaeckel P, Kröner A, Williams IS (1991). U/Pb isotopic systematics in single zircons from lower crustal rocks in Sri Lanka as revealed by ion microprobe and evaporation analysis. Terra Abstracts 3: 490
- Jacobs J, Fanning CM, Henjes-Kunst F, Olesch M, Paech HJ (1998). Continuation of Mozambique Belt into East Antarctica: Grenville age metamorphism and polyphase Pan-African high-grade events in Central Dronning Maud Land. J. Geol. 106: 385-406
- Kehelpannala KVW (1997). Deformation of high-grade Gondwana fragment, Sri Lanka. Gondwana Res. 1: 47-68
- Kleinschrodt R (1994). Large-scale thrusting in the lower crustal basement of Sri Lanka. Precam. Res. 66: 39-57
- Kretz R (1983) Symbols for rock forming minerals. Am. Mineral. 68: 277-279
- Kriegsman LM (1991a). Sapphirine-bearing granulite from central Sri Lanka-outcrop description and mineral chemistry. In: (Kröner A ed) the crystalline crust of Sri Lanka, part 1, summary of research of Sri Lankan-German Consortium (Kröner A ed). Geol. Surv. Dept. of Sri Lanka, Prof. Pap. 5: 178-187
- Kriegsman LM (1991b). Structural geology of the Sri Lankan basement. In: The crystalline crust of Sri Lanka, Part 1, Summary of the research of the German-Sri Lankan Consortium (Kröner A ed). Geol. Surv. Dept. Sri Lanka Prof. Pap 5: 52-68
- Kriegsman LM (1993). Geodynamic evolution of the Pan-African lower crust in Sri Lanka- Structural and petrological investigations into a high-grade gneiss terrain. PhD thesis, University of Utrecht, The Netherlands, pp207
- Kriegsman LM, Schumacher JC (2000). Petrology of sapphirine-bearing and associated granulites from central Sri Lanka. J. Petrol. 40: 1211-1239
- Kröner A (1991). African linkage of Precambrian Sri Lanka. Geol. Rundschau 80: 429-440
- Kröner A, Jaeckel P (1994). Zircon ages from rocks of the Wannu Complex: a crustal unit distinct from the Highland Complex. J. Geol. Soc. Sri Lanka 5: 21-36
- Kröner A, Williams AS (1993). Age of metamorphism of high-grade rocks of Sri Lanka. J. Geol. 101: 521-531

- Kröner A, Cooray PG, Vitanage PW* (1991). Lithotectonic subdivision of the Precambrian basement in Sri Lanka. In: The crystalline crust of Sri Lanka, Part 1. Summary of research of the German-Sri Lankan Consortium (*Kröner A* ed). Geol. Surv. Dept. Sri Lanka Prof. Pap. 5: 5-21
- Kröner A, Williams IS, Compston W, Baur N, Vitanage PW, Perera LRK* (1987). Zircon Ion Microprobe dating of High-grade rocks in Sri Lanka. *J. Geol.* 95: 775-791
- Liew TC, Milisenda CC, Hofmann AW* (1991). Isotopic characterization of the high-grade basement rocks in Sri Lanka In: The crystalline crust of Sri Lanka, Part 1. Summary of research of the German-Sri Lankan Consortium (*Kröner A* ed). Geol. Surv. Dept. Sri Lanka Prof. Pap. 5: 258-266
- Mathavan V, Fernando GVAR* (1991) Partial melting in cordierite-sillimanite gneiss from Dombawela, Matale, Sri Lanka. (abs), Proceed. 49th Ann Sess Sri Lanka Assoc. Adv. Sci. (SLAAS), 94
- Mathavan V, Fernando GVAR* (*in press*). Mineral Chemistry and Reaction Textures in Calc-Silicate Granulites from the Highland Complex of Sri Lanka: Evidence for Isobaric Cooling and Decompression Paths in the Metasediments (*Lithos*)
- Milisenda CC* (1991). Development of continental crust: a study of the high-grade terrain of Sri Lanka, Ph D thesis, University of Mainz, Germany, pp138
- Milisenda CC, Liew TC, Hoffman AW, Kröner A* (1988) Isotopic mapping of age provinces in Precambrian high-grade terrains: Sri Lanka. *J. Geol.* 96: 608-615
- Milisenda CC, Liew TC, Hoffman AW, Köhler H* (1994). Nd isotopic mapping of the Sri Lanka basement: update and additional constrains from Sr isotopes. *Precam. Res.* 66: 95-110
- Newton RC* (1986). Fluids of the granulite facies metamorphism. In: Fluid-rock interactions during metamorphism. (*Walther JV, Woods BJ* eds). *Advances in physical geochemistry* 5, Springer Verlag, New York, 36-59
- Newton RC, Hansen EC* (1986). The south India-Sri Lanka high-grade terrain as a possible deep crust section. In: The nature of the lower continental crust : (*Dawson DB, Carswell DA, Hall J, Wedepohl* eds). *Geol. Soc. Sp. Publ.* 24: 297-307
- Newton RC, Perkins D III* (1982). Thermodynamic calibration of geobarometers based on the assemblages garnet-plagioclase-orthopyroxene (clinopyroxene)-quartz. *Am. Mineral.* 67: 203-222

- Osanai Y* (1989). A preliminary report on sapphirine-kornerupine granulite from Highland Series, Sri Lanka (extended abstract), Seminar on recent advances in Precambrian geology in Sri Lanka
- Osanai Y, Owada M, Kagami H, Hamamoto T, Hensen J* (1996). Sapphirine granulite and related high-P-T metamorphic rocks from Highland Complex, Sri Lanka, In: Gondwana Research Group Misc. Publ. 4, (*Santosh M, Yoshida M* eds), 107-108
- Perera LRK* (1984). Co-existing cordierite-almandine – a key to the metamorphic history of Sri Lanka. *Precam. Res.* 25: 349-364
- Powell C Mac, Roosts SR, Veevers JJ* (1988). Pre-breakup continental extension in East Gondwanaland and the early opening of eastern Indian Ocean. *Tectonophysics* 155: 261-283
- Prame WKBN* (1991). Petrology of the Kataragama Complex, Sri Lanka: evidence for high P-T granulite facies metamorphism and subsequent isobaric cooling. In: The crystalline crust of Sri Lanka, Part 1. Summary of research of the German-Sri Lankan Consortium (*Kröner A* ed). *Geol. Surv. Dept. Sri Lanka Prof. Pap.* 5: 200-224
- Raase P, Schenk V* (1994). Petrology of granulite-facies metapelites of the Highland Complex, Sri Lanka: implications for the metamorphic zonation and the P-T path. *Precam. Res.* 66: 265-294
- Rubie DC* (1986). The catalysis of mineral reactions by water and restrictions on the presence of aqueous fluids during metamorphism, *Mineral. Mag.* 50: 399-415
- Rupasinghe MS, Dissanayake CB* (1987). New in-situ corundum deposits in Sri Lanka. *J. Gemmol. Assoc. Sri Lanka* 4: 2-5
- Sandiford M, Powell R, Martin SF, Perera LRK* (1988). Thermal and baric evolution of garnet granulites from Sri Lanka. *J. Metamorphic Geol.* 6: 351-364
- Schenk V, Raase P, Schumacher R* (1988). Very high temperatures and isobaric cooling before tectonic uplift in the Highland Series. *Terra Cognita* 8: 265
- Schenk V, Raase P, Schumacher R* (1991). Metamorphic zonation and P-T history of the Highland Complex in Sri Lanka. In: The crystalline crust of Sri Lanka Part 1. Summary of research in German-Sri Lankan Consortium (*Kröner A* ed). *Geol. Surv. Dept. Sri Lanka Prof. Pap.* 5: 150-163
- Schumacher JC, Robinson P* (1987). Mineral chemistry and metasomatic growth of aluminous enclaves in gedrite-cordierite-gneiss from southwestern New Hampshire, USA. *J. Petrol.* 28: 1033-1073

- Schumacher R, Schenk V, Raase P, Vithanage PW* (1990). Granulite facies metamorphism of metabasic and intermediate rocks in the Highland Series of Sri Lanka. In: High-grade metamorphism and crustal anatexis, (*Ashwarth JR, Brown M* eds), Unwin Hyman Ltd., London, 235-271
- Schumacher R, Faulhaber S* (1994). Summary and discussion of P-T estimates from garnet-pyroxene-plagioclase-quartz-bearing granulite-facies rocks from Sri Lanka. *Precam. Res.* 66: 295-308
- Silva KKMW, Siriwardena CHER* (1988). Geology and the origin of the corundum-bearing skarn at Bakamuna, Sri Lanka. *Mineral. Deposita* 23: 186-190
- Siriwardena CHER* (1988). Preliminary report of the survey of Rupaha serpentine deposit, Geol. Surv. Dept. (unpublished) pp15
- Soyza EG* (1986). An account of serpentine deposit of Rupaha, Sri Lanka. *J. Gemmol. Ass. Sri Lanka* 3: 30-34
- Touret JLR, Hartl THD* (1990). Syn-metamorphic fluid inclusions in granulites. In: *Granulites and crustal evolution.* (*Vielauf D, Vidal P* eds). NATO ASI Series C 311, Kluwer Publishers, Dordrecht, 397-417
- Valley JW, O'Neil JR* (1984). Fluid heterogeneity during granulite facies metamorphism in the Adirondacks: Stable isotope evidence. *Contrib. Mineral. Petrol.* 85: 158
- Valley JW, Bohlen SR, Essene EJ, Lamb W* (1990). Metamorphism in Adirondacks: II The role of fluids. *J. Petrol.* 31: 555-596
- Vithanage PW* (1972). Post-Precambrian uplifts and regional neotectonic movements in Ceylon. 24th IGC Montreal, Canada, 3: 642-654
- Vithanage PW* (1985). Tectonics and mineralization in Sri Lanka. *Geol. Soc. Finland Bull.* 57: 157-168
- Voll G, Kleinschrodt R* (1991). Sri Lanka: structural, magmatic and metamorphic development of Gondwana fragment. In: *The crystalline crust of Sri Lanka, Part -1.* Summary of research of the German-Sri Lankan Consortium (*Kröner A* ed). Geol. Surv. Dept. Sri Lanka Prof. Pap. 5: 22-51
- Voll G, Evangelakakis C, Kroll H* (1994). Revised two-feldspar geothermometry applied to Sri Lankan feldspars. *Precam. Res.* 66: 351-377
- Wells AJ* (1956). Corundum from Ceylon. *Geol. Mag.* 42: 25-31
- Yoshida M, Funaki M, Vithanage PW* (1992). Proterozoic to Mesozoic East Gondwana: the juxtaposition of India, Sri Lanka and Antarctica, *Tectonics.* 11: 381-391

Table 1.1 Geochronological and tectonic events of crystalline and non-crystalline rocks of Sri Lanka

Age (Ma)	WC	HC	VC	Major Tectonics
~3200-2400 (SHRIMP U-Pb detrital zircon)		Age of supracrustals (9)		
~ 2287 ± 108 (whole rock Rb-Sr, K-Ar)		Age of supracrustals (3,4)		
~2350-2000 (Sm-Nd model ages, U-Pb zircon fraction upper intercept)		Deposition of supracrustals in the Proterozoic basement (5, 6, 11, 12, 16, 17)		
~1942-1850 (U-Pb zircon fraction upper intercept)		Intrusion of granitoid rocks (1, 5, 6, 11,12, 16, 17)		
~1100 (Sm-Nd model ages)	Deposition of supracrustal rocks (5, 6, 12, 14, 16, 17)		Deposition of supracrustal rocks (11, 12, 16, 17)	
~1100-1000 (SHRIMP U-Pb detrital zircon)	Intrusion of granitoid rocks (6, 7, 8, 15)		Intrusion of granitoid rocks (5)	
~750 (U-Pb zircon)				Amalgamation of HC and WC (15)
~610-550 (U-Pb zircon fraction lower intercept, U-Pb monazite)	Regional granulite facies metamorphism, (1, 7, 12)	Regional granulite facies metamorphism (1, 5, 6)		Pan-African orogeny (collision between East- and West- Gondwana) (9, 10, 12, 18)
~580-550				Thrusting of HC-WC over VC (8)
~591-456 (U-Pb zircon fraction lower intercept)			Regional amphibolite facies metamorphism (5, 6, 11)	
~160-200	Deposition of Jurassic sediments on the crystalline rocks (2)			Crustal extension of East Gondwana (12,18, 20)
~26	Deposition of carbonates sediments in the Cauvery basin (2)			Separation of Sri Lanka from India (19)
(1). Bauer et al. (1991)	(2). Cooray (1984)	(3). Crawford (1969)		
(4). Crawford and Oliver (1969)	(5). Hölzl et al. (1991)	(6). Hölzl et al. (1994)		
(7). Jaeckel et al. (1991)	(8). Kleinschrodt (1994).	(9). Kriegsman (1991b)		
(10). Kriegsman (1993)	(11). Kröner et al. (1987)	(12). Kröner (1991)		
(13). Kröner et al. (1991)	(14). Kröner et al. (1994)	(15). Kröner and Jaeckel (1994)		
(16). Liew et al. (1991)	(17). Milisenda et al. (1988)	(18). Powell et al. (1988)		
(19). Vithanage (1985)	(20). Yoshida et al. (1992)			

FIGURE CAPTIONS

Fig. 1.1 Simplified geological map of the Sri Lanka showing all major litho-tectonic units (after Cooray 1994). The area outlined by the box is the studied area (Rupaha area), which is shown in greater detail in Fig. 1.3.

Fig. 1.2 P-T-t-D path for the granulites of the Highland Complex in Sri Lanka (after Kriegsman 1993). The prograde path is characterized by crustal thickening, and subsequent heating, while the retrograde path shows early isothermal decompression, followed by isobaric cooling.

Fig. 1.3 Geological map of the area around Rupaha. The Proterozoic rocks are composed of charnockites, charnockitic gneisses, quartzites, garnet-sillimanite-graphite gneisses (khondalites), garnet-biotite gneisses, and scattered marbles. The study concerns the metamorphosed ultramafic rocks, which are exposed at '*Garandu Kandura*' and their adjoining rocks. Geological map modified after Siriwardena (1988) and Geological Survey & Mines Bureau (1996). The study area given by the shaded box is shown in detail in Fig 1.4.

Fig. 1.4 Detailed geological and location map of the area around the main serpentinite body exposed at the '*Garandu Kandura*', Rupaha, Sri Lanka.

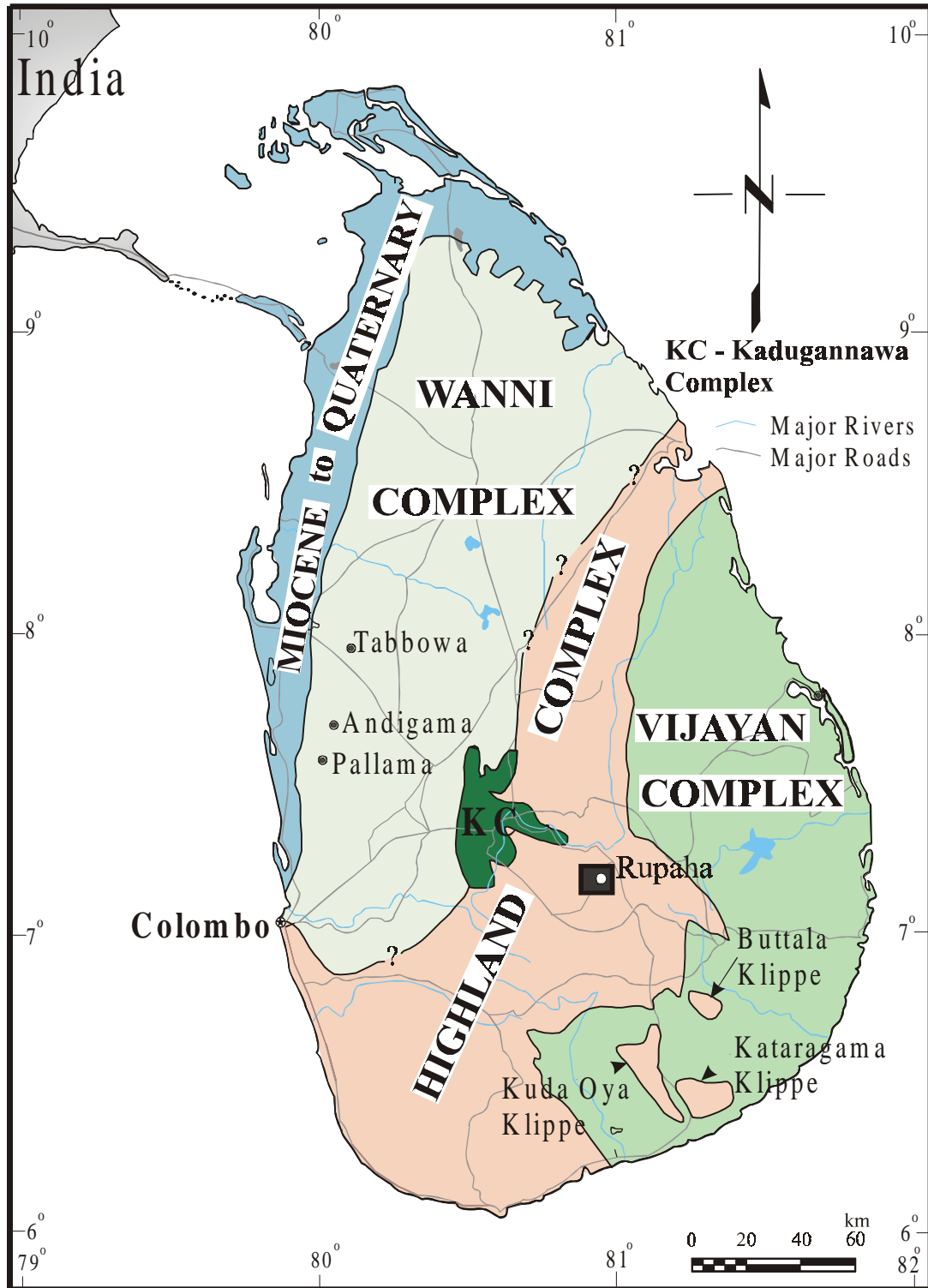
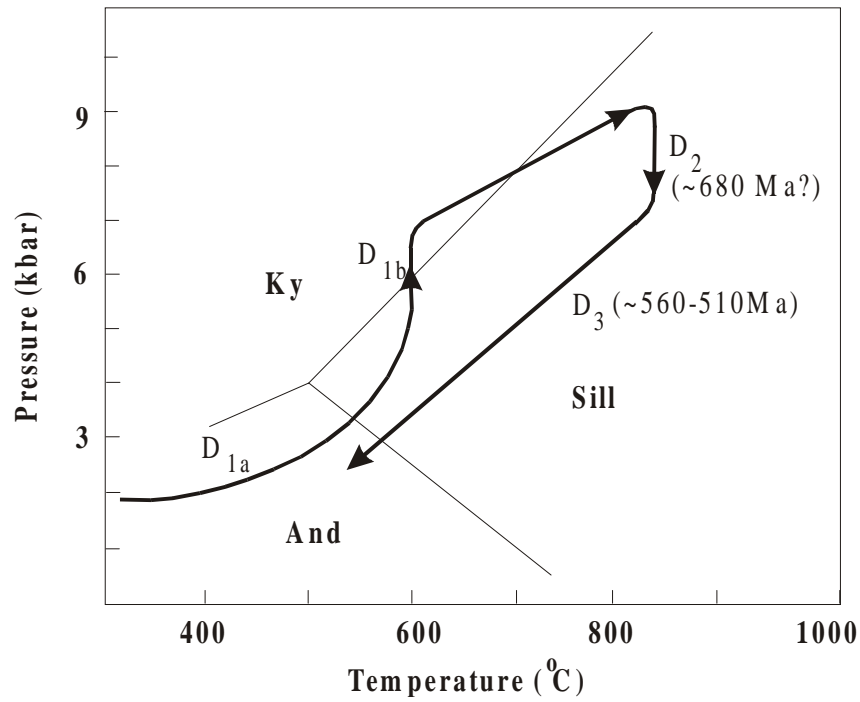


Fig 1.1



- | | |
|-----------------|--|
| D _{1a} | Early extension and low P /High-T metamorphism |
| D _{1b} | Crustal thickening |
| D ₂ | Extensional collapse- main deformation |
| D ₃ | Late folding and thrusting |

Fig.1.2

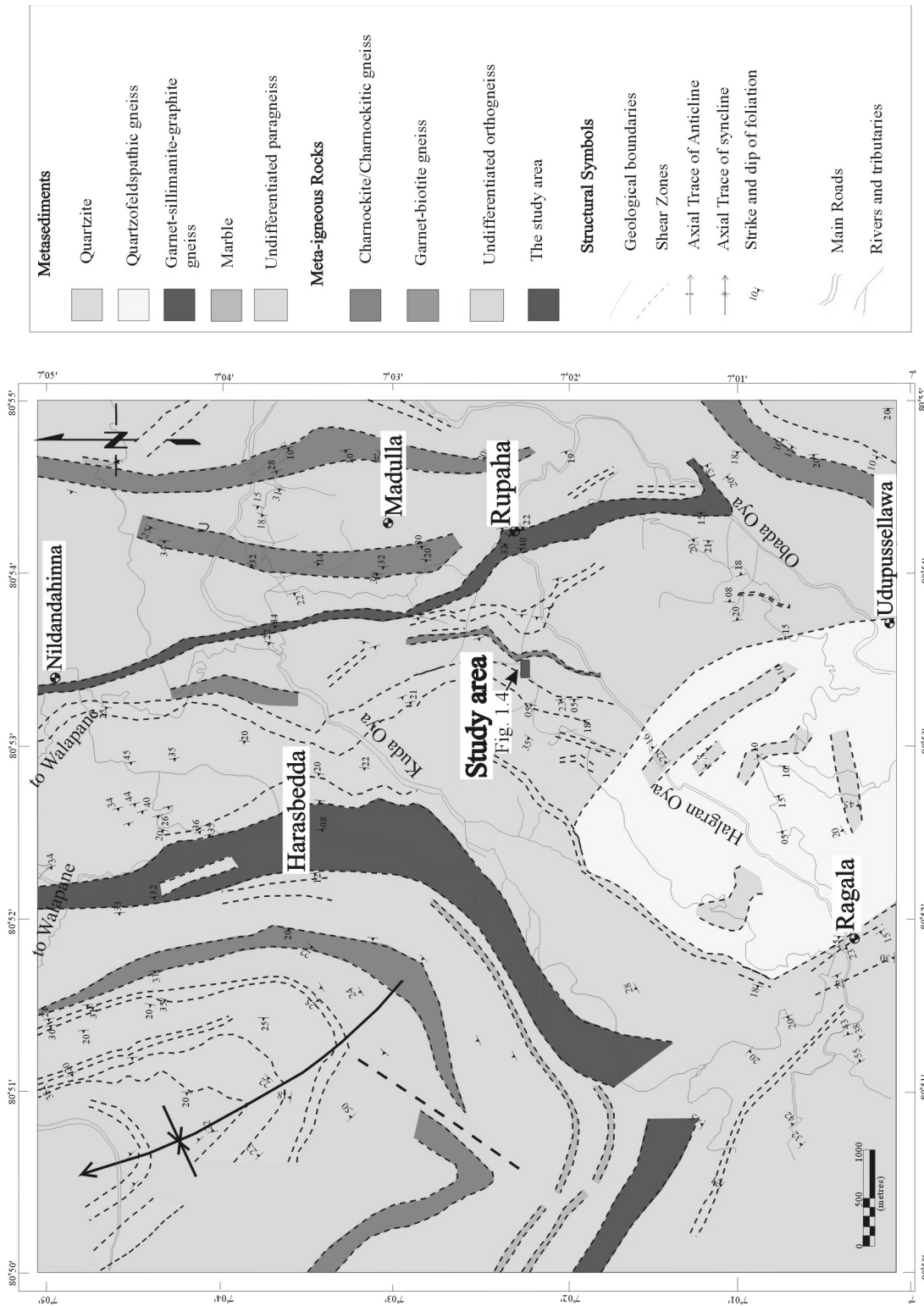


Fig. 1.3

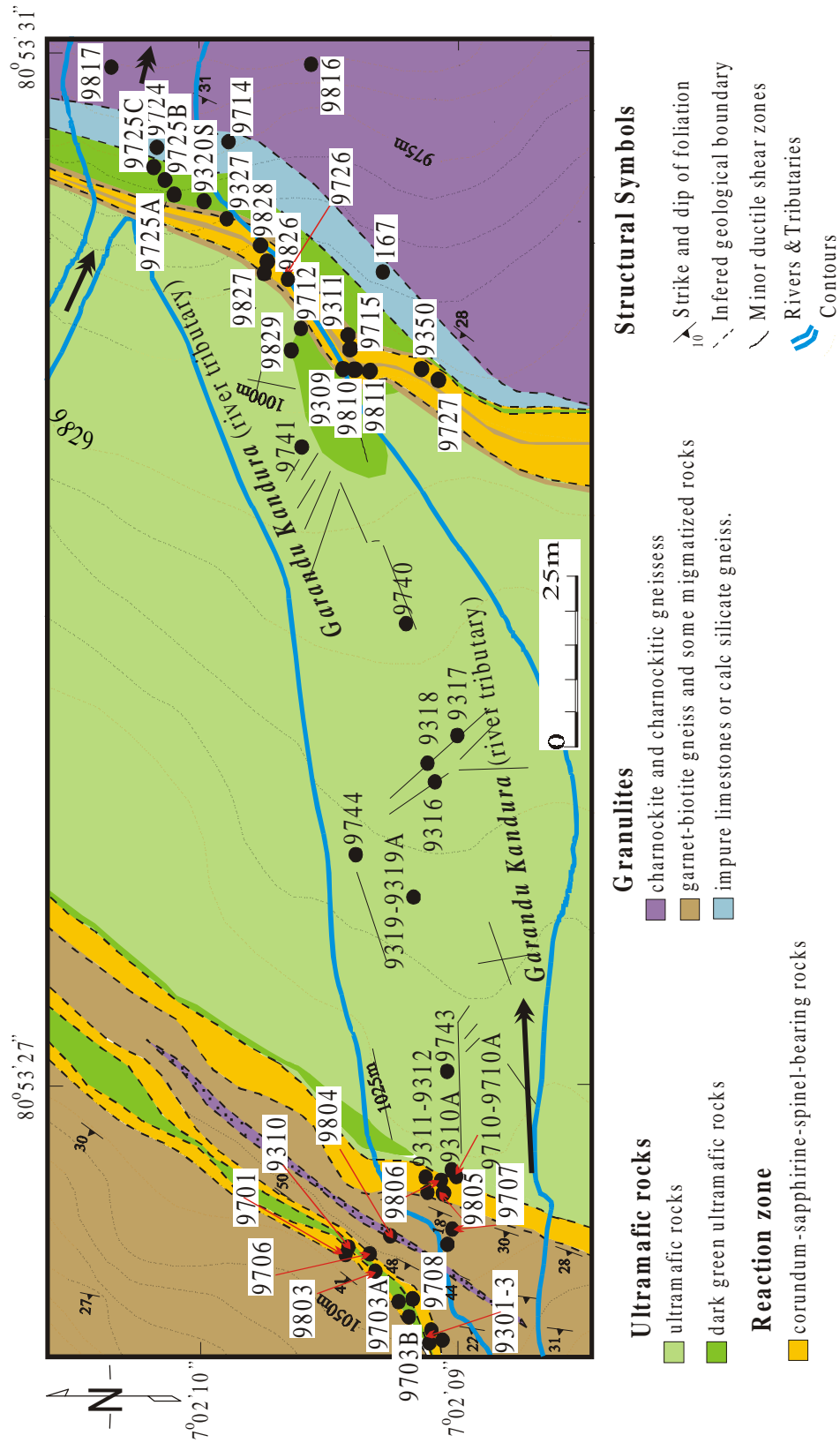


Fig. 1.4

Chapter 2

Retrograde diffusion zoning in garnet: Implications for three-stage cooling history of mafic granulites in the Highland Complex of Sri Lanka

ABSTRACT

Diffusion modeling of retrograded garnet rims from mafic granulites is used to estimate the cooling rates in the Proterozoic basement of Sri Lanka, which represents a small, but important fragment of the super-continent Gondwana. Metamorphic peak temperatures and pressures estimated with two-pyroxene thermometry and garnet-clinopyroxene-plagioclase-quartz (GADS) barometry, yield $875 \pm 4^\circ\text{C}$ and 8.7 ± 0.4 kbar, which is significantly higher than garnet-biotite Fe-Mg exchange thermometry of $820 \pm 20^\circ\text{C}$. Garnet rims exhibit narrow but regular retrograde zoning in terms of Fe and Mg exchange between garnets touching biotite and give temperature of 685°C .

The observed garnet zoning requires a three-step cooling history. Equilibrium was achieved along grain boundaries during the first cooling step. During the subsequent faster cooling, only local exchange between garnet and biotite occurs. A maximum cooling rate of $1^\circ\text{C}/\text{Ma}$ is estimated during the initial stage of cooling followed by a cooling rate of $\sim 30^\circ\text{C}/\text{Ma}$. The outermost rims of garnet indicate that cooling slowed down at or near the blocking temperature of garnet to about $10\text{-}15^\circ\text{C}/\text{Ma}$. The three-stage temperature-time history is not in agreement with the cooling history inferred from mineral radiogenic ages in the literature. The difference in cooling rates between our calculations and using thermochronology is mainly due to the lack of larger reliable set of geochronological results of different minerals and radiogenic isotope systems.

INTRODUCTION

One of the common features of granulite facies rocks is the textural and chemical equilibration during high-grade metamorphic conditions. Compositional zoning in minerals, if formed during the prograde path, is generally completely homogenized during granulite facies metamorphism. Existing mineral zoning in granulites is typically due to prolonged cooling and exhumation (e.g. Lasaga et al. 1977; Lasaga 1983; Giletti 1986; Essene 1989). Thus, mineral zoning in granulite terranes is critical for understanding the exhumation and uplift history of the specific terrane. This can be done by accurate determination of the pressure-temperature-time evolution path. If the compositions of mineral phases record and preserve peak equilibrium conditions, the time-temperature path (T-t) can be correctly pinpointed. But, if cores of zoned minerals do not represent the actual thermal peak, utilizing core compositions for geothermometry leads to meaningless results. On the other hand, if one can evaluate and estimate the correct peak compositions of minerals, the actual T-t history of the rocks can be tentatively estimated. Interpretation of the cooling history in granulites from Sri Lanka using garnet zoning and recovered peak compositions of garnets illustrate a well-constrained three-stage cooling history of the rocks.

Cooling rates of rocks are usually determined by three different ways; using closure temperature of minerals for radiogenic isotopes (e.g. Mezger et al. 1992) or for stable isotopes (e.g. Giletti 1986; Eiler et al. 1992, 1995) or diffusive zoning in metamorphic minerals (e.g. Dodson 1973; Lasaga 1983; Spear 1991; Lindström et al. 1991; Spear and Florence 1992; Florence and Spear 1995; Spear and Parrish 1996; Weyer et al. 1999).

To quantify the cooling history of rocks, many workers have discussed the use of garnet diffusion zoning patterns. Some have used the assumption of a large amount of (infinite) biotite, which implies a fixed biotite composition that is unaffected by diffusional exchange with the garnet (e.g. Dodson 1973). This assumption is correct for some granulites, where biotite makes up the bulk of the rock, and diffusion of grain boundaries is fast (e.g. Weyer et al. 1999). The other extreme is to balance the diffusional fluxes of the elements between touching biotite and garnet grains (e.g. Lasaga 1983; Spear and Florence 1992; Lindström et al. 1991; Florence and Spear 1995; Spear and Parrish 1996). The

diffusional gain or loss of garnet is balanced by the compositional change of its coexisting biotite.

The Fe-Mg inter-diffusion of more than two minerals in a rock like that exchange between garnet, biotite and clinopyroxene, for example, requires that all fluxes between these minerals are balanced in a closed system. Hence, the knowledge of interdiffusion coefficients of all individual phases, modal abundances and surface areas of these phases are required (see Eiler et al. 1992 for more details).

Lower crustal granulites are exposed in many places in Gondwana fragments, such as the small fragment of Sri Lanka. Granulites of Sri Lanka often have significant amounts of ferro-magnesian rocks, which are commonly interpreted as metamorphosed basic igneous rocks. These granulites, which show consistent isobaric cooling in the area around Rupaha within the Highland Complex (Fig.2.1), are used to evaluate its P-T and cooling history. Up to now only a few studies have presented cooling rates for Sri Lankan granulites (Hölzl et al. 1991; Burton and O'Nions 1990). There has been renewed interest to evaluate the internal consistency of cooling rates of Sri Lankan granulites because cooling and uplift history of Sri Lankan basement has been poorly defined by both methods.

We use garnet diffusion to determine the cooling rates. The interpretation is based on: (1) recovering of peak composition of garnets; (2) application of diffusion models to estimate the cooling rates using numerical zoning patterns. The results are combined with geochronology from the literature to describe the complete exhumation history of the granulites.

GEOLOGICAL SETTING

The Proterozoic basement of Sri Lanka exposes substantial parts of lower continental crust in which four different units were distinguished on the basis of isotopical, geochronological, geochemical and petrological constraints (Cooray 1994; Kröner et al. 1991; Milisenda et al. 1994)(Fig 2.1.): (1) the Highland Complex (HC); (2) the Vijayan Complex (VC); (3) the Wannu Complex (WC) and (4) the Kadugannawa Complex (KC). The WC consists mainly of metabasites and charnockites while the HC is comprised of

interbedded metapelites, quartzites and marbles in addition to rocks from WC. The VC is exposed in eastern Sri Lanka, consisting of meta-igneous gneisses of tonalitic to leucogranitic composition. The HC rocks yield relatively old crustal residence Sm-Nd model ages (2-3 Ga. Milisenda et al. 1994), while rocks from the other units give significantly younger residence times of 1-2 Ga. Metamorphic grade reaches granulite facies throughout the HC, the WC and the KC, albeit locally retrogressed to amphibolite facies, while the VC has amphibolite facies assemblages. The timing of peak metamorphism was estimated between ~550-~610 Ma (Hözl et al. 1991,1994; Kröner et al. 1991; Kröner and Williams 1993).

The area of this study is located in the central part of Sri Lanka, at Rupaha, within the central Granulite belt of the HC (Fig.2.1). It consists mainly of meta-igneous rocks (orthogneisses and charnockitic gneisses), which are intercalated with metasediments (quartzite, garnet-sillimanite-graphite gneisses, garnet-biotite gneisses, corundum-biotite gneisses and minor calc-silicates, marbles and ultramafics). The small-scale structures and geological units in the study area are illustrated in Fig. 2.1.

PETROGRAPHY

Two rock-types of mafic granulites, differing in mineral paragenesis and model proportions can be distinguished. Garnet-biotite-clinopyroxene-bearing gneisses (sample location No. 9708 in Fig. 2.1) are coarse-grained, dark and show a strong schistosity. Assemblages are typically $\text{Grt} + \text{Bt} + \text{Pl} \pm \text{Ilm}$; $\text{Grt} + \text{Bt} + \text{Cpx} + \text{Pl} \pm \text{Qtz} \pm \text{Ilm}$; $\text{Grt} + \text{Cpx} + \text{Pl} \pm \text{Qtz} \pm \text{Ilm}$ (for abbreviations see Kretz 1982). Garnet contains inclusions of plagioclase and biotite. Some parts of the rock are migmatized. Charnockites (sample location No. 9817 in Fig. 2.1) in the area are characterized by the mineral paragenesis $\text{Opx} + \text{Kfs} + \text{Pl} + \text{Qtz} \pm \text{Ilm} \pm \text{Ap}$; $\text{Hbl} + \text{Opx} + \text{Pl} + \text{Kfs} + \text{Qtz} \pm \text{Ilm} \pm \text{Ap}$; $\text{Opx} + \text{Cpx} + \text{Pl} + \text{Qtz} \pm \text{Ilm} \pm \text{Ap} \pm \text{Grt}$. The quartz content varies in these rocks from a few volume percent up to about 10%. In garnet-clinopyroxene-biotite-bearing gneisses, no reaction textures are observed. Garnet-quartz grain boundaries are absent suggesting that the reaction garnet + quartz to $\text{Cpx} + \text{plagioclase} + \text{ilmenite}$ has occurred. Biotite and garnet are in equilibrium in many places (Fig.2.2a). Both pyroxenes in charnockites are generally devoid of inclusions, though some small rounded grains of hornblende and plagioclase may be

present. Large elongated crystals of hornblende in the matrix have irregular shaped edges (Fig. 2.2b). A few grains of biotite are present in some samples of the two-pyroxene-hornblende-bearing assemblages. Some late stage chlorites replaced hornblende. The primary metamorphic mineral assemblages selected for thermobarometric study are Opx-Cpx-Pl-Hbl-Qtz and Grt-Bt-Cpx-Pl-Qtz along with minor amounts of magnetite, ilmenite, apatite, rutile and zircon.

ANALYTICAL TECHNIQUES

Thin sections from the two rock types showing the primary mineral assemblages with no or minor retrogression were selected for thermobarometry. After detailed optical inspection of polished thin sections, mineral analyses were performed on carbon-coated thin sections at the University of Mainz, Germany, using the JEOL microprobe (JEOL JXA 8900 RL) with operating conditions of 15keV accelerating voltage, 12nA beam current and 2 μ m beam diameter. Elements were calibrated against synthetic and natural standards. Online ZAF corrections were performed (Amstrong 1988, 1989). Mineral compositions of coexisting garnet-biotite, garnet-clinopyroxene, and garnet-clinopyroxene-plagioclase-quartz from garnet biotite gneisses and coexisting two-pyroxenes from charnockites were analyzed. Garnets were analyzed for both rim and core compositions, that physically contact with either biotite or clinopyroxene. Thermobarometric pairs were selected from adjacent grains in the view of separate thermobarometric calculations. Some representative garnets, adjacent to biotite were investigated for a probable zoning pattern by running microprobe line profile across the grain at 3 μ m spacing for Fe, Mg, Ca and Mn. A two-dimensional compositional map of Mg- distribution in garnet, which is in mutual contact with biotite, plagioclase and other garnet, was obtained with the automated JEOL microprobe using a wavelength dispersive spectrometer (WDS)(15kV, 30nA and 1 μ m probe diameter). All iron was assumed to be Fe²⁺ on recalculation.

MINERAL CHEMISTRY

Chemistry of mineral assemblages in one dataset used for thermobarometry of Rupaha granulites are presented in Table 2.1. The comprehensive analytical data set is attached in the Appendices C1-C4.

Garnets are mainly almandine-pyrope-grossular solid solutions, with average almandine content just about 50%. The pyrope content is around 21% while grossular and spessartine content are 16% and 13% respectively. They are typical about 700 μ m diameter on average. Fig.2.3a is a back-scattered image and Fig. 2.3b, a microprobe line profile of the same grain (Complete chemical data is attached in Appendix C5). Flat zoning of garnet is observed throughout most grains except in the vicinity of adjacent biotite, where X_{Mg} decreases and X_{Fe} increases slightly towards the garnet rim. The rims are approximately 20 μ m wide (Fig. 2.4). Garnet is typically unzoned towards non-Fe-Mg minerals (e.g. plagioclase) or other garnet. Garnet is not zoned with respect to Ca. Modal abundance of biotite is approximately half of the modal abundance of garnet. Biotite inclusions are preserved in some garnet grains. No zoning was found in clinopyroxene and there is no compositional zoning in contrast to the marked Fe/(Fe+Mg) gradient in garnet. Fe/(Fe+Mg) in clinopyroxene varies from 0.28-0.30 in biotite gneisses while it is between 0.51-0.53 in charnockitic rock. X_{Al} values range from 0.05-0.07. Orthopyroxene in charnockite is of homogeneous composition and has a Fe/(Fe+Mg) value of 0.64-0.67.

PRESSURE-TEMPERATURE ESTIMATES AND FLUID COMPOSITION

Results of ion exchange thermometry (Table 2.2) are based on the garnet-biotite (Dasgupta et al. 1991), the garnet-clinopyroxene (Sengupta et al. 1989) and the orthopyroxene-clinopyroxene (Brey and Köhler 1990) equilibria. The pressures were determined from the calibration of garnet-clinopyroxene-plagioclase-quartz (Eckert et al. 1991) assemblages. Temperature and pressure were calculated by simultaneous solving of the barometric and temperature equations, where applicable (Fig. 2.5). The highest P-T estimates were obtained for Opx-Cpx thermometry together with GADS barometer. Temperatures range from 870-882 $^{\circ}$ C, with pressures of 8.6-9.1 kbar. All three calibrations (Lindsley et al. 1981; Kretz 1982; Brey and Köhler 1990) yield identical results within the variation of mineral chemistry. Mineral equilibrium temperatures of 775-840 $^{\circ}$ C at this locality were obtained from Grt-Bt/GADS, using garnet cores, at pressures of 7.6 – 8.3 kbar. These are significantly lower than the Opx-Cpx/GADS thermobarometer values presented above. Pressure-temperature estimates obtained from garnet rim and adjacent biotite compositions with GADS barometer range from 685-795 $^{\circ}$ C and 6.7-7.8 kbar. Pressure-temperature estimates for Grt (rim)-Cpx (rim)/GADS are significantly lower (between 706-738 $^{\circ}$ C and

6.9-7.2 kbar). More than six calibrations (e.g. Ferry and Spear 1978; Hodges and Spear 1982; Perchuk and Lavent'eva 1983; Ganguly and Saxena 1984; Indares and Martignole 1985; Bhattacharya et al. 1992; Kleeman and Reinhardt 1994) were used to Grt(core)-Bt temperatures. While considerable scatter was observed (710-840°C), none of the calibrations indicates peak temperatures close to that of the Opx-Cpx thermometers.

Furthermore, no significant difference of the Grt-Cpx thermometer between the calibrations of Ellis and Green (1979) and Sengupta et al. (1989) was observed. The wide array of computed garnet-biotite temperatures is a function of the cooling history of the sample.

Fluid composition of charnockites can be calculated from the model buffering reactions of $2\text{Tr} = 4\text{Di} + 3\text{En} + 2\text{Qtz} + 2\text{H}_2\text{O}$ and $2\text{Ann} + 6\text{Qtz} = 3\text{Fs} + 3\text{San} + 2\text{H}_2\text{O}$ (Lamb and Valley 1988). The thermodynamic database of Holland and Powell (1998) was used together with activity model for a_{Tr} in Ca-amphiboles of Holland and Blundy (1994). The activity of anorthite was calculated after Holland and Powell (1992), while a_{San} in K-feldspar and a_{En} and a_{Fs} in Opx was obtained following Holland and Powell (1996). The calculated $a_{\text{H}_2\text{O}}$ is in the range of 0.05-0.09. These values indicate a low activity of water during peak metamorphism.

CONSTRUCTION OF FLUID SATURATED P-T GRIDS

An activity-corrected petrogenetic grid was calculated for the chemical system CaO-K₂O-FeO-MgO-Al₂O₃-SiO₂-H₂O (CKFMASH), using the phases Grt, Pl, Kfs, Cpx, Opx, Bt, Hbl and Qtz (Fig.2.6)(see abbreviations for mineral activities). They were calculated using the PeRpleX software of Connolly (1990). The diagram was constructed using the $X_{\text{H}_2\text{O}} = 0.1$, which corresponds to the calculated water activity of 0.05-0.09 (Holland and Powell 1991, 1998).

All possible reactions occurring in garnet-biotite-clinopyroxene gneiss and charnockites are shown here with the aim of unraveling the PT conditions of the area. On the basis of observed textural relationships in the rocks, a PT estimate of around 850-910°C and 7.5-9-0 kbars can be calculated (shaded area). The melting curve of the system Qtz-Ab-Or-H₂O-

CO₂ for X_{H₂O} = 0.1 was added to the diagram according to the experiments of Ebadi and Johannes (1991) and Johannes and Holtz (1996). The estimated PT conditions from the petrogenetic grid are in agreement with PT estimates from the Cpx-Opx/GADS ion-exchange thermobarometry.

The results of thermobarometry of our study compare well with the PT estimates of other areas of the HC. Schumacher and Faulhaber (1994) estimated the P-T condition of the Eastern, North-eastern and South-eastern part of the HC at 760-830°C and 9-10 kbar. Sandiford et al. (1988) used Gt-Cpx and Gt-Opx thermometry to illustrate the minimum temperature of metamorphism to be 670-730°C. They noted that the actual peak metamorphism could easily be much higher. Kriegsman (1993) obtained peak equilibrium temperatures for sapphirine-bearing granulites in HC at 830°C and 9 kbar using petrogenetic grids. Schenk et al. (1988) derived from two-pyroxene thermometry in the HC a maximum temperature of 900°C. Voll et al. (1994) estimated the peak temperatures of metamorphism between 850-900°C by using revised two-feldspar thermometry.

INTERDIFFUSION OF ELEMENTS DURING SLOW COOLING

The recent acquisition of diffusion coefficients for interdiffusion of Fe-Mg in garnet, biotite and pyroxene permits to quantify the effect of diffusion during slow cooling of rocks. A number of experimental values for interdiffusion of Fe and Mg in garnet have been published so far (e.g. Cygan and Lasaga 1985; Chakraborti and Ganguly 1992; Ganguly et al. 1998). Diffusion coefficients determined from the most recent experiments by Ganguly et al. (1998) are consistent with high-temperature systems and were used in our calculations.

The Fe-Mg interdiffusion rates of biotite, pyroxene and garnet are quite different. The diffusion coefficients of pyroxene, garnet and biotite differ by three orders of magnitude at 850°C, and the diffusion of Ca and Mg in pyroxene is even slower by over 2 orders of magnitude (Fig. 2.7). Similar inter-diffusion rates of Fe and Mg have been observed in pyroxenes and garnets (Ganguly and Tazzoli 1994; Ghose and Ganguly 1982), while biotite has much faster Fe-Mg interdiffusion. Minerals with relatively fast diffusion coefficients, like biotite, and to some degree, garnet and Cpx, will partially re-equilibrate

during cooling from granulite and amphibolite conditions. Therefore, one cannot expect to obtain the peak temperature from both garnet-clinopyroxene and garnet-biotite thermometry in granulite terranes. Hence, not surprisingly, these thermometers (e.g. Ellis and Green 1979; Sengupta et al. 1989; Dasgupta et al. 1991), yield temperatures that are 50-150°C lower than two-pyroxene thermometer for Rupaha granulites. These reset temperatures are '*apparent temperatures*' (Spear 1991; Spear and Florence 1992; Spear and Parrish 1996), since they correspond to neither closure temperature nor equilibrium peak temperature. Similar observation has been reported from the ultra-high temperature (UHT) terranes (~950-1000°C) of Enderby Land, which show the Grt-Cpx temperature of only 720°C (Ellis and Green 1985).

In summary, the two-pyroxene thermometer most likely records peak or near peak temperatures at Rupaha ($875 \pm 4^\circ\text{C}$), while garnet (core)-biotite ($820 \pm 20^\circ\text{C}$), Grt (rim)-Bt ($776 \pm 40^\circ\text{C}$) and Grt (rim)-Cpx ($734 \pm 10^\circ\text{C}$) documents slow cooling of the terrane. In the following chapters, we will retrieve information for the cooling history based on the Fe-Mg profiles in garnet.

COOLING RATES FROM GARNET PROFILES

The peculiarity of the Fe-Mg profile in garnet is that it is homogeneously reset throughout most of the crystal, with minor Fe increases and Mg decreases at the rim (Fig. 2.3b). This indicates a complete resetting of the garnet during an initial protracted cooling event, which was followed by a faster cooling, which resulted in the small Fe-Mg zoning at the rim.

The composition of the Fe-Mg minerals at peak pressure and temperature has to be calculated from thermodynamic and mass balance equations, since the garnet as well as biotite and clinopyroxene in the matrix changed their Fe/Mg composition throughout in the first cooling step. This was accomplished by using the modal abundances of garnet, biotite and clinopyroxene to calculate the bulk Fe-Mg of the rock. The equilibrium equations between the garnet, biotite and clinopyroxene were solved for Fe-Mg using this bulk composition at 875°C and 9kbar. This was achieved by simultaneously solving the mass balance equation for Fe and Mg and the mass action equations describing Fe-Mg

exchange. For these calculations it was assumed that no net transfer reaction occurred during cooling. This assumption is supported by fact that no retrograde growth of any high temperature phases can be observed in the studied sample. Modal mineralogy of the rock and the calculated Fe and Mg values of garnet at 875°C and 9 kbar are given in Table 2.3 and Table 2.4, respectively.

The diffusion model was set up based on the observed mineral zoning. During the first stage of cooling garnets are homogeneously changed, while during the second stage only garnet adjacent to biotite show appreciable zoning. Hence the first cooling step was modeled using 'bulk' diffusion model, assuming grain boundary diffusion is fast compared to that of volume diffusion in garnet (e.g. Joesten 1991; Eiler et al. 1992, 1995). In that case, diffusional fluxes should be balanced in representative volumetric elements, which are large compared to individual grains. Nevertheless, clinopyroxene occurs only in small quantities, therefore the diffusive fluxes have been balanced only between garnet and biotite. During the second cooling period diffusion along grain boundaries was limited, so that garnet zoning only developed where biotite contacted and shared grain boundaries. For this case we assume a model, which has a binary interdiffusion between garnet and adjacent biotite grains. For a further discussion of diffusive exchange modeling and the mathematical treatments see Dodson 1973; Lasaga 1983; Lindström et al. 1991; Eiler et al. 1992; Spear and Florence 1992; Florence and Spear 1995; Spear and Parrish 1996 and Weyer et al. 1999. We used the program Gibbs (Spear and Peacock 1990; Spear and Florence 1992; Florence and Spear 1995) to solve the resulting differential equations, mass action and flux balance equations.

The diameter of garnet used here is 668 μm . Both garnet and biotite are assumed to be homogeneous at starting temperatures (875°C). Significant zoning is predicted for garnets for cooling rates in excess of 1°C/Ma. Hence a maximum cooling of 1°C/Ma is estimated in the first step. During the second step, we have calculated the zoning profiles for linear cooling rates of 100, 50, 30, 20, 15, and 1°C/Ma for the starting temperature of 820°C. The starting temperature is obtained from apparent garnet (core)-biotite geothermometry. The zoning patterns calculated for the constant cooling rates is shown for these five cooling rates in Fig 2.8, along with the microprobe data. The calculated zoning profile for a cooling rate of 30°C/Ma is in excellent agreement with measured zoning profiles of garnet

at Rupaha. A consistent cooling rate is obtained over the temperature interval from 820°C to 500°C. However, X_{Mg} profile developed at the outermost rim (7-10 μm), indicated that the cooling rate has decreased, slightly probably at the temperatures below 650°C. The resulting cooling rate can be estimated around 15°C/Ma (Fig. 2.8).

DISCUSSION AND CONCLUSIONS

Ca-Fe-Mg exchange thermobarometry of co-existing Opx-Cpx and Grt-Cpx-Pl.Qtz is consistent with calculated PT phase diagrams for the rocks of the Rupaha area. They indicated that peak metamorphism occurred at $875 \pm 20^\circ\text{C}$ and pressures of 9.0 ± 0.1 kbar. Water activity is low <0.1 , as inferred from the charnockites. Fe-Mg exchange thermometry of Grt(core)-Bt resulted in $820 \pm 20^\circ\text{C}$. The garnet-biotite exchange temperatures are interpreted to represent apparent temperatures due to slow cooling.

The experimental studies on Opx-Cpx thermometry are primarily designed on the transfer of Ca-Mg components between co-existing Opx and Cpx (Lindsley et al. 1981; Kretz 1982; Carlson and Lindsley 1988). Brey and Köhler (1990) later used the Opx-Cpx thermometry in the account of Ca-Fe-Mg exchange. The results of Opx-Cpx geothermometry from all three methods were nearly identical to each other. The Ca-Mg interdiffusion of pyroxene is several orders lower than that of Fe-Mg diffusion in either garnet or pyroxenes (Fig. 2.7). Hence, one can speculate that the effect on Fe-Mg exchange is negligible when compared to the Ca-Mg exchange on pyroxene thermometry calculations. This is further supported by the observation that no retrograde zoning is present in pyroxene or garnet with respect to Ca. Therefore, we propose that the thermometer most likely to preserve peak metamorphic temperature is the Opx-Cpx thermometer.

Our insight for recovering of near-peak cooling history is very useful, since it is possible to refine the initial cooling of granulites from the Fe/Mg diffusion, which is an especially sensitive monitor of initial cooling at high temperatures. Results of diffusion modeling of Fe-Mg exchange between garnet, clinopyroxene and biotite suggest that the HC of Sri Lanka has undergone at least three cooling stages. The U-Pb dating from metamorphic zircons from syntectonic granitoids yields an age of $608 \pm 3\text{Ma}$, which is interpreted as the period of peak metamorphic event. The first cooling had occurred at a maximum cooling

rate of $1^{\circ}\text{C}/\text{Ma}$ in the first 55 Ma starting at 875°C and 9kbar. The slow cooling rate is probably due to a prolonged crustal residence time at the beginning of cooling until the temperature of 820°C . In the second step, cooling continues much faster at a rate of $\sim 30^{\circ}\text{C}/\text{Ma}$ until the temperature decreases below the $600\text{-}650^{\circ}\text{C}$. This may be related to rapid tectonic uplift of neighbouring Gondwana fragments during the Ordovician period. However, the third cooling rate can also be accounted because the measured zoning profile shows the slight deviation from the calculated zoning profile for $30^{\circ}\text{C}/\text{Ma}$ at the outermost garnet rim (Fig 2.8). This can be tentatively assumed to be around $15^{\circ}\text{C}/\text{Ma}$, which may perhaps continue until the garnet-biotite Fe-Mg exchange closed. The Rb-Sr biotite ages of 439 ± 10 Ma (Hözl et al. 1991), which is believed to record the time at temperatures around $300 \pm 30^{\circ}\text{C}$ (Spear 1993), indicates the final cooling during the uplift of the basement.

Some radiometric data available for Sri Lankan crystalline rocks provide a useful comparison with our results (Fig. 2.9). Hözl et al. (1991) have tentatively constructed a two stage cooling history from Sm-Nd garnet ages and Rb-Sr/whole rock biotite ages from the rocks of the HC. The cooling rate of 2 to $3^{\circ}\text{C}/\text{Ma}$ was determined from the garnet dating followed by a significantly higher rate of around 10 to $25^{\circ}\text{C}/\text{Ma}$ from biotite ages. These results are not in agreement with the conclusions of our results, especially the first step of cooling. This discrepancy has occurred probably because they derived the cooling rates assuming the blocking temperature of garnet at 800°C . Mezger et al. (1992) reported that the closure temperature for Sm-Nd exchange in garnet would be about 600°C , which is well below the temperature ($\sim 800^{\circ}\text{C}$) used to calculate the cooling rates by Hözl et al. (1991). This suggests that the first stage of cooling inferred from Sm-Nd garnet ages is misleading. The second step in the cooling history is in relatively good agreement with our findings. However, taking into account the few radiogenic ages and larger errors, cooling rates determined from geochronology may not be correctly representing the cooling history of the Sri Lankan granulites.

REFERENCES

- Amstrong JT* (1988) Quantitative analyses of silicate and oxide minerals: comparisons of Monte Carlo, ZAF and Phi-rho-z procedures. In: *Microbeam analysis-1988 (Newbury DE ed)*. San Francisco Press, San Francisco, 239-246
- Amstrong JT* (1989). CITZAF: combined ZAF and phi-rho (Z) electron beam correction programs. California Institute of Technology, Pasadena, CA
- Bhattacharya A, Mohanty L, Maji A, Sen SK, Raith M* (1992) Non-ideal mixing in the phlogopite-annite binary: Constraints from experimental data on Mg-Fe partitioning and a reformulation of the garnet-biotite geothermometer. *Contrib. Mineral. Petrol.* 111: 87-93
- Brady JB, McCallister RH* (1983) Diffusion data for clinopyroxenes from homogenisation and self-diffusion experiments. *Am. Mineral.* 68: 95-105
- Brey GP, Köhler T* (1990) Geothermobarometry in four-phase Lherzolites II. New thermobarometers and practical assessment of existing thermobarometers. *J. Petrol.* 31: 1353-1378
- Burton KW, O'Nions RK* (1990) The timescale and mechanism of granulite formation at Kurunegala, Sri Lanka. *Contrib. Mineral. Petrol.* 106: 66-89
- Carlson WD, Lindsley DH* (1988) Thermometry of pyroxenes on the join $Mg_2Si_2O_6$ - $CaMgSi_2O_6$. *Am. Mineral.* 73: 242-252
- Chakraborti S, Ganguly J* (1992) Cation diffusion in aluminosilicate garnets: experimental determination in spessartine-almandine diffusion couples, evaluation of effective binary diffusion coefficients, and applications. *Contrib. Mineral. Petrol.* 111: 74-86
- Connolly JAD* (1990) Multivariate phase diagrams: an algorithm based on generalized thermodynamics. *Am. J. Sci.* 290: 666-718
- Cooray PG* (1994) The Precambrian of Sri Lanka: a historic review. *Precam. Res.* 66: 3-18
- Cyan RT, Lasaga AC* (1985) Self-diffusion of magnesium in garnet at 750-900°C. *Am. J. Sci.* 285: 328-350
- Dasgupta S, Sengupta Pulak, Guha D, Fukuoka M* (1991) A refined garnet-biotite Fe-Mg exchange geothermometer and its application in amphibolites and granulites. *Contrib. Mineral. Petrol.* 109: 130-137
- Dodson MH* (1973) Closure temperature in cooling geochronological and petrological systems. *Contrib. Mineral. Petrol.* 40: 259-274

- Ebadi A, Johannes W* (1991) Beginning of melting and composition of first melts in the system Qtz-Ab-Or-H₂O-CO₂. *Contrib. Mineral. Petrol.* 106: 286-295
- Eckert JOJ, Newton RC, Kleppa OJ* (1991) The ΔH of reaction and recalibration of garnet-pyroxene-plagioclase-quartz geobarometers in the CMAS system by solution calorimetry. *Am. Mineral.* 76:148-160
- Eiler JM, Baumgartner LP, Valley JW* (1992) Intercrystalline stable isotope diffusion: a fast grain boundary model. *Contrib. Mineral. Petrol.* 112: 534-557
- Eiler JM, Valley JW, Graham CM, Baumgartner LP* (1995) The oxygen isotope anatomy of a slowly cooled metamorphic rock. *Am. Mineral.* 80: 757-764
- Ellis DJ, Green EH* (1979) An experimental study of the effect of Ca upon garnet-clinopyroxene Fe-Mg Exchange equilibria. *Contrib. Mineral. Petrol.* 71:13-22
- Ellis DJ, Green EH* (1985) Garnet-forming reactions in mafic granulites from Enderby Land, Antarctica-implication for geothermometry and geobarometry. *J. Petrol.* 26: 633-662
- Essene EJ* (1989). The current status of thermobarometry in metamorphic rocks In evolution of metamorphic belts. (*Daly JS, Cliff RA, Yardley BWD eds*). *Geol. Soc. London. Sp. Publ.* 43: 1-44
- Ferry JM, Spear FS* (1978) Experimental calibration of the partitioning of Fe and Mg between biotite and garnet. *Contrib. Mineral. Petrol.* 66:113-117
- Florence FP, Spear FS* (1995) Intergranular diffusion kinetics of Fe and Mg during retrograde metamorphism of a pelitic gneiss from the Adirondack Mountains Earth Planet Sci. Lett. 134: 329-340
- Ganguly J, Saxena SK* (1984). Mixing properties of aluminosilicate garnets: constraints from natural and experimental data, and applications to geothermobarometry, *Am. Mineral.* 69: 88-97
- Ganguly J, Tazzoli V* (1994) Fe²⁺-Mg interdiffusion in orthopyroxene: Retrieval from the data on intracrystalline exchange reaction. *Am. Mineral.* 79: 930-937
- Ganguly J, Cheng W, Chakraborti S* (1998) Cation diffusion in aluminosilicate garnets: experimental determination in pyrope-almandine diffusion couples. *Contrib. Mineral. Petrol.* 131:171-180
- Ghose S, Ganguly J* (1982) Mg-Fe order disorder in ferromagnesian silicates. In: *Advances in physical geochemistry 2* (*Saxena SK ed*), Springer Verlag New York, 3-100
- Giletti BJ* (1986) Diffusion effects on oxygen isotope temperatures of slowly cooled igneous and metamorphic rocks *Earth Planet Sci. Lett.* 77: 218-228

- Hodges KV, Spear FS* (1982). Geothermometry, geobarometry and Al_2SiO_5 triple point at Mt. Moosilauke, New Hampshire. *Am. Mineral.* 67: 1118-1134
- Holland TJB, Blundy J* (1994) Non-ideal interactions in calcic amphiboles and their bearing on amphibole-plagioclase thermometry. *Contrib. Mineral. Petrol.* 116: 433-447
- Holland TJB, Powell R* (1991). A compensated-Redlich-Kwong (CORK) equation for volumes and fugacities of CO_2 and H_2O in the Range 1 bar to 50Kbar and 100-1600°C. *Contrib. Mineral. Petrol.* 109: 265-273
- Holland TJB, Powell R* (1992) Plagioclase feldspars: activity-composition relations based upon Darken's quadratic formalism and Landau theory. *Am. Mineral.* 77: 53-61
- Holland TJB, Powell R* (1996) Thermodynamics of order-disorder in minerals:II. Symmetric formalism applied to solid solutions. *Am. Mineral.* 81:1425-1437
- Holland TJB, Powell R* (1998) An internally consistent thermodynamic data set for phases of petrological interest. *J. metamorphic Geol.* 16: 309-343
- Hözl S, Köhler H, Kröner A, Jaeckel P, Liew TC* (1991) Chronology of Sri Lankan basement. In: *The Crystalline crust of Sri Lanka, Part 1, summary of research of the German-Sri Lankan consortium, Part 1 (Kröner A ed).* Geol. Surv. Dep. Prof. Pap. 5: 237-257
- Hözl S, Hofmann AW, Todt W, Köhler* (1994).U-Pb geochronology of the Sri Lankan basement. *Precam. Res.* 66: 123-149
- Inderas A, Martignole J* (1985). Biotite-garnet geothermometry in the granulite facies: the influence of Ti and Al in biotite. *Am. Mineral.* 70: 272-278
- Joesten R* (1991) Grain boundary diffusion boundary kinetics in silicate and oxide minerals. In: *Diffusion, atomic ordering and mass transport; selected topics in geochemistry (Ganguly J ed)* Adv. Phys. Geochem. 8, Springer Verlag, 345-395
- Johannes W, Holtz F* (1996) Petrogenesis and experimental petrology of granitic rocks, Springer Verlag, Heidelberg, pp337
- Kleeman U, Reinhardt J* (1994). Garnet-biotite thermometry revisited: The effect of Al^{VI} and Ti in biotite. *Eu. J. Mineral* 6: 925-941
- Kretz R* (1982). Transfer and exchange equilibria in a portion of the pyroxene quadrilateral as deduced from natural and experimental data. *Geochim. Cosmochim. Acta* 46: 411-421
- Kretz R* (1983) Symbols for rock forming minerals. *Am Mineral* 68: 277-279
- Kriegsman LM* (1993) Geodynamic evolution of the Pan-African lower crust in Sri Lanka, PhD Thesis, University of Utrecht, The Netherlands, pp207

- Kröner A* (1991) African linkage of Precambrian Sri Lanka, *Geol. Rundschau* 80: 429-440
- Kröner A, Cooray PG, Vithanage PW* (1991) Lithotectonic sub divisions of Precambrian basement of Sri Lanka, In: *The Crystalline crust of Sri Lanka, Summary of research of the German-Sri Lankan consortium, Part 1* (*Kröner A* ed). *Geol. Surv. Dep. Prof. Pap.* 5: 5-21
- Kröner A, Williams AS* (1993) Age of metamorphism of high-grade rocks of Sri Lanka, *J. Geol.* 101: 521-531
- Lamb WM, Valley JW* (1988) Granulite facies amphibole and biotite equilibria, and calculated peak-metamorphic water activities. *Contrib. Mineral. Petrol.* 100: 349-360
- Lasaga AC* (1983) Geospeedometry: An extension of geothermometry. In: *Kinetics and equilibrium in mineral reactions* (*Saxena SK* ed). *Adv. Phys. Geochem.* 3, Springer Verlag, 243-284
- Lasaga AC, Richardson SM, Holland HD* (1977). The mathematics of cation diffusion and exchange between silicate minerals during retrograde metamorphism, In: *Energetics of geological process* (*Saxena SK, Bhattacharji S* eds), New York, Springer Verlag, 81-114
- Lindsley DH, Grover JE, Davidson PM* (1981) The thermodynamics of the $Mg_2Si_2O_6$ - $CaMgSi_2O_6$ join: A review and an improved model. In: *Thermodynamics of minerals and melts.* (*Newton RC, Novrotsky A, Wood BJ* eds) *Adv. Phys. Geochem.* 1 Springer Verlag, 149-175
- Lindström R, Viitanen M, Juhanoja J* (1991) Geospeedometry of metamorphic rocks: examples in the Rantasalmi-Sulkava and Kiuruvesi areas, eastern Finland. Biotite-garnet diffusion couples. *J. Metamorphic Geol.* 9: 181-190
- Mezger K, Essene EJ, Halliday AN* (1992) Closure temperature of the Sm-Nd system in metamorphic garnets *Earth Planet. Sci. Lett.* 113: 397-409
- Milicenda CC, Liew TC, Hofmann AW* (1994) Nd isotopic mapping of the Sri Lanka basement: update and additional constraints from Sr isotopes. *Precam. Res.* 66: 95-110
- Pattison DRM* (1994) Are reversed Fe-Mg exchange and solid solution experiments really reversed? *Am. Mineral.* 79: 938-950
- Perchuk LL, Lavrent'eva IV* (1983). Experimental investigation of exchange equilibria in the system cordierite-garnet-biotite. In: *Kinetics and equilibrium in mineral reactions* (*Saxena SK* ed). *Adv. Phys. Geochem.* 3, Springer Verlag, 199-239
- Sandiford M, Powell R, Martin SF, Perera LRK* (1988). Thermal and baric evolution of garnet granulites from Sri Lanka. *J. Metamorphic Geol.* 6: 351-364

- Schenk V, Raase P, Schumacher R* (1988) Very high temperatures and isobaric cooling before tectonic uplift in the Highland Series. *Terra Cognita* 8: 265
- Schumacher R, Faulhaber S* (1994) Summary and discussion of P-T estimates from garnet-pyroxene-plagioclase-quartz-bearing granulite-facies rocks from Sri Lanka. *Precam. Res.* 66: 295-308
- Sengupta Pulak, Dasgupta S, Bhattacharya PK, Hariya Y* (1989) Mixing behaviour in quaternary garnet solid solution and an extended Ellis and Green garnet-clinopyroxene geothermometer. *Contrib. Mineral. Petrol.* 103: 223-227
- Spear FS* (1991) On the interpretations of peak metamorphic temperatures in light of garnet diffusion during cooling. *J. Metamorphic Geol.* 9: 379-388
- Spear FS* (1993) Metamorphic phase equilibria and pressure-temperature-time paths Monograph series, Mineral. Soc. Am, Washinton D.C., pp799
- Spear FS, Florence FP* (1992) Thermobarometry in granulites: pitfalls and new approaches. *Precam. Res.* 55: 209-241
- Spear FS, Parrish RR* (1996) Petrology and cooling rates of the Valhalla Complex, British Columbia, Canada. *J. Petrol.* 37:733-765
- Spear FS, Peacock SM* (1990) Metamorphic P-T-t paths: Program manual and computer exercises for the calculation of metamorphic phase equilibria, pressure-temperature-time paths and thermal evolution of orogenic belts. *Geol. Soc. Am. Short Course*, Dallas, Texas, pp188
- Voll G, Evangelakakis C, Kroll H* (1994) Revised two-feldspar geothermometry applied to Sri Lankan feldspars. *Precam. Res.* 66: 351-377
- Weyer S, Jarick J, Mezger K* (1999) Quantitative-temperature-time information from retrograde diffusion zoning in garnet: constraints for the P-T-t history of the central Black Forest, Germany. *J. Metamorphic Geol.* 17: 449-461

Table 1.1 Chemistry of mineral assemblages used to calculate the thermobarometry at Rupaha

Assemblage Sample no.	Grt-Bt assemblages RU 9708				Grt-Cpx assemblages RU 9708			Opx-Cpx assemblages RU 9817			Grt-Cpx-Pl-Qtz assemblages RU 9708A				
	Grt rim	Grt core	Bt at Grt contact	Bt matrix	Grt rim	Cpx rim	Opx core	Opx core	Cpx core	Grt core	Pl matrix	Cpx core	Grt core	Pl matrix	Cpx core
No. of Oxygens	12	12	11	11	12	6	6	6	6	12	8	6	12	8	6
SiO ₂	38.24	37.95	37.18	38.07	38.65	52.19	48.33	48.33	50.65	38.52	61.45	52.04	38.52	61.45	52.04
TiO ₂	0.06	0.08	5.67	5.26	0.08	0.11	0.08	0.08	0.09	0.04	0.00	0.22	0.04	0.00	0.22
Al ₂ O ₃	21.43	21.21	13.18	12.89	21.15	1.57	0.68	0.68	1.22	21.32	23.80	2.00	21.32	23.80	2.00
Cr ₂ O ₃	0.05	0.06	0.10	0.00	0.10	0.00	0.05	0.05	0.05	0.05	0.05	0.06	0.05	0.05	0.06
FeO	23.61	22.98	14.63	14.35	23.30	9.52	38.03	38.03	18.44	23.50	0.05	10.20	23.50	0.05	10.20
MnO	5.91	5.81	0.05	0.14	6.25	1.00	0.89	0.89	0.38	6.27	0.00	1.23	6.27	0.00	1.23
MgO	5.48	5.66	14.12	13.55	5.44	13.54	10.66	10.66	8.45	5.59	0.02	13.14	5.59	0.02	13.14
CaO	5.92	5.96	0.21	0.16	6.05	21.39	0.87	0.87	20.75	5.99	5.57	21.09	5.99	5.57	21.09
Na ₂ O	0.07	0.11	0.21	0.22	0.19	0.34	0.01	0.01	0.51	0.01	8.40	0.52	0.01	8.40	0.52
BaO	nd	nd	0.31	0.24	0.00	0.00	nd	nd	nd	nd	0.00	nd	nd	0.00	nd
K ₂ O	nd	nd	9.08	8.65	0.00	0.02	nd	nd	nd	nd	0.48	0.02	nd	0.48	0.02
F	0.00	0.09	1.63	1.55	0.13	0.00	nd	nd	nd	0.00	nd	nd	0.00	nd	nd
Cl	0.01	0.03	0.31	0.35	0.08	0.00	nd	nd	nd	0.02	nd	nd	0.02	nd	nd
Total	100.78	99.94	96.66	95.43	101.43	99.68	99.61	99.61	100.55	101.30	99.83	100.51	101.30	99.83	100.51
Cations															
Si	2.97	2.97	2.66	2.73	2.99	1.96	1.97	1.97	1.96	2.98	2.74	1.95	2.98	2.74	1.95
Al	1.96	1.96	1.11	1.09	1.93	0.07	0.03	0.03	0.06	1.94	1.25	0.09	1.94	1.25	0.09
Ti	0.00	0.01	0.31	0.28	0	0.00	0	0	0	0	0	0.01	0	0	0.01
Cr	0	0	0.01	0	0.01	0.00	0	0	0	0	0	0	0	0	0
Fe	1.53	1.50	0.88	0.86	1.51	0.30	1.29	1.29	0.60	1.52	0	0.32	1.52	0	0.32
Mg	0.64	0.66	1.51	1.45	0.63	0.76	0.65	0.65	0.49	0.64	0	0.73	0.64	0	0.73
Mn	0.39	0.39	0.01	0.01	0.41	0.03	0.03	0.03	0.01	0.41	0	0.04	0.41	0	0.04
Ba	0	0	0.01	0.01	0	0.00	0	0	0	0	0	0	0	0	0
Ca	0.49	0.50	0	0.01	0.50	0.86	0.04	0.04	0.86	0.50	0.27	0.85	0.50	0.27	0.85
Na	0.01	0.02	0.03	0.03	0.03	0.03	0	0	0.04	0	0.73	0.04	0	0.73	0.04
K	0	0	0.83	0.79	0	0.00	0	0	0	0	0.03	0	0	0.03	0
Total Cations	8	8	7.36	7.25	8	4	4.02	4.02	4.02	8	5.01	4.02	8	5.01	4.02
F	0	0.02	0.37	0.35	0.03	0	0	0	0	0	0	0	0	0	0
Cl	0	0	0.04	0.04	0.01	0	0	0	0	0	0	0	0	0	0
X _{almandine}	0.50	0.49			0.49					0.49			0.49		
X _{pyrope}	0.21	0.22			0.21					0.21			0.21		
X _{grossular}	0.16	0.16			0.16					0.16			0.16		
X _{spessartine}	0.13	0.13			0.13					0.13			0.13		
Fe/(Fe+Mg)			0.37	0.37		0.28	0.67	0.67	0.55						0.30

Table 2.2 Results of thermobarometry estimates for granulites from the Rupaha, Sri Lanka

	Temperature (°C)	Pressure (kbar)
Grt-Bt / GADS		
Dasgupta et al. (1992) and Eckert et al. (1991)		
garnet core	774-840 (820 ± 20)	7.6-8.3 8.1 ± 0.2)
garnet rim	685-821 (780 ± 40)	6.2-8.1 7.6 ± 0.6)
Grt-Cpx / GADS		
Sengupta et al. (1989) and Eckert et al. (1991)		
	706-738 (724 ± 10)	6.9-7.2 7.1 ± 0.1)
Opx-Cpx / GADS		
Brey and Köhler (1990) and Eckert et al. (1991)		
	870-882 (874 ± 4)	8.6-9.1 8.7 ± 0.4)

Table 2.3 Modal mineralogy of Rupaha mafic granulites

Mineral		Modal Percentage
		Radius/half length (µm) of mineral grains
Garnet	47.8	300
Biotite	27.2	300
Plagioclase	14.6	300
Cpx	7.4	200
Quartz	3.0	300
Total	100.00	

Table 2.4 Calculated peak compositions of garnet, biotite and clinopyroxene

	Peak	Apparent	Reset
	temperature	temperature	temperature
	calculated	core	rim
	875°C	820°C	685°C
garnet			
Fe	1.503	1.528	1.605
Mg	0.670	0.645	0.479
Fe/(Fe+Mg)	0.692	0.703	0.770
Mg/(Fe+Mg)	0.308	0.297	0.230
biotite			
Fe	0.967	0.928	0.928
Mg	1.551	1.590	1.590
Fe/(Fe+Mg)	0.384	0.369	0.369
Mg/(Fe+Mg)	0.616	0.631	0.631
Cpx			
Fe	0.341	0.311	0.311
Mg	0.697	0.727	0.727
Fe/(Fe+Mg)	0.329	0.300	0.300
Mg/(Fe+Mg)	0.671	0.700	0.700

FIGURE CAPTIONS

Fig. 2.1 Simplified geological map of the area around Rupaha, Sri Lanka (after Cooray 1994; Kröner et al. 1991)

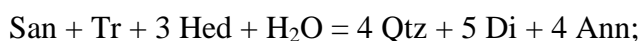
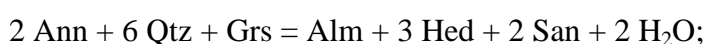
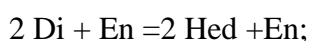
Fig. 2.2 (a). Photomicrograph showing relationship of model garnet to the rock and other phases in the sample. Inclusions of biotite in garnets evidence for early phase of biotite. (b). Photomicrograph illustrates small hornblende inclusions in orthopyroxene in two-pyroxene-bearing gneiss. Note the co-existing Opx-Cpx assemblage in the upper right corner.

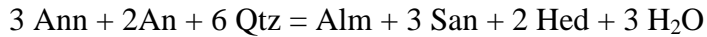
Fig. 2.3 (a). Backscattered electron image of co-existing garnet-biotite in granulites at Rupaha, Sri Lanka. A chemical composition profile was run across the garnet along the drawn line A-B. (b). Profiles are showing mole fractions of almandine, pyrope, grossular and spessartine along the line depicted in Fig 2.3a. Profiles were assembled from 174 closely spaced quantitative spot analyses of garnet. Note that X_{Mg} decreases and X_{Fe} and X_{Mn} increases at the biotite contacts while no significant X_{Ca} change is observed.

Fig. 2.4 (a). Compositional map showing the Mg distribution of garnet contacting biotite, plagioclase and garnet with a resolution of 1 μ m (the area is as indicated in the box in Fig. 2.3a). Note that Mg decreases of Mg at the rims of garnet touching biotite.

Fig. 2.5 Summary of the results of combined ion-exchange thermobarometries of granulites at Rupaha, Sri Lanka.

Fig. 2.6 Schreinemakers grid (CKFMASH) calculated at $X_{H_2O} = 0.1$ using the thermodynamic database of Holland and Powell (1998) (shaded area is representative of Rupaha granulites). The following reactions represent the respective numbers in the diagram: Note that reaction equations are written such at the high temperature assemblage is on the right of the ' = ' sign





The experimentally determined solidus curve of the system Qtz-Ab-Or-H₂O-CO₂ at X_{H₂O} = 0.1 is from (Ebadi and Johannes 1991; Johannes and Holtz 1996). Abbreviations as in Kretz (1992) [Calculated activities used: *orthopyroxene*: a_{En} = 0.11, a_{Fs} = 0.39; *clinopyroxene*: a_{Di} = 0.40, a_{Hed} = 0.44; *biotite*: a_{Ann} = 0.013, a_{Phl} = 0.16; *feldspar*: a_{An} = 0.28, a_{Ab} = 0.75, a_{San} = 0.82; *garnet*: a_{Prp} = 0.017, a_{Grs} = 0.007, a_{Alm} = 0.089; *hornblende*: a_{Tr} = 0.005].

Fig. 2.7 Arrhenius plots of Fe-Mg and Ca-Mg interdiffusion coefficients used in this study: garnet (Ganguly et al. 1998), biotite (Pattison, 1994), orthopyroxene and clinopyroxene (Fe-Mg: Ganguly and Tazzoli 1994; Ghost and Ganguly 1982), clinopyroxene (Ca-Mg: Brady and McCallister 1983).

Fig. 2.8 Comparisons of geospeedometry simulations of Diff-Gibbs profiles with different cooling rates and measured Mg/(Fe+Mg) of garnets in granulites at Rupaha. The best-fit model assumed at the cooling rate of 30°C/Ma (see text for more details).

Fig. 2.9 Calculated cooling paths of granulites from Sri Lanka from this study compares with the geochronological cooling rates from Hölzl et al. 1991. Peak metamorphism was estimated from U-Pb zircon ages (608 ± 3Ma) (Hölzl et al. 1991, 1994). The geochronological cooling paths are inferred from: (1) blocking temperatures of garnet from Sm-Nd garnet ages (561±12Ma) (Hölzl et al. 1991), (2) blocking temperatures of biotites from Rb-Sr ages (439 ± 10Ma) (Hölzl et al. 1991), (3) Rb-Sr blocking temperature of biotite (300 ± 30°C) from Spear (1993).

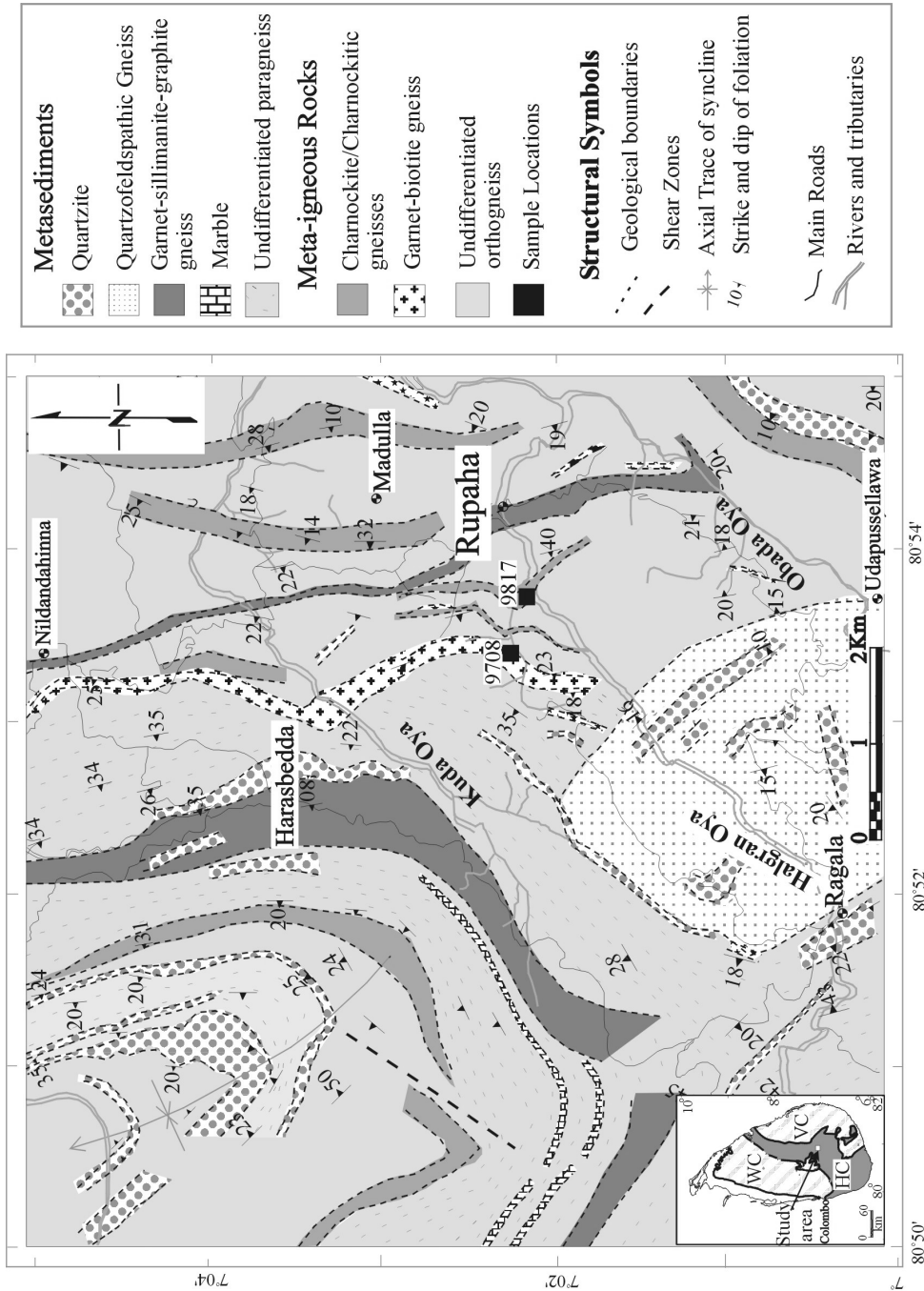


Fig. 2.1

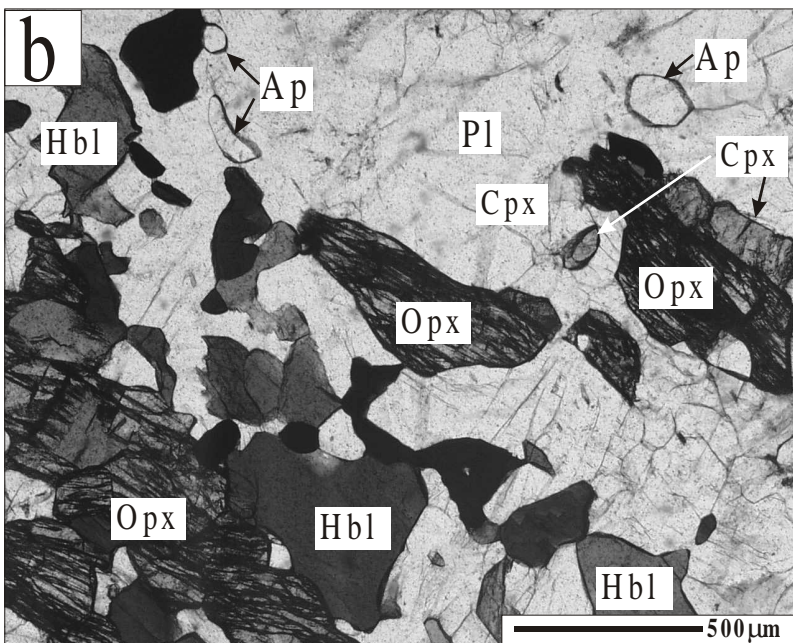
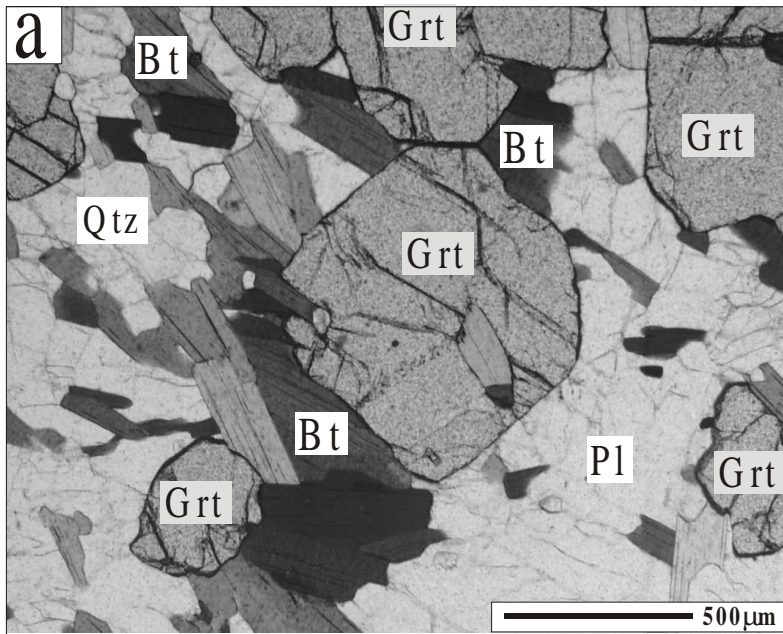


Fig. 2.2

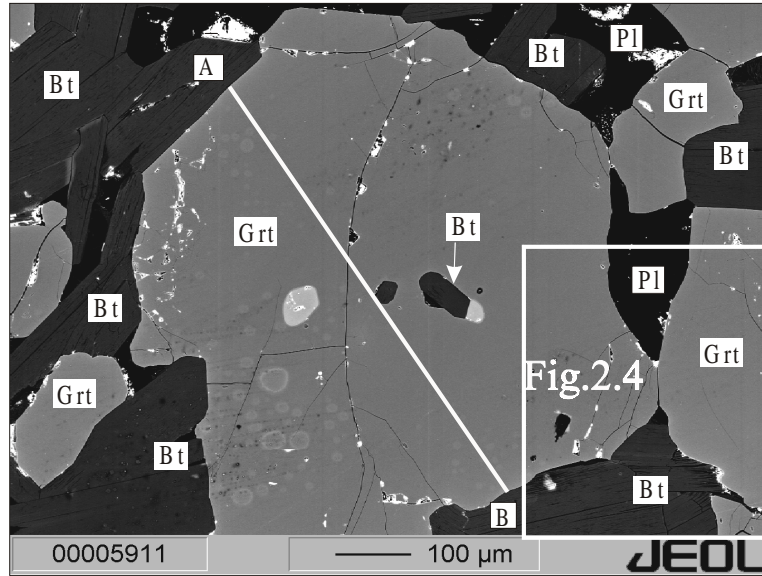


Fig.2.3a

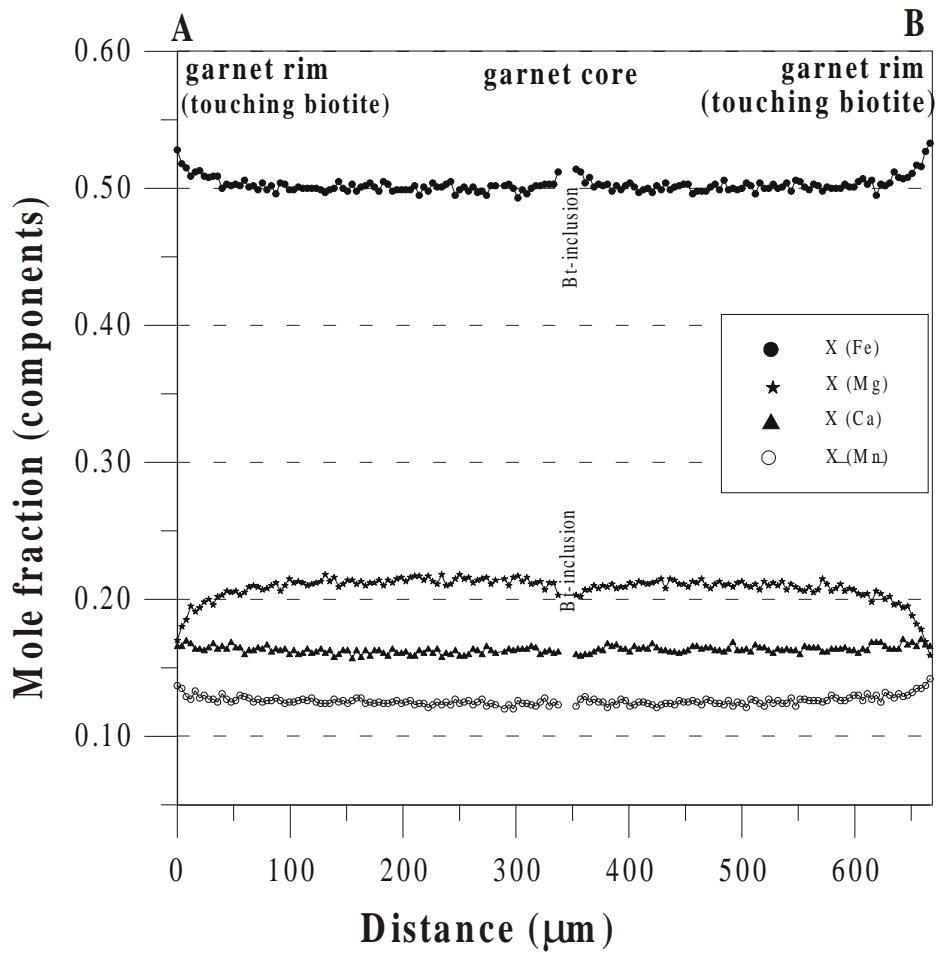


Fig. 2.3b

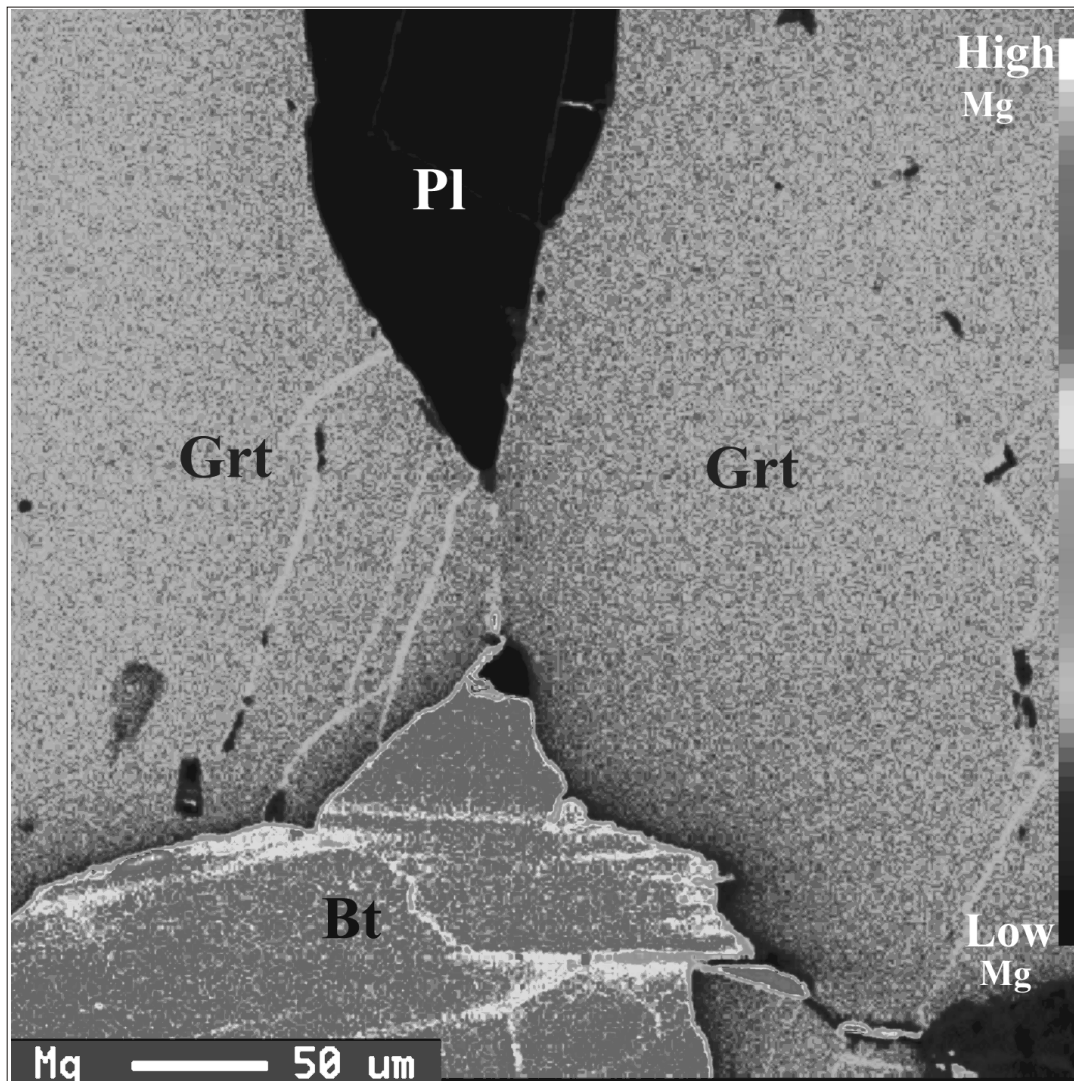


Fig. 2.4

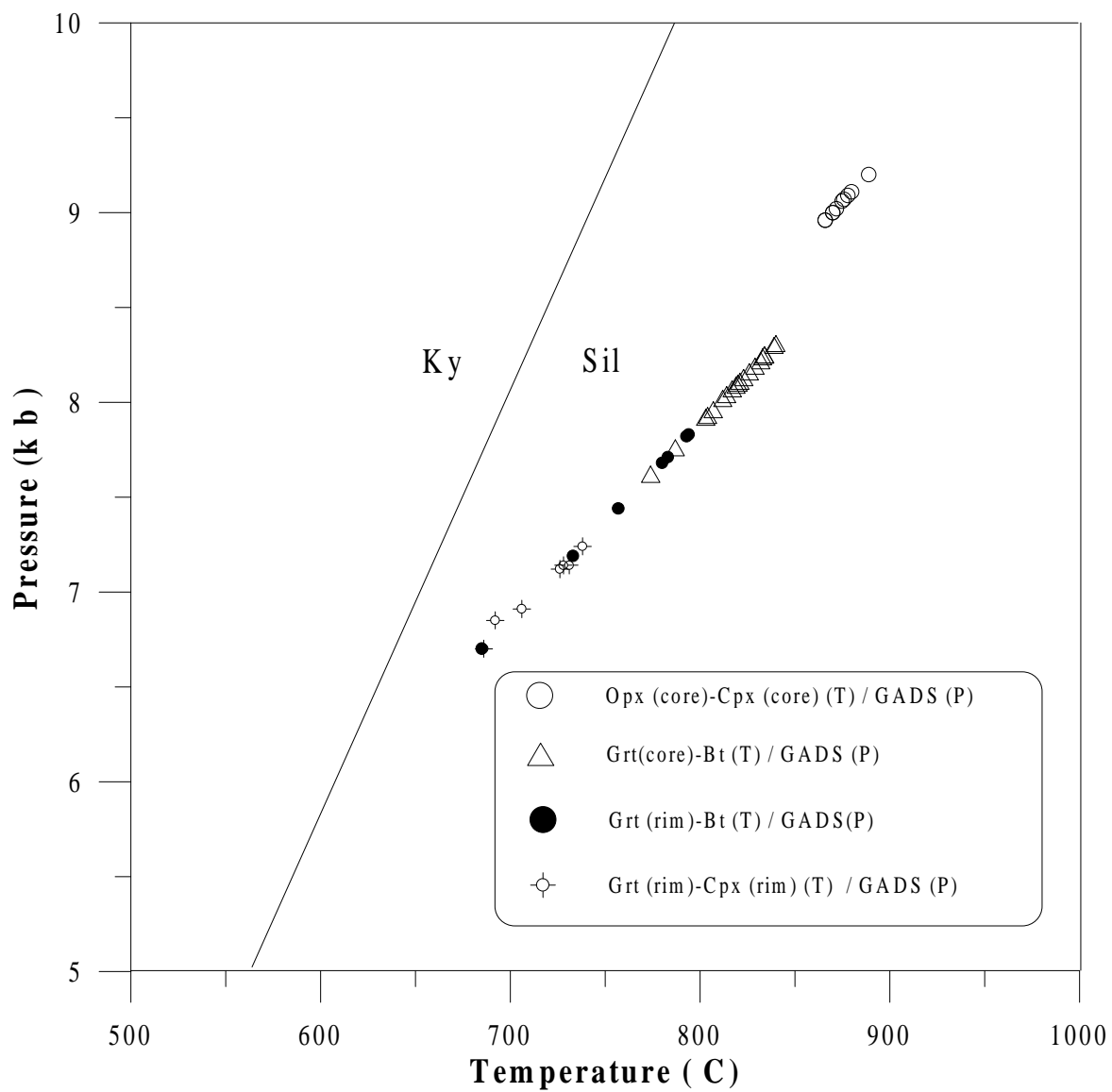


Fig. 2.5

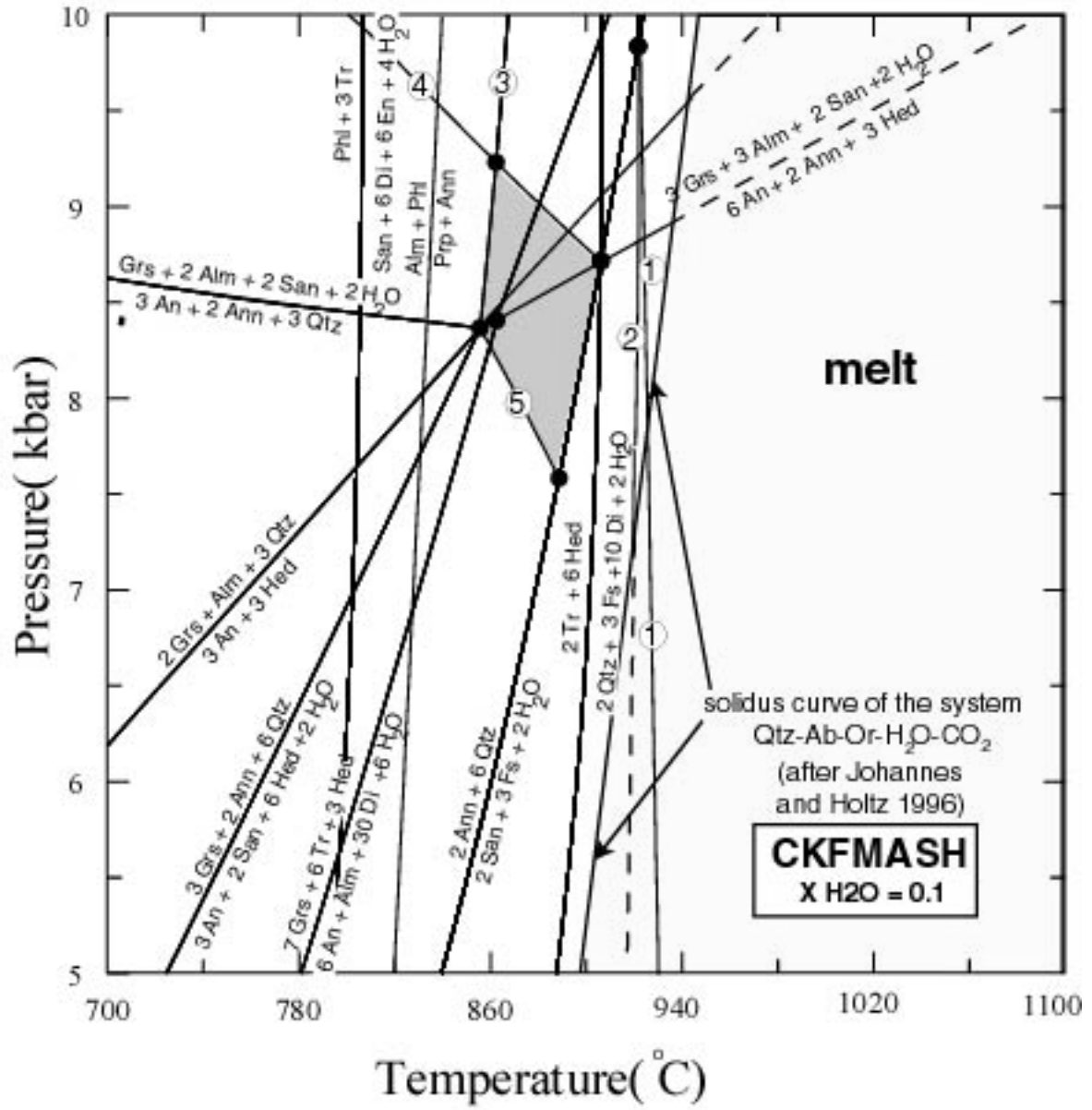


Fig 2.6

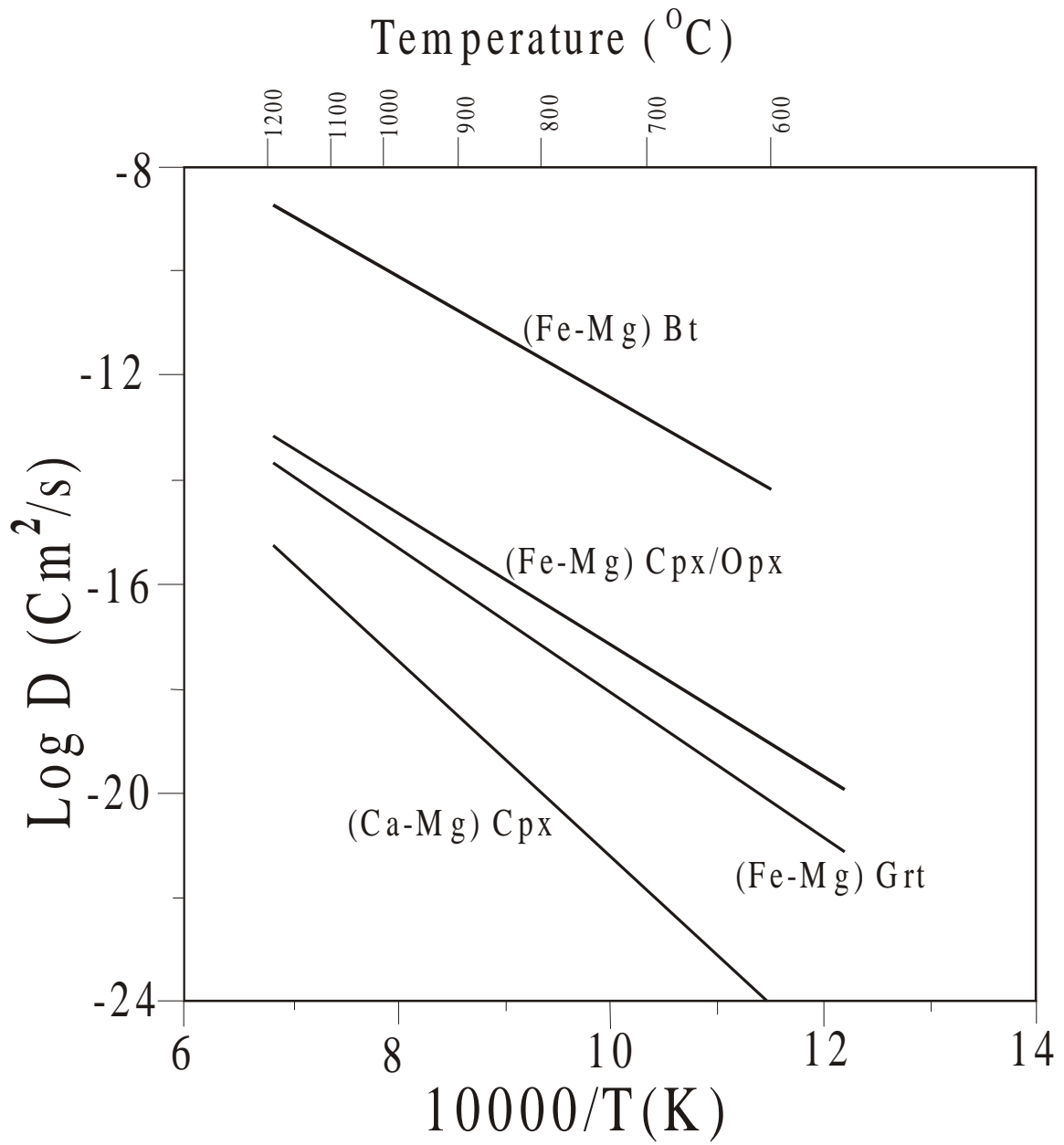


Fig. 2.7

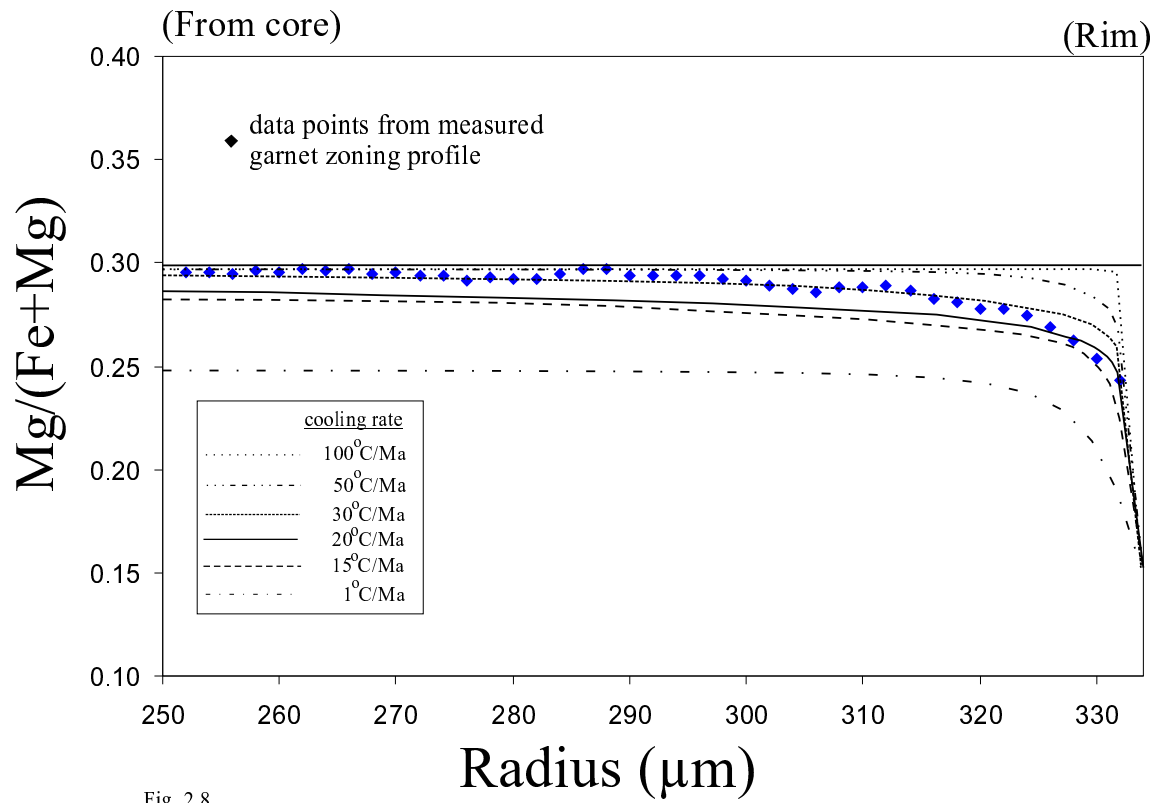


Fig. 2.8

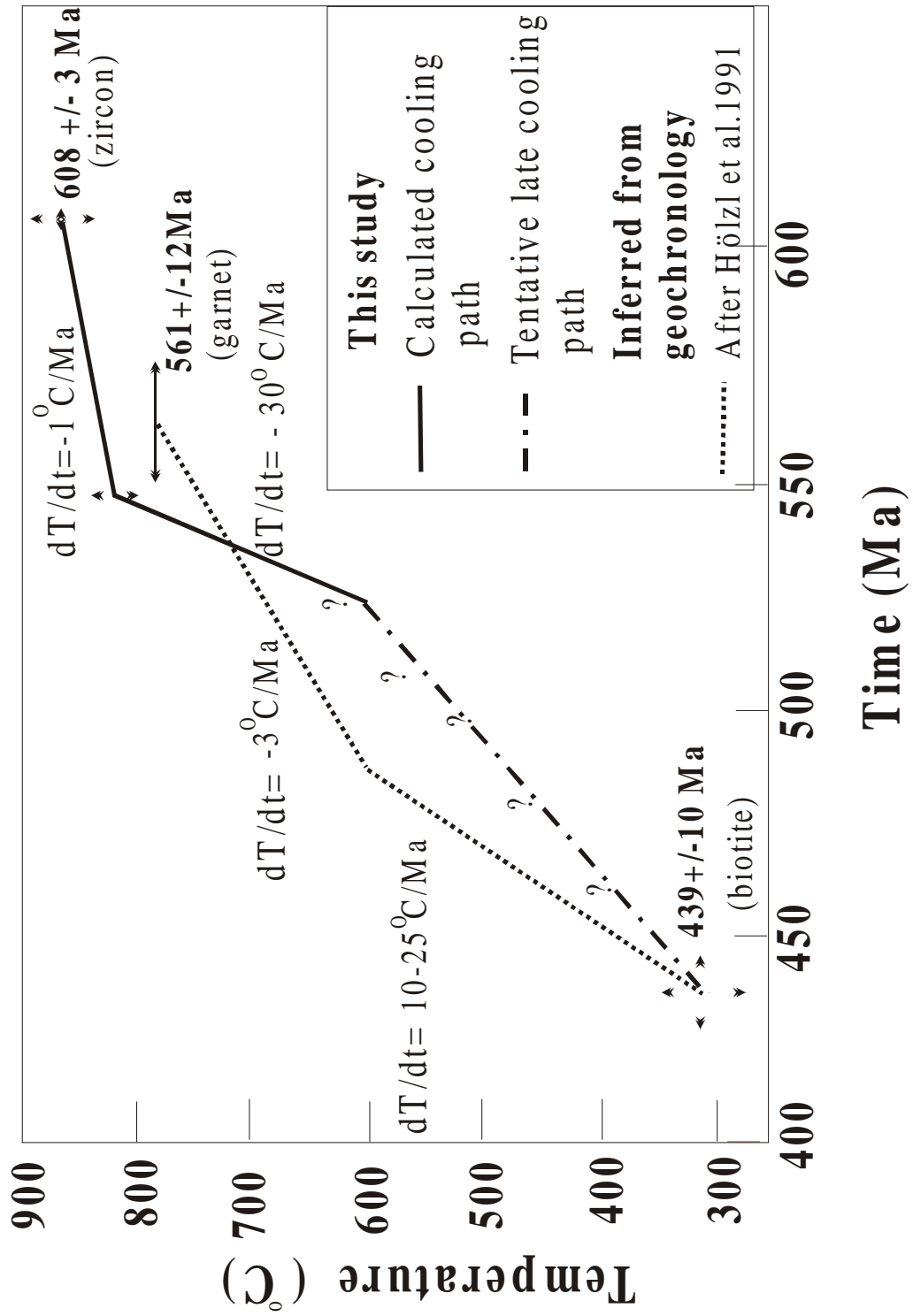


Fig.2.9

Chapter 3

**High-temperature metasomatism and retrogression of granulite facies
ultramafics from the Highland Complex of Sri Lanka: Field
relationships, phase equilibria and fluid fluxes**

ABSTRACT

The ultramafic rocks at Rupaha, Sri Lanka were emplaced early into the Proterozoic basement and subjected to deformation and granulite facies metamorphism at 850°C at 9 kbar. The results of two-pyroxene thermometry are consistent with geothermobarometric results obtained from the surrounding granulites. Structures, textures and the mineralogy of the blackwall suggest that the K-Si-metasomatism took place contemporaneous to the granulite facies metamorphism. Fluid circulating at the deep crust would result in several types of metasomatic processes. The metasomatic reaction was started by infiltration of K₂O and SiO₂ along the lithological contacts between ultramafic rocks and surrounding granulites or diffusion of these components from the surrounding granulites. As the ultramafic rock cooled together with surrounding granulites, the retrograde overprints and the carbonation and hydration textures are produced. These textures involve a partially retrogression of enstatite and forsterite to tremolite and dolomite, which formed through introduction of CaO and CO₂. The stability of tremolite + dolomite at 730–640°C and 9kbar condition records a $0.40 \geq X_{\text{CO}_2} \geq 0.15$ for the fluid phase.

INTRODUCTION

Ultramafic rocks found in metamorphic terranes are frequently exposed as suites of small bodies but are of special petrological interest. They may lose their original mineralogical, structural, textural and bulk chemical properties on their way to the surface with advancing metamorphism. Nevertheless, the understanding of the relationship of pressure, temperature, fluid history, mineral transformation and reaction textures of ultramafic rocks can provide many clues to its original nature. Ultramafics are often intercalated with host gneisses in granulite terranes, which have chemistry different from those of ultramafics. The contrast in chemistry between two adjacent rocks in such a terrane could often lead to metasomatism. Significant advances in understanding the process of such metamorphic ultramafic rocks have come from several previous studies (e.g. Evans and Trommsdorf 1970; Trommsdorf and Evans 1974; Springer 1974; Pinsent and Hirst 1977; Evans 1977; Desmarais 1981; Kimball et al. 1985; Peretti et al. 1992; Kassoli-Fournaraki et al. 1995; Dasgupta et al., 1997).

Until recently, attention has been focused on pressure and temperature conditions of the rocks as a major cause of metamorphism. The finding of fluid inclusions in minerals (see reviews by Roedder 1984; Crawford and Hollister 1986) and recent discussions on the role of fluids in regional metamorphic and contact metamorphic environments (e.g. Rice and Ferry 1982; see also reviews by Barton et al. 1991 and Ferry 1991) reveal that fluids play an important role in these environments. The study of fluid–rock ratio of rocks and the nature of fluid flow during metamorphism has been discussed extensively in recent times (e.g. Walther and Wood 1986; Rumble 1989; Baumgartner and Ferry 1991; Newton et al. 1998). Mineral assemblages and the stable isotopic compositions of metamorphic rocks are routinely used as a monitor of metamorphic fluid flow. In particular, most mineralogical investigations are focussed on the role of fluid flow in driving prograde reactions (e.g. Labotka et al. 1988; Bickle and Barker 1990; Baumgartner and Ferry 1991; Nabelek 1991; Cartwright and Buick 1995). However, the role of retrograde fluid flow, which usually involves hydration and carbonation, following peak conditions, has not received much attention (but Ferry 1996; Roselle 1997). The goal of this study is to discuss field relationships, petrology and geochemistry of ultramafic enclaves that characterize the pressure-temperature and fluid compositions at Rupaha, Sri Lanka. Using this data, we will

present evidences for the high temperature and retrograde fluid-rock interactions of ultramafic rocks.

The ultramafic rocks in the Rupaha area are generally massive. They crop out as a series of discontinuous lenses and pods enveloped by surrounding granulites (Fig. 3.1). Peak metamorphic assemblages (e.g. enstatite-forsterite-diopside) are observed only in few places. These rocks often show evidences for retrograde overprints in which peak metamorphic assemblages are replaced by tremolite, dolomite and talc in many places. Therefore, the path of retrograde fluid flow can be evaluated on the basis of retrograde mineral assemblages of the ultramafic rocks at Rupaha.

GEOLOGICAL SETTING AROUND RUPAHA ULTRAMAFIC BODY

The Proterozoic basement of Sri Lanka consists mostly of granulite to amphibolite facies rocks. Sm-Nd model ages, determined for a variety of lithology, define three distinct crustal units: the Highland Complex (HC); the Wannai Complex (WC); and the Vijayan Complex (VC) (Fig.3.1) (Milisenda et al. 1988, 1994; Cooray 1994). The rocks of the area around Rupaha lie within the HC of Sri Lanka. The principle rock units in the area are ortho- and para-gneisses. The meta-sediments and the meta-igneous charnockitic rocks are intimately intercalated in the field on all scales (from metre to kilometre). The meta-sediments include quartzites, marbles, pelitic gneisses and calc-silicate granulites. Ortho-gneisses are present as charnockites, charnockite gneisses and biotite gneisses. At least three major phases of structural events (D_1 , D_2 and D_3) have been recognized (Berger and Jayasinghe 1976; Kriegsman 1993). The D_1 event is believed to predate peak metamorphic conditions, while the D_2 event is contemporaneous with it. D_3 is believed to form during the early retrogression.

Field mapping in the area of Rupaha showed, that the ultramafic bodies are exposed discontinuously as elongated belts along most of the western part of Rupaha. Its length is about 2 km, with a thickness ranging from a few metres (northern part of the body) to several hundred metres (in the river tributary '*Garandu Kandura*') where it is best exposed (Fig. 3.1). Apparently the ultramafic rocks acted as a competent unit during deformation of the area. The planes of foliation and the direction of dips within the ultramafic rocks are

difficult to identify. But when it is visible, the foliation is similar to the regional striking trend, approximately N-S. Metasomatic mineral reaction zones are observed at contacts between ultramafic rocks and siliceous granulites. Similar contact relations are repeated in at least six places, all within the main exposure at '*Garandu Kandura*'. Further north of the river basement, ultramafic rocks can again be traced discontinuously in four places. Here, morphological, physical and textural features of all rock types are similar to those at *Garandu Kandura*.

The ultramafic rocks at Rupaha are composed primarily of the metamorphic equivalent of dunites and peridotites. Based on their physical and textural appearance, and mineral paragenesis, four rock types have been divided (Fig. 3.1): (1). Pale green coloured ultramafic rocks (PG) (e.g. sample numbers 9740, 9744 in Fig 3.1), (2). Dark green coloured ultramafics (DG) (e.g. sample numbers 9320S, 9703 in Fig 3.1), (3). Phlogopite dominate ultramafic rocks at the physical contacts of the surrounding granulites known as *blackwall zone* (BW) (e.g. sample numbers 9710A, 9712 in Fig 3.1), (4). Late carbonatized and brecciated veins (CV) (e.g. sample numbers 9316, 9317, 9318 in Fig 3.1).

Olivine is the main constituent in all rock types, except the late carbonatized and brecciated veins, where serpentine is the dominant constituent. Colourless, porphyroblastic orthopyroxenes are present in most fresh PG rocks (Fig 3.2a). The DG rocks include accessory Fe-oxides, some phlogopites and scanty relicts of spinel. The colour of spinel varies from dark blue to purple. The spinel occurs as subhedral crystals, smoothly bounded clots and frequently as clusters of grains of 1 to 2 mm size. Clots are elongated resulting in micro-scale pinch and swell structures (e.g. sample No. 9320S in Fig 3.1). Although two different ultramafic rocks have been observed, there does not seem to be any spatial relationship or distribution of the different types.

The blackwall rocks (BW) often exhibit a planar fabric and are confined to the physical contacts of the ultramafic body with the surrounding granulites (e.g. 9710A in Fig 3.1). These rocks occur as thin lenses about 10-50 cm wide, they are also composed of predominantly olivine with lesser amounts of phlogopite, and traces of clinopyroxene and spinel, but significantly porphyroblastic orthopyroxene is absent here. Pronounced changes in modal abundances of minerals occur as phlogopite increases progressively within this

zone, and clinopyroxene and olivine decrease. With further deformation, elongated phlogopite crystals lie along grain boundaries defining a distinct fabric. Both field relationships and textures suggest that phlogopite formed during the blackwall alteration (cf. Dubińska and Wiewióra 1999).

Carbonate-serpentine veins (CV) dissect the ultramafic rocks (Fig. 3.1). The carbonate-dominated veins are a few millimetres to several centimetres thick. In addition to these veins, blackish-green, frequently brecciated sheet-like bodies are well developed along brittle fractures and shear zones (Fig. 3.2b). The orientations of these sheet-like bodies are random. Shearing in the rocks is confined only to the PG part of the rock (e.g. 9316, 9317, 9318 in Fig. 3.1). The extensive occurrences of late carbonate veins in pale green ultramafic rocks perhaps lead earlier workers to describe this unit as 'serpentine marble' (e.g. Coomaraswamy 1904; Soyza 1986; Rupasinghe and Dissanayake 1987; Siriwardena 1988).

METHOD OF INVESTIGATION

The Rupaha ultramafic body was surveyed on aerial photographs, mapped in detail in the field. The geological mapping was carried out on the scale of 1:500 near the ultramafic unit during the course of this study. As far as possible, all ultramafic units, not only from the main exposure but also from other isolated locations were identified and mapped. Twenty-five samples representing every ultramafic unit were collected from 18 locations in the ultramafic rocks, exposed at '*Garandu Kandura*' (Fig. 3.1). At each outcrop care was taken to collect the least altered, freshest samples. Mineral parageneses of each sample were identified by petrographic observations and microprobe measurements. Modes of every representative rock types were measured by counting 2000 points in thin section. The major and trace element analyses of whole rocks were determined by X-ray Fluorescence spectroscopy (Philips-PW1404) at the University of Mainz, Germany. Mineral compositions were measured with a JEOL microprobe (JEOL JXA 8900 RL) at the University of Mainz, Germany with analytical operating conditions of 15 keV accelerating voltage, 12nA beam current and 2 μ m beam diameter. Synthetic and natural standards were used. Halides were calibrated with tugtupite, $\text{Na}_4\text{AlBeSi}_4\text{O}_{12}(\text{Cl}, \text{S})$ (7.58

wt % Cl) and F-phlogopite (9.20 wt % F). An online ZAF correction was used for data processing (Amstrong 1988, 1989).

WHOLE ROCK CHEMISTRY

The all whole rock major and trace element compositions are listed in Table 3.1. All the samples examined are silica poor, with SiO₂ composition ranging from 37-45%. High amounts of total Fe are characteristic for dark-green ultramafics, in which secondary magnetite is responsible for this high Fe content. Fig. 3.3 illustrates the compositional variability of different zones in ultramafics. A marked increase in K₂O, TiO₂, Al₂O₃, and volatiles along with a decrease in MgO is observed for samples close to the border of the ultramafic rocks (blackwall zone). This is reflected by the increased modal abundance of phlogopite, and a decrease in the modal abundance of olivine, orthopyroxene and clinopyroxene (Table 3.1). Samples from late carbonatized and brecciated veins (CV) have low Mg and high volatile concentrations (Fig. 3.3a, b). Table 3.1 also includes some lithophile trace element data for Rupaha ultramafic samples. Concentrations of fluid immobile trace elements are below detection limit in many of our samples. Ni and Cr concentrations, which are compatible with olivine and spinel, show a large increase in the dark coloured ultramafics (Table 3.1) while Ba and Rb significantly increase towards the blackwall zone of the ultramafic rocks. The high Ni and Cr of the DG rocks suggest that original protoliths environment of the ultramafic would be earth's upper mantle (see also review from Evans 1977), but now have been completely metamorphosed.

MINERAL CHEMISTRY

Compositions of the minerals found in the ultramafics are listed in Table 3.4. *Olivine* composition in pale green rocks is Fo₍₉₈₋₉₉₎, while dark green rocks have Fo₍₉₅₋₉₆₎ (Table 3.4a). *Orthopyroxene* is enstatite with En₍₉₈₋₉₉₎, while *clinopyroxene* consist of 99% of diopside component.

Spinel belongs close to the spinel end member of the spinel-hercynite solid solution with X_{Mg} = 0.91-0.92 (Table 3.4a). It has very low Cr contents [(Cr/(Cr + Al) = 0.001] and (recalculated) Fe³⁺ (0.003-0.021) contents. These values are comparable with the spinels from the high-grade meta-peridotite bodies of Ruby Range Montana (Desmarais 1981;

$X_{Mg} = 0.48-0.63$ and $[Cr/(Cr + Al) = 0.02-0.15]$, but differ from the primary igneous spinels found in the low grade metamorphic terranes of British Columbia (Pinsent and Hirst 1977; $X_{Mg} = 0.05-0.62$ and $Cr/(Cr + Al) = 0.58-0.76$). The same chemistry of spinel in igneous rocks was observed by Basu and MacGresor (1974), Evans and Frost (1974), Sack and Ghiorso (1991) and Clynne and Borg (1997).

Phlogopites in the BW and PC are high in Mg ($X_{Mg} = 0.985-0.995$), compared with phlogopite in the DG, which are poorer in Mg ($X_{Mg} = 0.970-0.978$). No significant difference between the two groups has been observed with respect to Cl (0.04-0.08 pfu) (Table 3.4b). Phlogopite in DG rocks has a much higher Al content (2.50-2.85 pfu) compared to that of PG and BW variety (2.00–2.45 pfu). Fe content is also significantly high in the dark green rock (Table 3.4b). A remarkably high F content is observed in some phlogopites. Phlogopite found at the BW rocks shows the highest values of F, ranging from 0.813 - 0.899 pfu. This indicates high F/ F+OH in the fluids (Table 3.4b). High F increases the stability of biotite towards higher temperatures (Hensen and Osanai 1994).

Amphibole is a nearly pure tremolite with a formula of $Ca_{1.94}Mg_{4.90}Si_{7.90}O_{22}(OH_{1.93}F_{0.06}Cl_{0.01})$. *Talc* is low in Al and Fe and, has a X_{Mg} of 0.98-0.99. Talc is too fine-grained to obtain proper analyses in the shear zone. Antigorite, which is a high temperature and pressure form of *serpentine*, is perhaps the major serpentine mineral present within the assemblages.

PETROGRAPHY

Mineral assemblages

Mineral associations in different lithologies and the textural evidence for mineralogical equilibrium and disequilibrium are discussed in the next sections. Mineral associations of four different lithologies are listed in Table 3.2 and illustrated in Fig 3.4 in the composition map of $MgO-SiO_2-CaO-(H_2O-CO_2)$. The mineral association does not only include presumed primary minerals, but also late-stage minerals appearing in the reaction textures. Modes of eight samples in four different units of ultramafic rocks are listed in Table 3.3. The peak-metamorphic minerals and secondary minerals have been identified from textures, where secondary minerals commonly overprint peak-metamorphic minerals.

Pale green ultramafic rocks (PG)

Pale green ultramafic rocks are distinguished by the presence of forsterite, diopside, enstatite and also tremolite and dolomite. The observed mineral associations are; Fo + Di + En, Fo + Tr + Dol, and En + Tr + Dol. Mineral abbreviations are those of Kretz (1983). Textural evidences suggest that forsterite; enstatite and diopside are from early metamorphic phases (Fig. 3.4a) while tremolite and dolomite overprint the former (Fig.3.4d).

Dark green ultramafic rocks (DG)

Mineralogy of DG zone differs from PG zone by the appearance of spinel and phlogopite (Table 3.2). Where DG rocks consist of phlogopite, this is always confined to the BW zone (e.g. 920S). The occurrence of orthopyroxene has been observed in DG rocks few places (e.g. 9824), but at the PG zone. Mode of phlogopite increases up to ~6% due to replacement of many early metamorphic minerals. The DG consists the assemblages of Fo + Phl, Spl + Phl, Spl + Di + Phl, Fo + Di + Phl, Fo + Di + Dol and Fo + Phl + Dol, where phlogopite and dolomite appear as late overprints. This zone is the least altered zone among all ultramafic lithologies showing an average mode of secondary minerals of about 6%.

Phlogopite-bearing blackwall rocks (BW)

The phlogopite-bearing blackwall rocks, in general, are medium- to coarse-grained, and composed predominantly of olivine (~60%) with lesser phlogopite (~12%). The main changes occur within BW zone, they are summarized in the Table 3.3. Mineral associations of this zone are almost identical with the DG zone, but differ significantly with the modes of phlogopite and olivine and the state of alterations (Table 3.2). The formation of coarse-grained phlogopite is quite advanced in this zone at the expense of forsterite and spinel. Oriented phlogopites are well interlocked with olivine. The marked increase of hydrated minerals at the physical contact indicates a flux of fluid, accompanied by potassium and silicon.

Late carbonatized and brecciated veins (CV)

These veins contain variety of mineral assemblages that are interpreted as having formed during retrogression. The observed mineral assemblages in the late veins are Dol + Tlc +

Srp and Tlc + Tre + Dol. Ninety percent of forsterite has been completely altered to serpentine within this zone.

Textural relations

From structural and textural relationships it is clear that the Rupaha ultramafic body has been completely transferred to new phases under high-grade metamorphic conditions. Crystallization outlasted penetrative D₂ deformation, which is the major fabric-forming event in the region. The following evidences pointed to this conclusion; No typical igneous textures and structures have been observed through out the ultramafic body; minerals have irregular anhedral habits; absence of mineral relicts; no mineral zoning; and the presence of micro-scale pinch and swell structures in spinel and lineated phlogopite in the BW zone, which follow the D₂ deformation of the region.

Peak and near-peak metamorphic assemblages

The earliest, high temperature assemblages are forsterite-enstatite-diopside, and forsterite-spinel (Fig. 3.5a, b). They are preserved in the less altered portions of the body. Both assemblages can be stable at granulite facies temperatures and pressures. Olivine is variably serpentinized, whereas some olivine grains are altered into the serpentine minerals along cleavage fractures and borders. The other high-temperature assemblages in ultramafic rocks are phlogopite-bearing assemblages, which are apparently restricted to BW zone of ultramafic rocks (Fig.3.5c). These are mostly developed within a metre of the body contact. In places, phlogopite commonly replaced spinel and forsterite, forming thin coronas separating them (Fig 3.5b). The phlogopite is aligned with regional foliation, interpreted to be D₂. The D₂ deformation fabric has been shown to be near-peak metamorphism. Hence, phlogopite formed in ultramafics close to, or at, Peak PT. The formation of phlogopite at the physical contacts of the body indicates that mass transport between ultramafics and host granulites occurred during granulite facies metamorphism.

Retrograde metamorphic assemblages

Several retrograde reaction textures overprint peak mineral assemblages within the pale green ultramafics (PG). The stable mineral assemblages are illustrated in Fig. 3.4 The most common is the replacement of enstatite by tremolite and dolomite (Fig. 3.5d). Tremolite also occurs as well-formed prismatic crystals, which grow within the forsterite matrix as

well. Tremolite overprints has been observed at the forsterite-forsterite grain boundaries as well (Fig. 3.5e). These textures provide an unequivocal sense of tremolite formed either from enstatite or from forsterite or both ways with infiltration of Ca-rich fluids.

Talc quite often replaces tremolite in late carbonatized veins (CV) (Fig 3.5f). Here talc formed through the infiltration of H₂O and CO₂-bearing fluids. The source of these fluids is external to the ultramafics. The last prominent retrograde alterations are veins of serpentine minerals. In general, the abundance of serpentine is greatest in samples that have abundant late veins (Table.3.3). Here forsterites are altered to serpentine completely in almost every sample. Nevertheless, the degree of alteration is less in zone of DG lithology.

CONDITION OF METAMORPHISM

Peak metamorphic temperature

Unaltered portions of the rocks, together with mineral fabrics discussed indicate that the earliest assemblage was orthopyroxene + clinopyroxene + olivine ± spinel. Peak metamorphic temperatures were estimated using the two-pyroxene geothermometry of Kretz (1982) and Brey and Köhler (1990). Thirteen pyroxene pairs were chosen for thermometry. Selected data used for Opx-Cpx calculations are given in the Table 3.4a (mineral pairs 30-46, 32-48, 34-53). The calibration of Brey and Köhler (1990) yields temperatures of $750 \pm 41^\circ\text{C}$ while Kretz's (1982) calibration gives higher values of $842 \pm 68^\circ\text{C}$ at 9kbar conditions. A pressure estimate of 9kbar was used, based on the surrounding granulites (see chapter 2). The temperature estimates of the ultramafic rocks are consistent with those of the surrounding granulites. This supports the view, which is based on field and petrological observations that ultramafic rocks have equilibrated under granulite facies conditions.

Evolution of the mineral paragenesis and mineral fluid-reactions

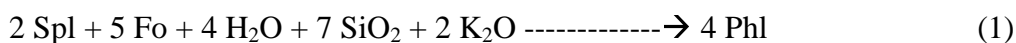
Mineralogical changes and reaction textures observed in the ultramafic rocks have several important implications in response to change in temperature, fluid and bulk composition. The growth of phlogopite in the ultramafic rocks was investigated by comparing phlogopite assemblages with phase equilibria for the simplified system MgO-SiO₂-K₂O-

$\text{Al}_2\text{O}_3\text{-H}_2\text{O-CO}_2$. We used the $\mu\text{SiO}_2\text{-}\mu\text{K}_2\text{O}$ diagram and $\text{T-}\mu\text{K}_2\text{O}$ diagram to illustrate the peak metamorphic conditions, including the effect of fluids during the formation of phlogopite. The fluid induced retrograde metamorphic conditions are illustrated from $\mu\text{CO}_2\text{-}\mu\text{CaO}$ and $\text{T-}\mu\text{CaO}$ diagrams. All diagrams were calculated with the PerPleX software (Connolly 1990). Reduced activities were used for diopside, enstatite, forsterite, talc, spinel, phlogopite, and tremolite that measurably deviated from pure substances while talc, dolomite, brucite, K-feldspar, plagioclase and periclase were considered as pure phases. The thermodynamic data of Holland and Powell (1998) were used together with the following activity models; The a_{Tr} in Ca-amphiboles was calculated after Holland and Blundy (1994) while a_{En} and a_{Fs} in enstatite were computed after Holland and Powell (1996). Activity models for diopside, talc, spinel and olivine are from Holland and Powell (1998). Fluids were considered $\text{CO}_2\text{-H}_2\text{O}$ solutions that obey the equation of state given by Holland and Powell (1991, 1998). We used the 'ionic solution model' [$a_{\text{Phl}} = (\text{X}_{\text{Mg}})^{3*} (\text{X}_{\text{OH}})^2$] to calculate the activity of phlogopite because of the high F content that is measured in phlogopites.

Peak metamorphic conditions

The mineral assemblages of forsterite-enstatite-diopside are recognized as the peak assemblage in the rock and may represent the metamorphic episode that took place during the highest temperature attained by the rock (Fig. 3.5a). These mineral assemblages are also graphically presented in the H_2O saturated CaO-MgO-SiO_2 ternary diagram (Fig. 3.4a).

The reaction texture of a phlogopite corona around spinel suggests a reaction involving forsterite + spinel to form phlogopite (Fig. 3.5b). A model explaining the formation of phlogopite from forsterite and spinel is shown in the $\mu\text{SiO}_2\text{-}\mu\text{K}_2\text{O}$ diagram in the Fig. 3.6. It relates the formation of phlogopite in an open system. The influx of K_2O and also SiO_2 is required to produce phlogopite. Therefore, the reaction (1) could be the most reasonable explanation for phlogopite formation at the given PT condition.



The geometry of blackwall zones and mineral assemblages also suggests a localized fluid flow along the physical contacts. The Si and K must have been added from outside to the system during the reaction in order to form phlogopite. The influx of H₂O-rich fluid, which was probably saturated in SiO₂, triggered the reaction leading to the formation of phlogopite.

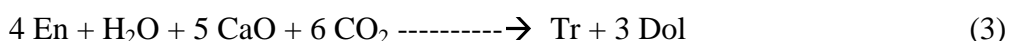
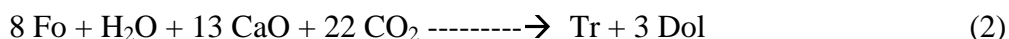
The possible temperature conditions involving hydration and the activity of K₂O, projecting from SiO₂, is shown by the T- μ K₂O diagram (Fig 3.7), which was calculated for 9kbar. This diagram illustrates that the formation of phlogopite requires at least a temperature of 800°C. This is close to the peak metamorphic conditions of the ultramafic rocks. This result is consistent with the temperature calculations of two-pyroxene thermometry of ultramafics.

The phases of muscovite, sanidine, anorthite, clinocllore, brucite and periclase were included to highlight the conditions under which these minerals would not be expected.

Retrograde metamorphic conditions

Phase relations of retrograde mineral assemblages are plotted in the fluid saturated (H₂O-CO₂) ternary diagrams of CaO-MgO-SiO₂ (Figs 3.4b and 3.4c), This illustrates the typical phase relations of retrograde minerals in the zones of PG and CV. Retrograde minerals like tremolite, dolomite, talc and antigorite from enstatite, forsterite and diopside have formed in these zones.

Abundance of hydrated minerals like phlogopite at the rocks from BW suggests water must have been present in the pore fluids in the high-temperature conditions. And also, the evidence for CO₂ + H₂O in fluids during retrogression is indicated by the overprints of tremolite + dolomites over enstatite (Fig. 3.5d) and the formation of tremolite in the forsterite-forsterite grain boundaries (Fig. 3.5e). The reaction producing tremolite either from forsterite or from enstatite requires Ca²⁺. For tremolite and dolomite, such a reactions may be simplified to;



Significantly, diopside is absent in any of tremolite-bearing samples (see also Table 3.2). Hence, the transition of tremolite and dolomite additionally involved the Ca and CO₂ in the reactions. The calculation of the chemical potential diagram of CO₂ Vs CaO, shown in Fig. 3.8, illustrates the stability of Tr-Dol-Fo-Tlc-Di-En-Qtz in a system CaO-MgO-SiO₂-H₂O at 750°C and 9kbars. Diagrams were calculated with measured mineral compositions converted to activities. The resulting diagram reproduces mineral reactions, which are very similar to the observed products of retrograde reactions. For example, the influx of CO₂ and CaO is required to form Tr + Dol from En or Fo.

Further evolution is governed by constant MgO activity and progressively decreasing activity of CO₂ and CaO while passing the Tr + Dol, finally arriving at the Tlc + Dol zone (as shown in the dark line in Fig. 3.8). This path attributed to form Tlc from Tr in the late veins. The activity change of CaO and CO₂ indicates the strong gradient in chemical potential. These calculations, support interference from the arguments detailed above, are obviously the factors controlling the retrograde overprints of the ultramafic rocks.

The activity corrected T- μ CaO diagram is calculated for the system MgO-SiO₂-H₂O-CO₂ at 9kbar conditions, using the thermodynamic database of Holland and Powell (1998) (Fig. 3.9). The shaded area marks the stability fields of En + Tr + Dol, Fo + Tr + Dol and Tr + Dol + Tlc. Fig. 3.9 was calculated for X_{CO₂} [=CO₂/(CO₂+H₂O)] = 0.30. The univariant point A overlapped with univariant point B for X_{CO₂} of 0.40, indicating forsterite is unstable, when X_{CO₂} > 0.40. Insomuch, the univariant point A overlapped with the univariant point C, when X_{CO₂} < 0.15. No enstatite can be formed with X_{CO₂} < 0.15 at the given pressure conditions. Hence, it can be concluded that the stability fields of En + Tr + Dol and Fo + Tr + Dol occur together at the fluid condition of 0.40 ≥ X_{CO₂} ≥ 0.15 at 9kbar conditions. Therefore, T- μ CaO diagram provides a reasonable estimate of 640-750°C for En + Tr + Dol and Fo + Tr + Dol assemblages of ultramafic rocks at 9 kbar conditions during the granulite-amphibolite retrograde condition.

When summarising the retrograde history of ultramafic rocks, it can be pointed out that with the progressing of retrograde reactions (2) to (3), the pervasive CO₂ fluid flow ($0.52 \geq X_{\text{CO}_2} \geq 0.21$) accompanied with the influx of Ca²⁺ to the ultramafic rocks may have been retrogressed at temperatures between 730 and 640°C. The equilibrium assemblages should contain talc instead of tremolite at lower temperatures. The stability of talc rather than tremolite in the low-grade assemblages at Rupaha shows evidence for the presence of water-rich fluid conditions. The first appearance of antigorite marks a pervasive hydration event in later stages. The antigorite event therefore reflects infiltration of H₂O into host rock at temperatures below 640°C through the brittle fractures.

SUMMARY AND DISCUSSION

Metamorphism

Although mineralogically complex, the metamorphosed ultramafic rocks at Rupaha are compositionally simple, permitting a relatively straightforward interpretation of their metamorphic evolution. Such rocks are commonly mantle-derived silica-undersaturated rocks. The low concentrations of Cr, Ni and Fe in spinel, olivine and diopside indicate that their protoliths have been completely transformed into a metamorphic rock during granulite facies. They formed as alpine type peridotites in the metamorphic terranes (Evans 1977).

K-Si-metasomatism

There are several lines of chemical evidences for a high temperature metasomatism at the out side most part of the body. The direction of the planer structural elements suggests that the phlogopite growth took place contemporaneous with the major deformation episode (D₂), which in turn is believed to be syn-peak metamorphic (Berger and Jayasinghe 1976; Kriegsman 1993). The formation of phlogopite during deformation requires infiltration of potassium and silica. Similar circumstances have been discussed by many other workers (e.g. Harker 1932; Beach 1973, 1976; Gresens 1966; Kerrich et al. 1977; Brodie 1980). The enrichment of K, Ti, Al, Rb and Ba measured for whole rocks also supports this hypothesis (see also Fig. 3.3).

Application of μSiO_2 - $\mu\text{K}_2\text{O}$ and T- $\mu\text{K}_2\text{O}$ diagrams illustrate the near-peak K-Si-metasomatism in the ultramafic rocks at the physical contacts from potassium-rich granulites. The reaction was started by K_2O , SiO_2 and H_2O infiltration along the granulite-ultramafic contact or diffusion of these elements from the surrounding granulites. The stability field of phlogopite, as illustrated in T- $\mu\text{K}_2\text{O}$, suggest the K-metasomatism may have occurred contemporaneous to the granulite facies metamorphism.

Fluid flow during retrogression

The replacement of enstatite and forsterite by tremolite and dolomite confirms the presence of CO_2 -rich infiltrating fluids ($0.40 \geq X_{\text{CO}_2} \geq 0.15$) at elevated temperatures (730-640°C) at 9kbar. The retrogression can be modelled assuming the chemical potential gradients in Ca and CO_2 , which may possibly have served to modify the peak metamorphic mineral assemblages. The second, but widespread hydration occurred at much lower temperatures and is marked by the formation of serpentine from forsterite.

Field evidences and textures of the formation of retrograde minerals like, tremolite, dolomite and talc within the ultramafic rocks suggests that the formation was, in general, not localized by fault-controlled influx. Retrograde metamorphism simply corresponds to a progressive opening of the system, whenever fluid circulation introduces H_2O and CO_2 to more permeable zones. However, it is clear that the massive brecciation and carbonation allowed fluid interaction with large volumes of rocks, as opposed to the retrogression, where minor brecciation occurred and fluid flowed mainly along the grain boundaries.

Mechanism of the emplacement

Any model for the mechanism of emplacement of the ultramafics should account for the sequence of metamorphism, metasomatism as well as retrograde events. The ultramafic rocks at Rupaha are the only locality so far found in the entire Highland Complex of Sri Lanka, in which they have been metamorphosed at granulite facies. One possible explanation for the observations is that a piece of the mantle was faulted up to the lower crust (cf. Dick 1979). The fluid circulating at the deep crust would result in several types of metasomatic processes. As the ultramafic rock cooled together with surrounding granulites, the retrograde overprints and the carbonation and hydration textures are produced.

REFERENCES

- Amstrong JT* (1988). Quantitative analyses of silicate and oxide minerals: comparisons of Monte Carlo, ZAF and Phi-rho-z procedures. In: (*Newbury DE* eds). Microbeam analysis-1988, San Francisco Press, San Francisco, 239-246
- Amstrong JT* (1989). CITZAF: combined ZAF and phi-rho (Z) electron beam correction programs. California Institute of Technology, Pasadena, CA
- Barton MD, Ilchik RP, Marikos MA* (1991) Metasomatism. In: Contact metamorphism, *Reviews in Mineralogy (Kerrick M ed)*, Mineral. Soc. Am. 26: 321-345
- Basu AR, MacGregor ID* (1975). Chromite spinels from ultramafic xenoliths. *Geochim. Cosmochim. Acta* 39: 937-945
- Baumgartner LP, Ferry JM* (1991). A model for coupled-fluid flow and mixed-volatile mineral reactions with applications to regional metamorphism. *Contrib. Mineral. Petrol.* 106: 273-285
- Beach A* (1973). The mineralogy of high temperature shear zones at Scourie, N.W. Scotland. *J. Petrol.* 14: 231-248
- Beach A* (1976). The interrelations of fluid transport, deformation, geochemistry and heat flow in the early Proterozoic shear zones in the Lewisian Complex. *Phil. Trans. R. Soc. A280*: 569-604
- Berger AR, Jayasinghe NR* (1976). Precambrian structure and chronology in the Highland Series of Sri Lanka. *Precam. Res.* 3: 559-576
- Bickle MJ, Barker J* (1990). Advective-diffusive transport of isotopic fronts: an example from Naxos, Greece. *Earth Planet. Sci. Lett.* 97:78-93
- Brey GP, Köhler T* (1990) Geothermobarometry in four-phase Lherzolites II. New thermobarometers and practical assessment of existing thermobarometers. *J. Petrol.* 31: 1353-1378
- Brodie KH* (1980). Variation in mineral chemistry across a shear zone in phlogopite peridotite. *J. Structural Geol.* 2: 265-272
- Cartwright I, Buick IS* (1995). Formation of wollastonite-bearing marbles during regional metamorphic channelled fluid flow in the Upper Calc-silicate unit of the Reynolds Range Group, central Australia. *J. Metamorphic Geol.* 13: 397-413
- Clynne MA, Borg LE* (1997). Olivine and chromian spinel in primitive calc-alkaline and theolitic lavas from the southernmost Cascade range, California: a reflection of relative fertility of the source. *Canadian Mineral.* 35: 453-472

- Coomaraswamy AK* (1904) Administrative report. Mineral. Surv. Ceylon
- Cooray PG* (1994) The Precambrian of Sri Lanka: a historic review. *Precam. Res.* 66: 1-18
- Connolly JAD* (1990). Multivariate phase diagrams: an algorithm based on generalized thermodynamics. *Am. J. Sci.* 290: 666-718
- Crawford ML, Hollister LS* (1986). Metamorphosis fluids: The evidence from fluid inclusions. In: Fluid-rock interactions during metamorphism In: *Advances in physical geochemistry 5* (*Walther JV, Wood BJ* eds), Springer Verlag, 1-35
- Dasgupta S, Ehl J, Raith M, Sengupta Pranesh, Sengupta Pulak* (1997). Mid-crustal contact metamorphism around the Chimakurthy mafic-ultramafic Complex, eastern Ghats, India. *Contrib. Mineral. Petrol.* 129: 182-197
- Desmarais NR* (1981). Metamorphosed Precambrian ultramafic rocks in the Ruby range, Montana. *Precam. Res.* 16: 67-101
- Dick HJB* (1979). Alteration and metamorphism of peridotite at Islas Orcades Fracture zone (abs) *EOS Trans, Am. Geophys. Un.* 60: 973
- Dubińska E, Wiewióra A* (1999). Layer silicates from a rodingite and its blackwall from Przemiłów (Lower Silesia, Poland): mineralogical record of metasomatic processes during serpentization and serpentinite Recrystallization. *Mineral. Petrol.* 67: 223-237
- Evans BW* (1977). Metamorphism of alpine peridotite and serpentinite. *Ann. Rev. Earth. Planet. Sci.* 5: 397-447
- Evans BW, Frost BR* (1974). Chrome-spinel in progressive metamorphism - a preliminary analysis. *Geochim. Cosmochim. Acta* 39: 959-972
- Evans BW, Trommsdorf V* (1970). Regional metamorphism of ultramafic rocks in the central Alps: Paragenesis in the system CaO-MgO-SiO₂-H₂O. *Schweiz. Min. Petrol. Mitt.* 50: 481-492
- Ferry JM* (1991) Dehydration and decarbonation reactions as a record of fluid infiltration. Metasomatism. In: Contact metamorphism, *Reviews in Mineralogy* (*Kerrick M* ed), Mineral. Soc. Am. 26: 351-391
- Ferry JM* (1996). Prograde and retrograde fluid flow during contact metamorphism of siliceous carbonate rocks from the Ballachulish aureole, Scotland. *Contrib. Mineral. Petrol.* 124: 235-254
- Gresens RL* (1966). The effect of structurally produced pressure gradients on diffusion in rocks. *J. Geol.* 74: 307-321
- Harker A* (1932). *Metamorphism*, Chapman and Hall, London, pp362

- Hensen BJ and Osanai Y* (1994). Experimental studies in dehydration melting of F-bearing biotite in model pelite compositions. *Mineral. Mag.* 58A: 410-411
- Holland TJB, Blundy J* (1994) Non-ideal interactions in calcic amphiboles and their bearing on amphibole-plagioclase thermometry. *Contrib. Mineral. Petrol.* 116: 433-447
- Holland TJB, Powell R* (1991). A compensated-Redlich-Kwong (CORK) equation for volumes and fugacities of CO₂ and H₂O in the Range 1bar to 50 Kbar and 100-1600°C. *Contrib. Mineral. Petrol.* 109: 265-273
- Holland TJB, Powell R* (1996) Thermodynamics of order-disorder in minerals:II. Symmetric formalism applied to solid solutions. *Am. Mineral.* 81:1425-1437
- Holland TJB, Powell R* (1998) An internally consistent thermodynamic data set for phases of petrological interest. *J. metamorphic Geol.* 16: 309-343
- Kassoli-Fournaraki A, Filippidis A, Kolcheva K, Hatzipanayotou K, Koepke J, Dimadis E* (1995). Multi-stage alteration of the Gorgona Ultramafic body, central Rhodope massif, Greece. *Chem. Erde* 55: 331-344
- Kerrick R, Fyfe WS, Gorman BE, Allison I* (1977). Local modification of rock chemistry by deformation. *Contrib. Mineral. Petrol.* 65: 183-190
- Kimball KL, Spear FS, Dick HJB* (1985). High temperature alteration of Abyssal ultramafics from the Islas Orcadas Fracture zone, South Atlantic. *Contrib. Mineral. Petrol.* 91: 307-320
- Kretz R* (1982). Transfer and exchange equilibria in a portion of the pyroxene quadrilateral as deduced from natural and experimental data. *Geochim. Cosmochim. Acta* 46: 411-421
- Kretz R* (1983) Symbols for rock forming minerals. *Am. Mineral.* 68: 277-279
- Kriegsman LM* (1993). Geodynamic evolution of the Pan-African lower crust in Sri Lanka- Structural and petrological investigations into a high-grade gneiss terrain. PhD thesis, University of Utrecht, The Netherlands, pp207
- Labotka TC, Nabelek PI, Papike JJ* (1988). Fluid infiltration through the Big Horse limestone member in the North Peak contact aureole, Utah. *Am. Mineral.* 73:1302-1324
- Milisenda CC, Liew TC, Hofmann AW, Kröner A* (1988) Isotopic mapping of age provinces in Precambrian high-grade terrains: Sri Lanka. *J. Geol.* 96: 608-615
- Milisenda CC, Liew TC, Hofmann AW* (1994) Nd isotopic mapping of the Sri Lanka basement: update and additional constraints from Sr isotopes. *Precam. Res.* 66: 95-110
- Nabelek PI* (1991). Stable isotope monitors. In: Contact metamorphism. Reviews in Mineralogy, 26 (*Kerrick D* ed), Mineral. Soc. Am. Washington DC, 395-436

- Newton RC, Aranovich L Ya, Hansen EC, Vandenheuvel BA* (1998). Hypersaline fluids in Precambrian deep-crustal metamorphism. *Precam. Res.* 91: 41-63
- Peretti A, Dubessy J, Mullis J, Frost R, Trommsdorf V* (1992). Highly reducing conditions during Alpine metamorphism of Malenco peridotite (Sandrio, northern Italy) indicated by mineral paragenesis and H₂ in fluid inclusions. *Contrib. Mineral. Petrol.* 112: 329-340
- Pinsent RH, Hirst DM* (1977). The metamorphism of Blue River Ultramafic Body, Cassiar, British Columbia, Canada. *J. Petrol.* 18: 567-594
- Roedder E* (1984). Fluid inclusions, *Reviews in Mineralogy* 12, (*Ribbe Paul H* ed), Mineral. Soc. Am. Washington DC, pp646
- Roselle GT* (1997). Integrated petrologic, stable isotopic and statistical study of fluid-flow in carbonates of the Ubehebe Peak contact aureole, Death Valley National Park, California, PhD dissertation, University of Wisconsin-Madison, pp239
- Rice JM, Ferry JM* (1982). Buffering, infiltration and the control of intensive variables during metamorphism, In: *Characterization of metamorphism through mineral equilibria*, *Reviews in Mineralogy* 10, (*Ferry JM* ed). Mineral. Soc. Am. Washington DC, 263-326
- Rumble D III* (1989). Evidences of fluid flow during regional metamorphism. *Eu. J. Mineral.* 1: 731-737
- Rupasinghe MS, Dissanayake CB* (1987). New in-situ corundum deposits in Sri Lanka. *J. Gemmol. Assoc. Sri Lanka* 4: 2-5
- Sack RO, Ghiorso MS* (1991). Chromian spinel as petrogenetic indicators: Thermodynamics and petrological applications. *Am. Mineral.* 76: 827-847
- Sriwardena CHER* (1988). Preliminary report of the survey of Rupaha serpentine deposit, Geol Surv Dept (unpublished) pp.15
- Soyza EG* (1986). An account of serpentine deposit of Rupaha, Sri Lanka, *J. Gemmol. Ass. Sri Lanka* 3: 30-34
- Springer RK* (1974). Contact metamorphosed ultramafic rocks in the western Sierra Nevada foothills, California. *J. Petrol.* 15: 160-195
- Trommsdorf V, Evans BW* (1974). Alpine metamorphism of ultramafic rocks. *Schweiz. Min. Petrol. Mitt.* 54: 333-352
- Walther JV, Wood BJ* (eds) (1986). Fluid-rock interactions during metamorphism, *Advances in physical geochemistry* 5, Springer Verlag, 1-35

Table 3.1. Major and trace element abundance of typical ultramafic rock types

	pale green rocks (PG)				dark green rocks (DG)				blackwall rocks (BW)			late carbonatized veins (CV)					
	9740	9741	9744	9743	9710.00	9829	9320	9703	9320A	9710A	9710B	9712	9712A	9316	9317	9318	9318
SiO ₂ %	38.78	37.74	37.13	37.31	39.15	39.17	37.60	40.61	36.90	38.76	37.92	38.63	38.45	44.37	40.96	42.17	45.23
Al ₂ O ₃ %	0.17	0.16	0.15	0.14	0.16	0.10	0.06	0.15	0.19	2.32	2.41	2.30	2.45	0.42	0.41	0.52	0.55
Fe ₂ O ₃ %	1.32	1.47	1.50	1.42	1.42	1.62	4.69	5.56	4.30	1.37	1.39	1.40	1.54	0.82	0.98	0.98	0.91
MnO %	0.04	0.04	0.04	0.04	0.04	0.04	0.09	0.10	0.10	0.04	0.04	0.05	0.05	0.07	0.06	0.04	0.08
MgO %	50.19	49.01	49.25	50.24	52.70	50.85	49.07	48.78	49.22	45.69	46.02	46.08	46.23	35.92	41.32	42.78	38.79
CaO %	0.64	0.70	0.66	0.32	0.38	0.34	0.08	0.08	0.04	0.41	0.40	0.40	0.39	3.22	1.36	0.50	1.23
Na ₂ O %	0.01	0.01	0.01	0.01	0.01	0.22	0.36	0.13	0.18	0.00	0.00	0.01	0.01	0.23	0.19	0.25	0.23
K ₂ O %	0.01	0.01	0.00	0.00	0.01	0.02	0.02	0.07	0.02	1.43	1.33	1.28	1.32	0.03	0.03	0.04	0.04
TiO ₂ %	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.07	0.07	0.07	0.06	0.02	0.03	0.03	0.03
P ₂ O ₅ %	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.01
LOI %	10.34	10.53	10.40	11.21	7.79	8.58	9.41	5.17	9.56	9.98	10.01	9.62	9.22	15.42	14.91	14.26	13.93
Total %	101.53	99.69	99.17	100.72	101.69	100.97	101.41	100.68	100.50	100.09	99.61	99.86	99.74	100.53	100.25	101.59	101.04
Cr	3	5	2	3	bdl	bdl	233	364	230	1	2	2	1	nd	nd	nd	nd
Ni	4	4	2	3	3	3	13	11	14	2	2	2	2	nd	nd	nd	nd
Zn	30	31	31	30	32	30	54	78	52	34	36	30	32	nd	nd	nd	nd
Rb	bdl	bdl	bdl	bdl	bdl	bdl	bdl	4	bdl	112	120	100	108	nd	nd	nd	nd
Ba	15	12	12	12	18	17	16	25	17	212	189	198	208	nd	nd	nd	nd

nd-not detected; bdl-below detection limit; all iron as Fe₂O₃

Uncertainties for major oxides (%): Si = 0.13, Al = 0.25, Fe = 0.11, Mn = 0.88, Mg = 0.23, Ca = 0.16, Na = 0.61, K = 0.45, Ti = 0.16, P = 0.48

Uncertainties for trace elements (%): Cr = 1.2, Ni = 0.8, Zn = 1.3, Rb = 2.4, Ba = 0.6

Detection limits of trace elements (ppm): Cr = 2.1, Ni = 1.1, Zn = 1.8, Rb = 1.3, Ba = 6.6

Sample No.	Fo	En	Di	Spl	Phl	Tr	Dol	Tlc	Mag
pale green ultramafics (PG)									
9744	X	X	X						
9710		X				X ^r	X ^r		
9710	X					X ^r	X ^r		
9740	X	X					X ^r		
9825	X	X				X ^r	X ^r	X ^r	
dark green ultramafics (DG)									
9320S			X	X	X				
9320S	X		X		X				X
9703	X				X		X		X
9320S	X		X				X		
9824	X	X							
blackwall rocks (BW)									
9710A			X	X	X				
9710A	X		X		X				
9710B	X				X		X		
carbonatized veins (CV)									
9316							X	X	
9317						X	X	X	
9318	X						X		
X- occurs as matrix assemblages									
X ^r - early retrograde phase									
X ^a - occurs as alterations									

Table 3.3. Modes of selected samples of metamorphosed ultramafic rocks

(PG-pale green, DG-dark green, BW-blackwall, CV-carbonatized veins)

	9710	9311	9720S	9703A	9712	9310A	9316	9318
rock type	PG	PG	DG	DG	BW	BW	CV	CV
olivine	63.6	68.2	72.6	78.8	56.2	64.2	4.0	4.6
opx	1.9	1.6	0.0	0.0	0.0	0.0	0.0	0.0
cpx	0	0.3	0.0	1.3	0.5	0.3	0.0	0.0
spinel	0	0.0	13.4	8.2	0.5	0.2	0.0	0.0
phlogopite	0.1	0.1	5.8	7.0	14.5	10.1	0.0	0.0
tremolite ^a	1.1	2.7	0.0	0.0	0.0	0.0	5.2	5.8
ddomite ^a	5.2	4.3	1.2	0.1	2.3	0.2	8.4	7.6
serpentine ^a	28.1	22.8	6.8	4.2	26.0	25.0	55.2	54.2
Fe-oxide ^a	0	0	0.2	0.4	0.0	0.0	0.0	0.0
talc ^a	0	0	0.0	0.0	0.0	0.0	27.2	27.8

^a Secondary phases

Table 3.4b Some selected phlogopite, tremolite, talc and serpentine analyses of different zones in the ultramafic rock (PG-pale green, DG-dark green, BW-blackwall, CV-carbonatized veins)

mineral rock type sample No.	phlogopite			tremolite			talc			serpentine			carbonate					
	PG	DG	BW	PG	DG	BW	PG	DG	BW	PG	DG	BW	PG	DG	BW			
analyses No.	33	111	117	66	72	72	5	6	8	12	14	27	28	29	1	2	3	20
SiO ₂	41.95	40.98	39.22	39.79	41.33	41.23	58.83	57.81	57.05	59.91	57.79	40.82	40.62	42.06	nd	nd	nd	nd
TiO ₂	0.43	0.35	0.48	1.46	0.43	0.34	0.00	0.03	0.02	0.06	0.00	0.00	0.02	0.00	nd	nd	nd	nd
Al ₂ O ₃	12.70	14.82	17.41	15.74	15.34	14.71	0.57	1.29	1.56	0.58	0.57	0.04	0.34	0.35	0.00	0.26	0.00	0.00
FeO	0.45	0.46	1.10	1.14	0.40	0.52	0.48	0.56	0.34	0.46	0.65	1.31	0.78	0.34	0.27	0.00	0.20	0.27
Cr ₂ O ₃	0.07	0.00	0.03	0.04	0.00	0.02	0.09	0.03	0.06	0.03	0.01	0.01	0.06	0.00	0.00	0.06	0.00	0.00
MnO	0.04	0.02	0.02	0.00	0.02	0.00	0.04	0.01	0.00	0.01	0.00	0.06	0.04	0.03	0.03	0.06	0.06	0.04
MgO	28.94	27.58	25.69	25.96	27.33	27.57	24.47	24.18	23.82	31.51	31.82	42.38	41.75	42.01	22.78	22.62	22.25	23.25
CaO	0.00	0.00	0.00	0.00	0.00	0.00	13.38	13.38	14.34	0.07	0.08	0.04	0.02	0.05	32.88	32.64	32.67	32.40
Na ₂ O	0.12	0.84	0.29	0.46	0.53	0.53	0.12	0.26	0.45	0.27	0.24	0.03	0.10	0.06	0.00	0.01	0.08	0.00
K ₂ O	9.14	10.07	9.82	9.31	9.81	9.92	0.01	0.06	0.11	0.06	0.00	0.01	0.09	0.05	0.01	0.00	0.00	0.00
BaO	0.08	0.07	0.38	0.47	0.35	0.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.04	0.09	0.00	0.00
SrO	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.10	0.10	0.09	0.05
F	1.21	1.76	1.37	1.41	1.89	2.08	0.13	0.20	0.31	0.08	0.08	0.00	0.00	0.00	nd	nd	nd	nd
Cl	0.28	0.66	0.20	0.20	0.26	0.33	0.03	0.04	0.08	0.08	0.08	0.19	0.08	0.17	nd	nd	nd	nd
CO ₂	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	43.89	44.23	44.65	43.98
Total	95.42	97.59	95.99	95.96	97.70	97.50	98.155	97.843	98.141	92.951	91.163	84.89	83.89	85.19	100.00	100.00	100.00	100.00
	formula for 22 oxygens															formula based on (Ca+Mg+Fe+Mn)=1		
Si	5.813	5.607	5.453	5.532	5.625	5.633	7.952	7.862	7.782	7.837	7.734	3.912	3.922	3.982	0	0	0	0
Ti	0.044	0.036	0.050	0.152	0.044	0.035	0.000	0.003	0.002	0.006	0.000	0.000	0.002	0.000	0	0	0	0
Al	2.074	2.390	2.853	2.579	2.460	2.368	0.091	0.206	0.250	0.089	0.089	0.004	0.038	0.040	0	0	0	0
Cr	0.008	0.000	0.003	0.004	0.000	0.002	0.010	0.003	0.007	0.004	0.001	0.000	0.004	0.000	0	0	0	0
Mg	5.978	5.626	5.325	5.380	5.545	5.615	4.931	4.902	4.844	6.145	6.348	6.054	6.008	5.930	0.489	0.490	0.485	0.498
Fe	0.052	0.052	0.128	0.132	0.046	0.060	0.054	0.063	0.039	0.050	0.073	0.104	0.062	0.026	0.003	0.000	0.003	0.003
Mn	0.005	0.002	0.003	0.000	0.003	0.000	0.005	0.001	0.000	0.001	0.000	0.004	0.004	0.002	0.004	0.001	0.001	0.000
Ca	0.000	0.000	0.000	0.000	0.000	0.000	1.938	1.950	2.096	0.009	0.012	0.004	0.002	0.004	0.004	0.001	0.001	0.000
Na	0.033	0.221	0.078	0.123	0.141	0.140	0.032	0.069	0.118	0.069	0.063	0.006	0.018	0.012	0	0	0	0
K	1.616	1.758	1.742	1.651	1.703	1.729	0.002	0.011	0.020	0.010	0.000	0.002	0.010	0.006	0	0	0	0
Ba	0.004	0.004	0.020	0.025	0.019	0.013	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0	0	0	0
sum-cat	15.628	15.695	15.655	15.579	15.586	15.594	15.015	15.070	15.158	14.220	14.320	10.094	10.072	10.006	1.003	0.999	1.000	1.000
F	0.530	0.761	0.601	0.619	0.813	0.899	0.055	0.086	0.136	-	-	-	-	-	-	-	-	-
Cl	0.066	0.152	0.046	0.047	0.060	0.076	0.008	0.009	0.019	-	-	0.062	0.026	0.054	-	-	-	-
OH	1.404	3.086	1.353	1.334	1.126	1.026	1.938	1.906	1.846	-	-	3.984	3.993	3.987	-	-	-	-
X _{Fe}	0.009	0.009	0.023	0.024	0.008	0.010	0.011	0.013	0.008	-	-	-	-	-	-	-	-	-
F/(F+OH)	0.274	0.198	0.308	0.317	0.419	0.467	-	-	-	-	-	-	-	-	-	-	-	-
X _{Mg}	0.991	0.991	0.977	0.976	0.992	0.990	0.989	0.987	0.992	0.992	0.989	-	-	-	-	-	-	-

OH was calculated by stoichiometry

n.d. not detected

FIGURE CAPTIONS

Fig. 3.1 Geological and Structural map of the area around Rupaha. The Proterozoic rocks are composed of charnockites, charnockitic gneisses, quartzites, garnet-sillimanite-graphite gneisses (khondalites), garnet-biotite gneisses, and little scattered marbles.

Fig. 3.2 (a). Photograph of the pale green coloured fresh-looking ultramafic rock has coarse-grained colourless porphyroblast orthopyroxene in its fresh-looking samples; (b). Photograph of dark blue to black coloured massive late-veins cross cutting the ultramafic body.

Fig. 3.3 Whole rock analyses of different zones plotted against: (a). MgO vs SiO₂, (b). LOI vs SiO₂.

Fig. 3.4 Chemographic diagrams for the CaO-MgO-SiO₂ system projected from H₂O and CO₂. These diagrams illustrate the different mineral assemblages found in different zones in the ultramafic rock.

Fig. 3.5 Photomicrographs of ultramafic rocks showing different prograde and retrograde disequilibrium mineral textures: (a). The appearance of olivine-forsterite-enstatite in the same thin section (as relicts phase?) marks the early peak metamorphic history of the rock, (b). Phlogopite corona around spinel marks the possible reaction between forsterite and spinel to form phlogopite, (c). Aligned phlogopite at the blackwall zone marks the major deformation fabric of the blackwall rock, (d). Poikiloblastic enstatite has numerous inclusions. Enstatite has commonly retrograde to tremolite, (e). Formation of retrograde tremolite along forsterite-forsterite grain boundaries. Also note the occurrences of late stage carbonate veins, (f). Reaction textures of talc after tremolite marks the fluid present retrogression of the rock.

Fig. 3.6 $\mu\text{K}_2\text{O}$ - μSiO_2 diagrams at 850°C/9kbar. The arrows indicate possible infiltration pathway of phlogopite formation at the blackwall zone. The diagram was calculated from PerPleX software (Connolly, 1990) using the thermodynamic database of Holland and Powell (1998).

Fig. 3.7 T- $\mu\text{K}_2\text{O}$ diagrams at 9kbar. Activity corrected diagram suggest that phlogopite is stable in the temperatures above 800°C , which corresponds to peak metamorphism of ultramafic rocks.

Fig. 3.8 Chemical potential diagram of μCaO vs μCO_2 showing a gradient of CaO and CO_2 at $750^\circ\text{C}/9\text{kbar}$. The dark line indicates the existence of a chemical potential gradient during the formation of retrograde mineral assemblages (shaded area). The diagram was calculated from PerPleX software (Connolly, 1990) using the thermodynamic database of Holland and Powell (1998).

Fig. 3.9 T- μCaO diagram for the system $\text{CaO-MgO-SiO}_2\text{-H}_2\text{O-CO}_2$ calculated at 9 kbar. The retrograde assemblages of tremolite, dolomite and talc document the stability limit of $640\text{-}730^\circ\text{C}$ at X_{CO_2} of 0.30. See text for more details.

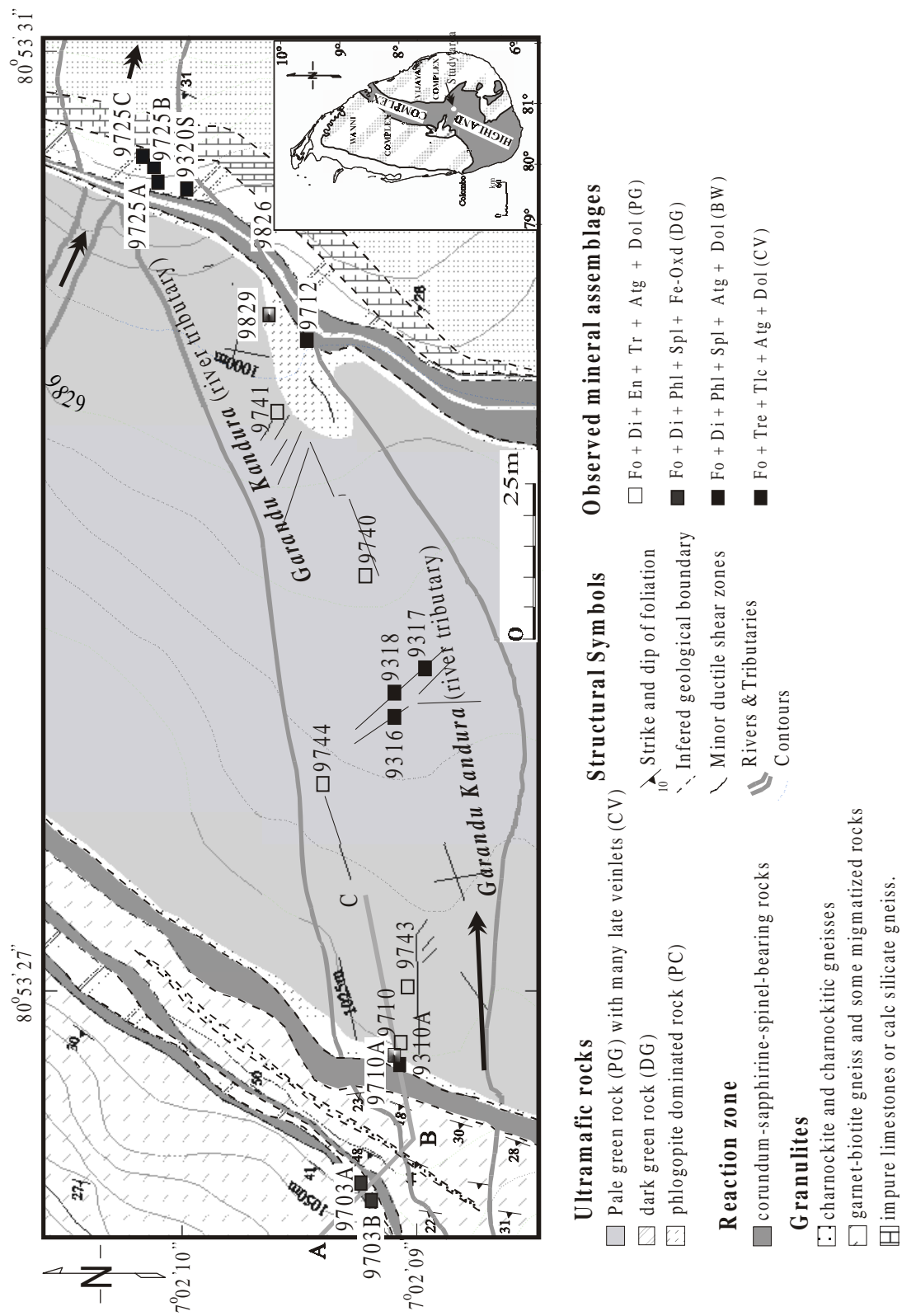


Fig.3.1

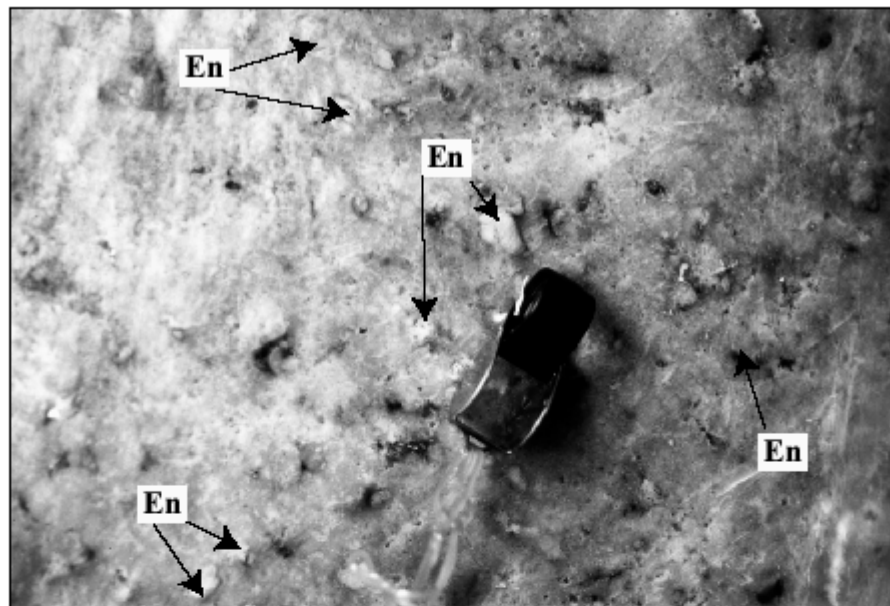


Fig. 3.2a

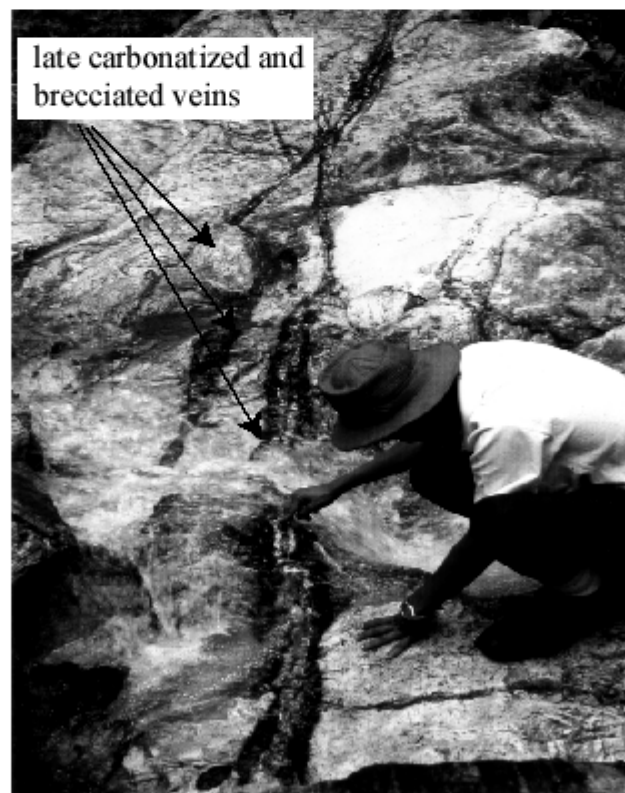


Fig. 3.2b

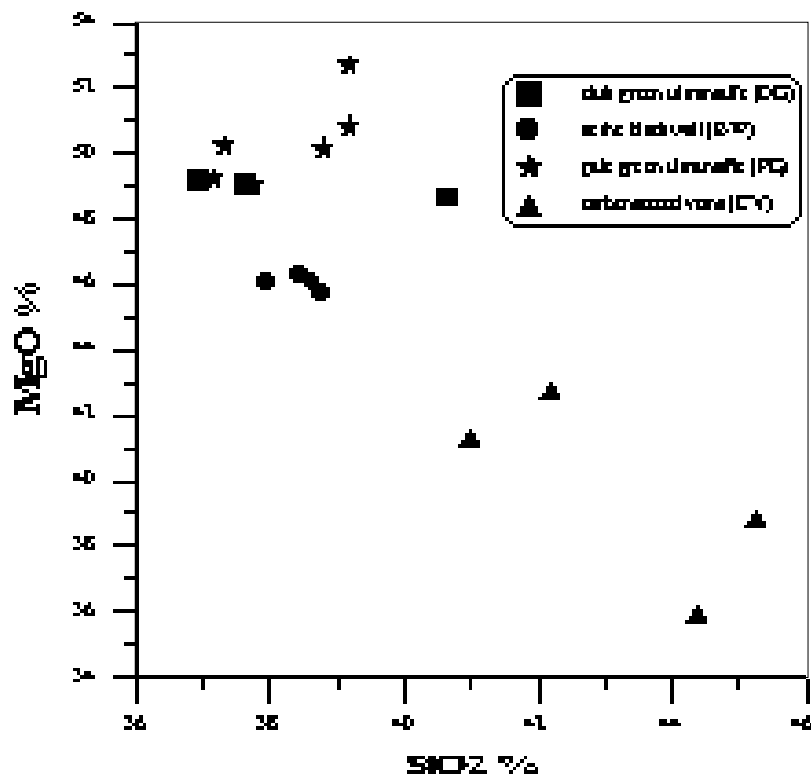


Fig.3.3a

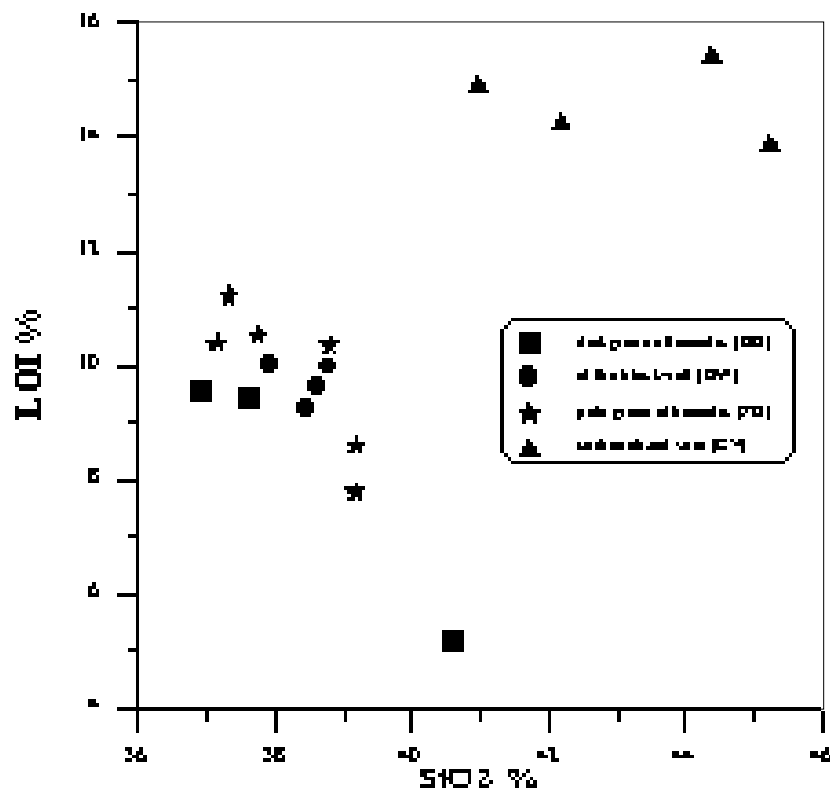


Fig.3.3b

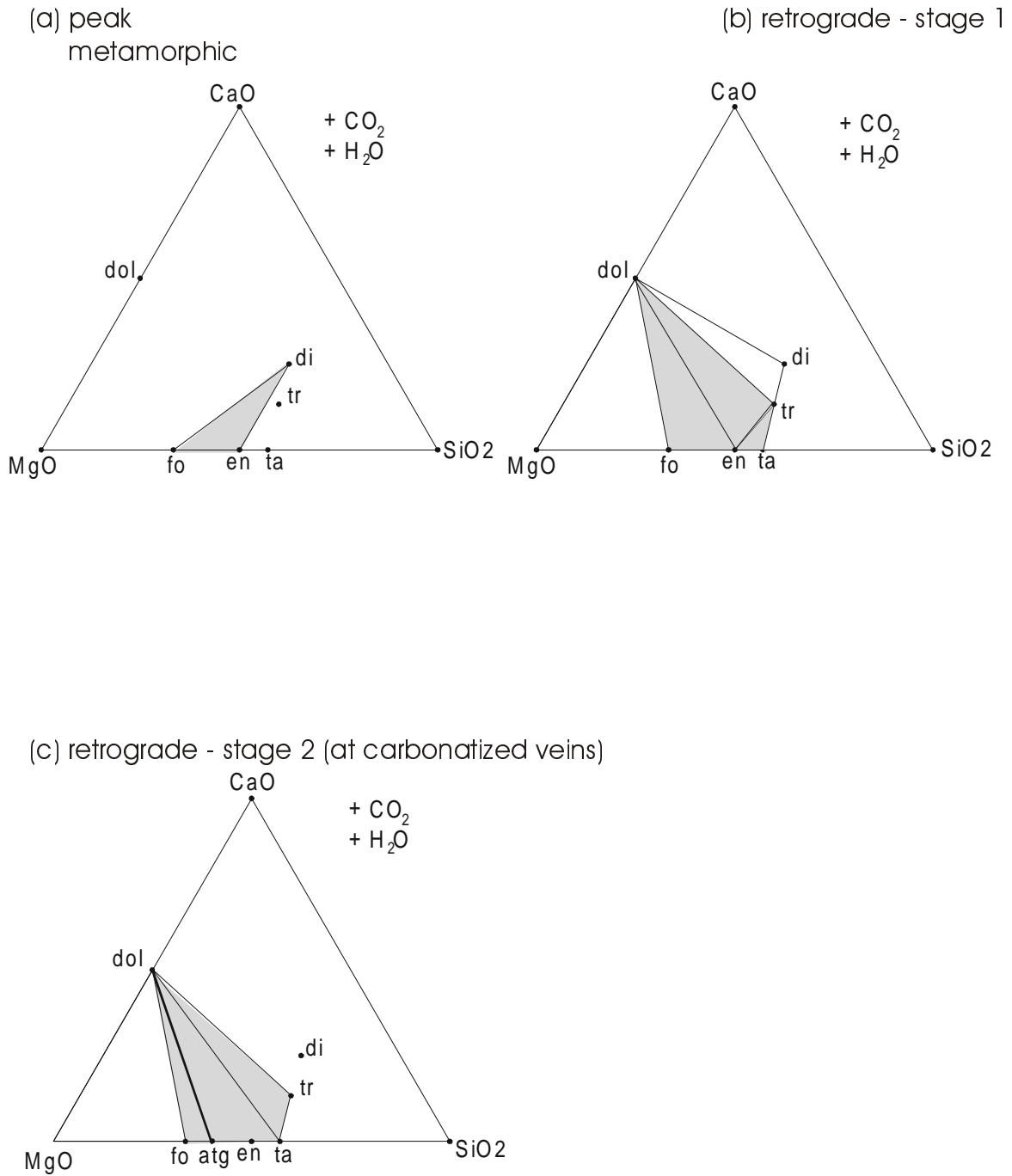


Fig. 3.4

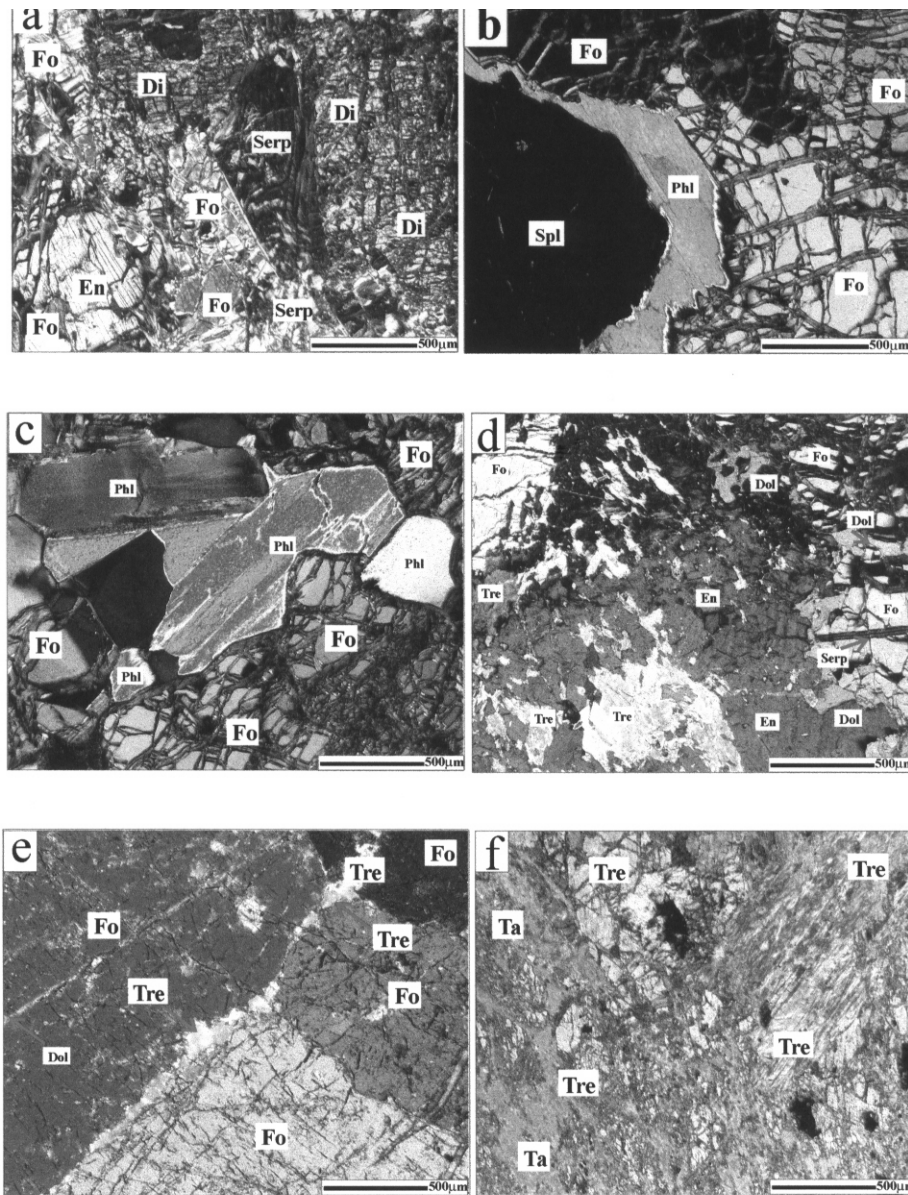


Fig. 3.5

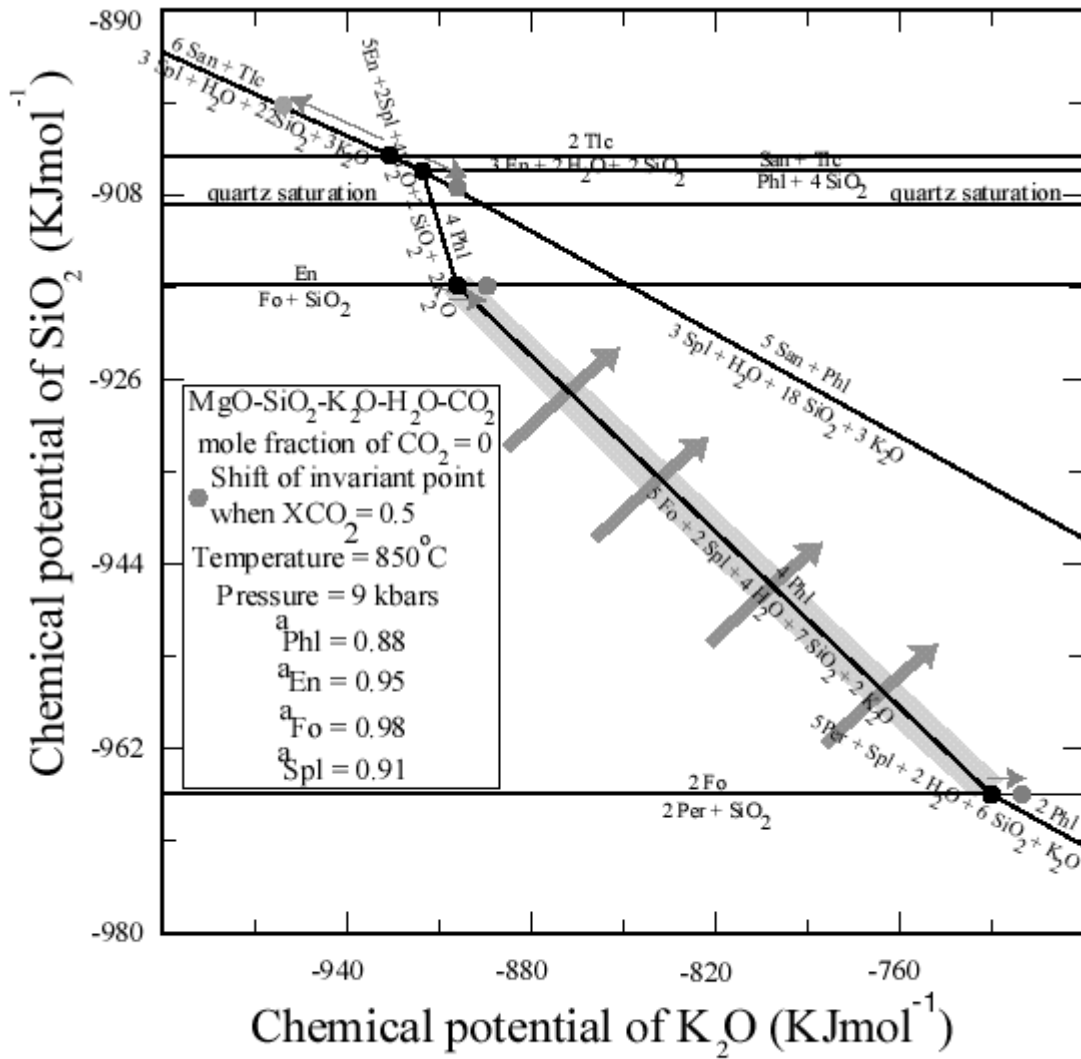


Fig. 3.6

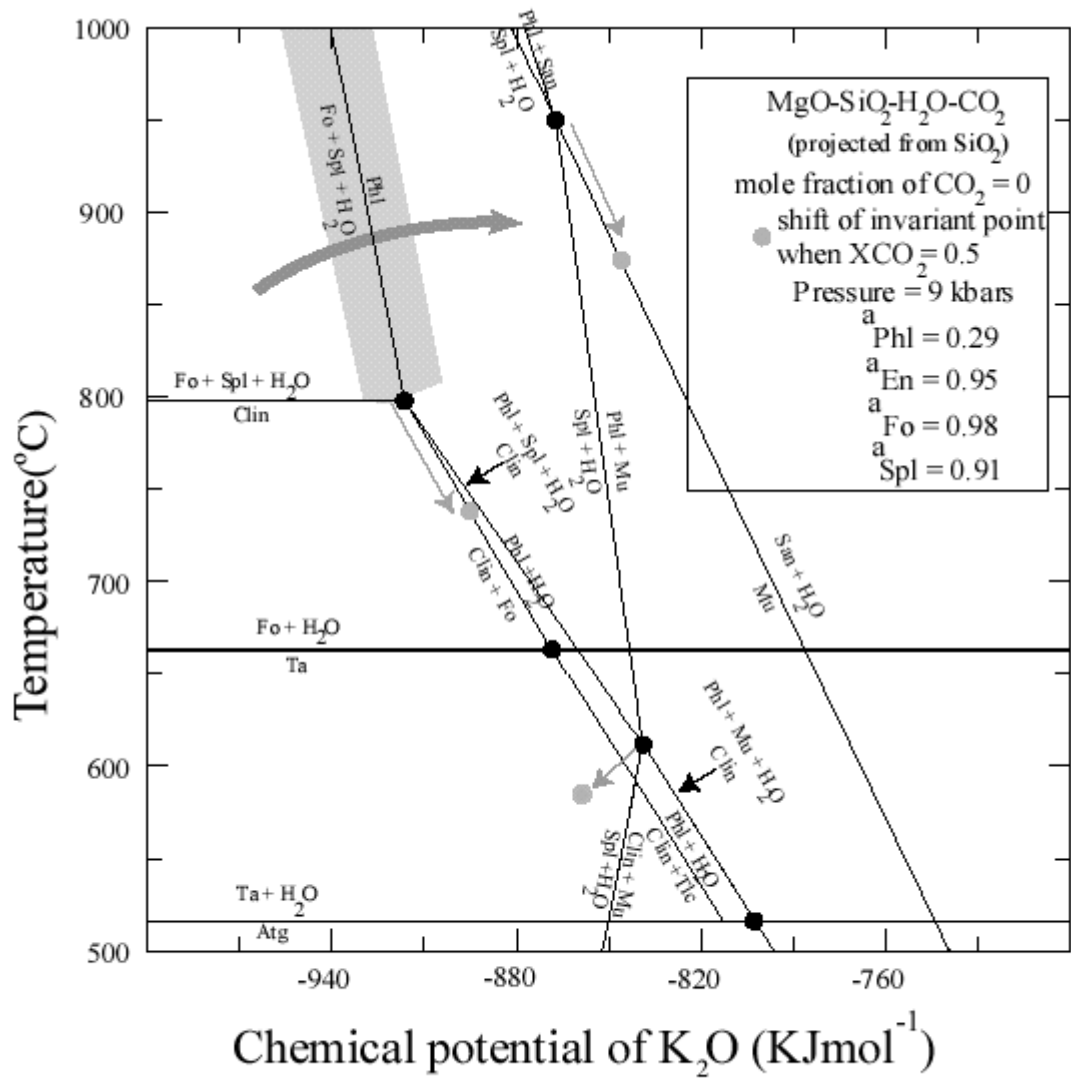


Fig. 3.7

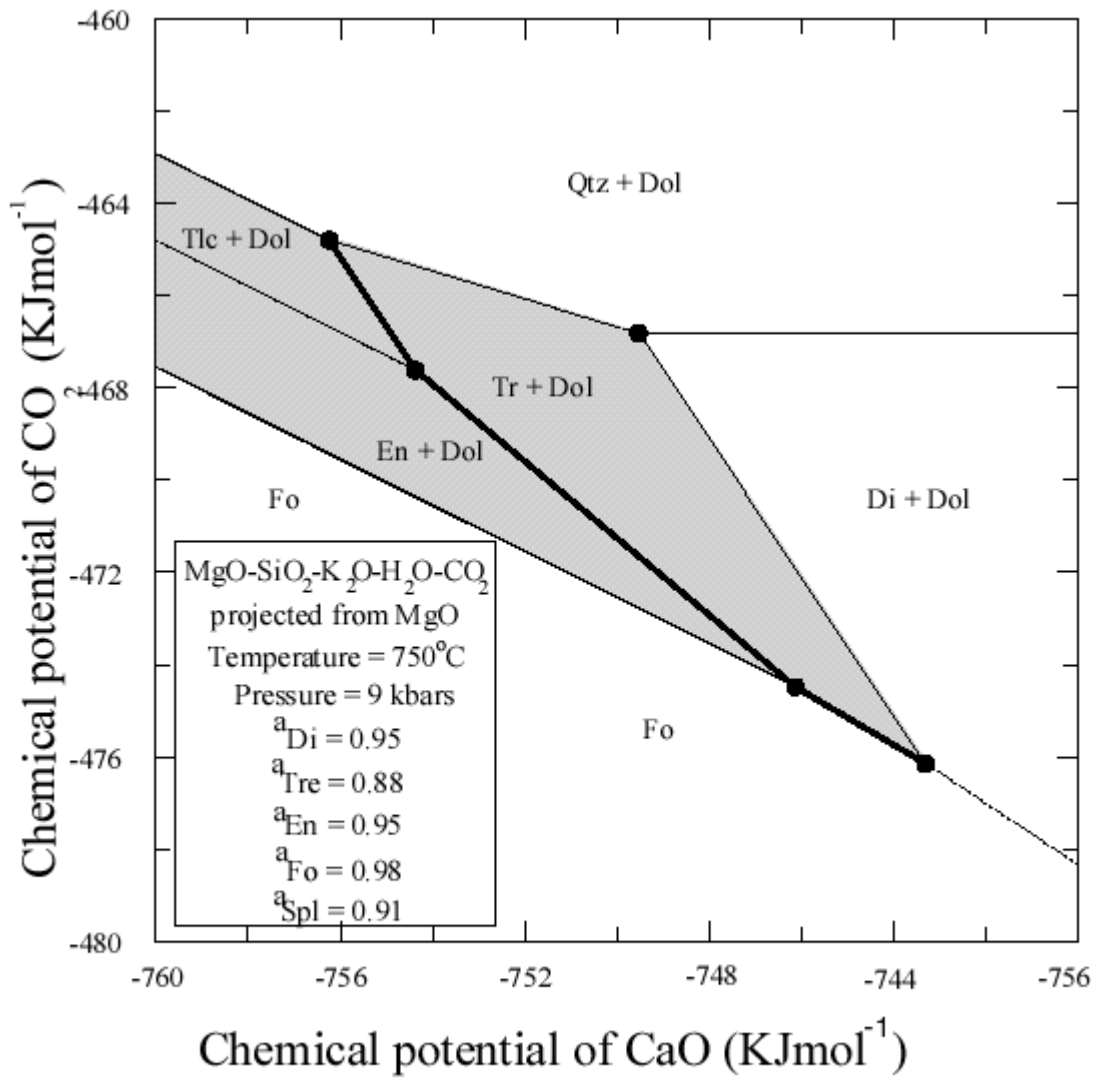


Fig. 3.8

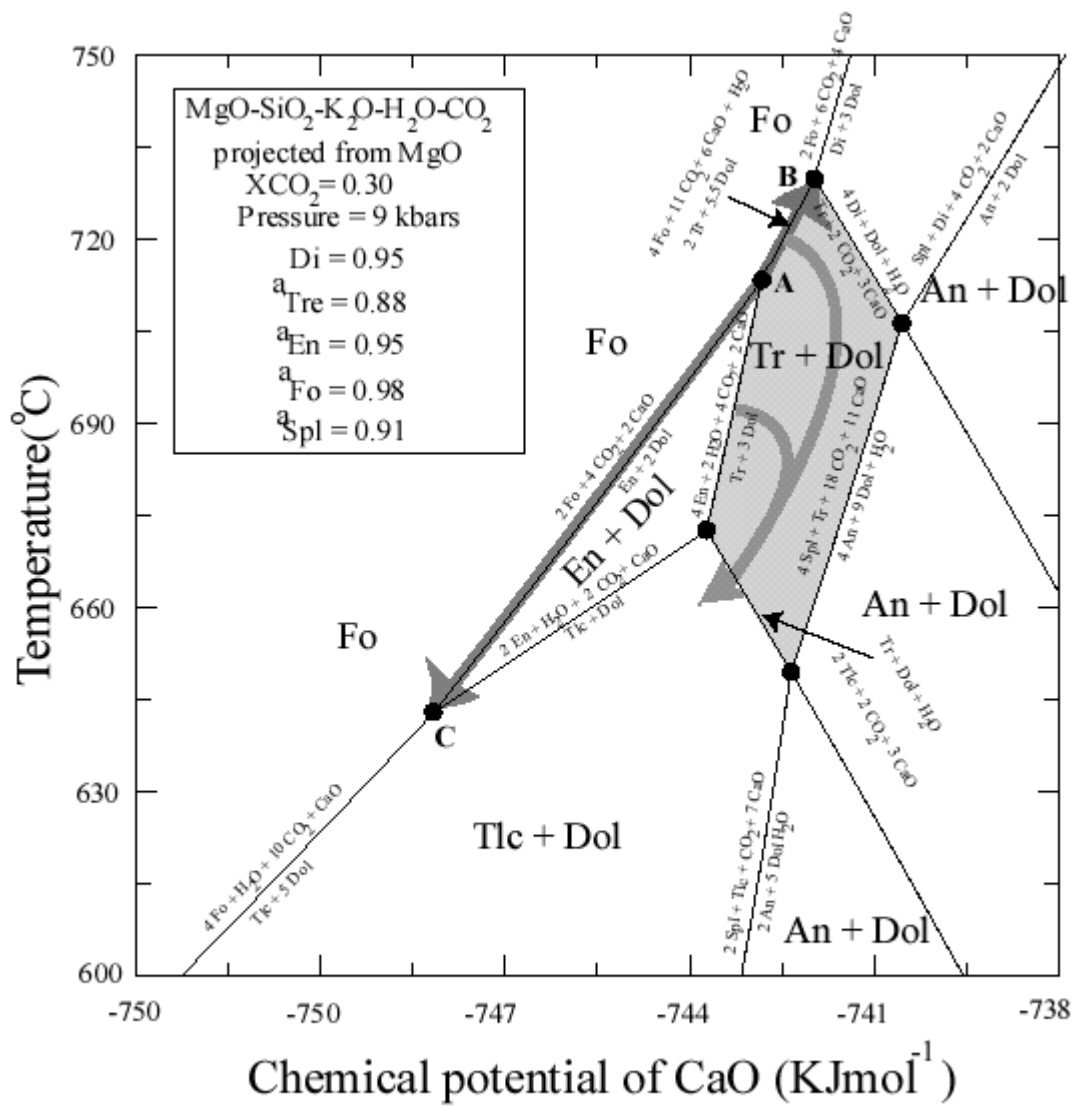


Fig. 3.9

Chapter 4

Genesis of silica-undersaturated sapphirine-corundum-spinel-bearing reaction zones from Rupaha, Sri Lanka

ABSTRACT

Field and petrological observations of ultramafic enclaves in granulites from 10 localities at Rupaha in the Highland Complex of Sri Lanka, place critical constraints on mass transfer mechanisms in the lower crust. Mineral reaction zones are observed at contacts between ultramafic rocks and siliceous granulites. The reaction zones developed between these units from ultramafic to siliceous granulites are: phlogopite + spinel + sapphirine, spinel + sapphirine + corundum and corundum + biotite + plagioclase. Spinel-sapphirine thermometry yields a temperature of $820 \pm 40^\circ\text{C}$, which is in agreement with the peak-temperatures recorded in the adjacent crustal granulites and ultramafics rocks.

The sequences of mineral zones, containing a variety of Al-rich, silica undersaturated minerals in the reaction zones separating the ultramafic rocks from the silica-rich rocks can be explained by a diffusion model. This involves the diffusion of Mg from ultramafic rocks across the layers, and K and Si diffuse in opposite direction. Chemical potential of Mg generated continuous monotonic gradient, allowing steady state diffusional transport across the profile. The strong enrichment in Al, and the considerable loss of Si, during the formation of reaction bands can be inferred from isocon diagrams. Some Al was probably added to the reaction zones, while Si was lost. This is most likely due to fluids percolating parallel to the zones at the boundary of the rock units. High temperature supercritical fluids, especially Chlorine and Fluorine, present in the pore spaces are also responsible for the transport of U and Th to- and LIL elements from the reaction zones.

INTRODUCTION

Studies of metasomatism during high-grade regional metamorphism have focussed attention on the mechanism of the mass transfer in the lower crust. Metamorphic fluids may act as a medium for mass transport (see also Fyfe et al. 1978; Ferry and Dipple 1991). The most striking example for metasomatism is the developing of distinct reaction zones (e.g. Korzhinskii 1970; Braddy 1977; Frisch and Helgeson 1984). The present paper discusses the constraints on the mechanism of mass transfer between enclaves of ultramafic rocks interbedded within thick layers of siliceous granulites at Rupaha, Sri Lanka. Several silica-undersaturated mineral assemblages containing spinel, sapphirine and corundum separate the ultramafic from granulites. Here, the fourth occurrences of sapphirine in the Sri Lankan Proterozoic basement is reported (Osanai 1989; Kriegsman 1991, Osanai et al. 1996; Kriegsman and Schumacher 2000). Formation of sapphirine in metasomatic zones has been reported in a few instances (Schumacher and Robinson 1987; Dunkley et al. 1999; Hokada et al. 1999).

Understanding of mass transfer for metasomatic processes for geologic systems requires information about mineral paragenesis, spatial distribution of minerals, relative abundances, and chemical composition of minerals and fluids. Here, we report data on the formation of reaction zones from field observations, lateral changes in mineral chemistry, chemical potential diagrams and mass balance. Variations of biotite chemistry and halogen contents in biotites in closely spaced samples of a complete profile (cross-section of ultramafic rocks, reaction zones and siliceous granulites) provide insight into fluid composition. These data permit calculation of the extent to which chemical components have been introduced, removed, and/or redistributed during metasomatism. The results suggest that reaction bands were formed during high-temperature and pressure. Diffusion most likely was the dominant mechanism of transport across layers, whereas significant Si leakage is proposed parallel to the layers.

REGIONAL GEOLOGY AND P-T EVOLUTION

The study area (Fig. 4.1) is located in the central part of the Highland Complex, which is also the part of Proterozoic belt in the Sri Lankan lower crust (Cooray 1994). The other important metamorphic units of Sri Lankan basements are the Wannai Complex and the Vijayan Complex. The Highland Complex shows a prolonged crustal history (~3.2 - 2.4 Ga). It consists of granulite facies rocks, as does the younger rocks from the Vanni Complex (~1.1 Ga) (Kröner et al. 1991; Milisenda et al. 1994). Evidence from the U-Pb system dates granulite facies metamorphism at ~610-550Ma (Bauer et al. 1991; Hölzl et al. 1994). The Vijayan Complex shows Amphibolite facies assemblages. Three major phases of structural events have been recognized (Berger and Jayasinghe 1976; Kriegsman 1993). The first event (D_{1a} and D_{1b}) are believed to predate peak metamorphic conditions, while the D_2 event is contemporaneous with peak PT. The D_3 is believed to form during the early retrogression.

Supracrustal sequences, consisting of marbles, garnet-sillimanite-graphite gneisses and quartzites constitute about 50% of the HC terrane. The remainder of the terrane is composed of orthogneisses. Peak temperature was estimated to be between 760-830°C at a pressure of 9-10kbar in the east and southeast part. Lower temperatures around ~700°C/5-6kbar are indicated in the northwest (e.g. Faulhaber and Raith 1991; Schumacher and Faulhaber 1994). Schenk et al. (1988) and Voll et al. (1994) derived a maximum temperature of 900°C for granulite assemblages from two-pyroxene and two-feldspar thermometry respectively. Metamorphic peak temperatures and pressures estimated from the rocks at Rupaha with two-pyroxene thermometry and garnet-clinopyroxene-plagioclase-quartz barometry, yield temperatures of $875 \pm 20^\circ\text{C}$ and pressures of 9.0 ± 0.1 kbar respectively (chapter 2).

This study focuses on the region of ultramafic rocks that crop out as a series of discontinuous lenses and pods, enveloped by surrounding granulites at Rupaha. Lithological layering strikes $030-040^\circ$ and dips $20-40^\circ$ to west (Fig 4.1). In all mapped exposures, the strike is broadly parallel to regional foliation. The present orientation of lithological layering was that attained at the peak of the metamorphic event. Metasomatic reaction zones separate granulite rocks from those of ultramafic enclaves. Reaction zone sequences are repeated at least in 10 places in the area. The sequence is best exposed at the

river tributary named *Garandu Kandura* (Fig. 4.2). The thickness of reaction zones varies significantly from locations to location (10-150cm). The mineral assemblages and textural characteristics of the reaction zones are described in the following paragraph.

ANALYTICAL METHODS

The chemical composition of the various parts of the reaction zones relative to their original protoliths was used to evaluate the gain and losses of materials that occurred. Rock samples were taken from a traverse across the sampling points of 9805-9806 (Fig. 4.2 and Fig. 4.3), where the least altered samples can be found. Rock slabs were cut roughly perpendicular to main foliation from each sample. Thin sections were cut, so that profiles covering the entire samples were obtained. Nine samples from siliceous granulites, six from corundum gneisses and three each from the reaction zones were analysed for 34 elements and loss of ignition (LOI) at the XRF laboratory at the University of Mainz, Germany, using a PHILIPS PW 1404 spectrometer. Mineral analyses were performed with a JEOL microprobe (JEOL JXA 8900 RL) with 15kV voltage and a 12nA beam current with a beam diameter of 2 μ m. Elements were calibrated against synthetic and natural standards. Fluorine and chlorine were calibrated with Tugtupite, $\text{Na}_4\text{AlBeSi}_4\text{O}_{12}(\text{Cl}, \text{S})$ (7.58 wt % Cl) and F-phlogopite (9.20 wt% F). Online ZAF corrections were performed using the technique of Armstrong (1988, 1989).

PETROGRAPHY OF THE RUPAHA SPINEL-SAPPHIRINE-CORUNDUM OCCURRENCES

Two complete profiles of relatively fresh samples (profile 9805-9806, profile 9715-9311) were selected for petrographic study. A schematic diagram of profile 9805-9806 and a photograph of hand specimen of the reaction zone are shown in Figs. 4.3a and b. Different mineral zones were identified on the basis of mineral assemblages and textures. These zones depicted in the Fig 4.3a are shown in the insets labelled A, B, C and D. In each case, progressing from ultramafic to siliceous granulites the following mineral assemblages sequences occur:

- (1) En Fo Di - - - - - (ultramafic rocks)
- (2) - Fo Di Phl Spl - - - - - (ultramafic rocks)
- (3) - - - Phl Spl Spr - - - - - (zone A)
- (4) - - - Phl Spl Spr Crn - - - - - (zone B)
- (5) - - - - - Crn Pl Bt - - - - - (Crn ~30%)(zone C)
- (6) - - - - - Crn Pl Bt - - - - - (Crn ~ 5%)(zone D)
- (7) - - - - - Pl Bt Qtz Kfs - Sil (siliceous granulites)
- (8) - - - - - Pl Bt Qtz Kfs Cpx Grt (siliceous granulites)

(for abbreviations see: Kretz 1983)

Ultramafic rocks

The peak metamorphic mineral assemblages in the ultramafic rocks is presented by forsterite + diopside + enstatite (Fig. 4.4a). Olivine is the dominant phase, which contains about 65% of mode (without alteration). Many of olivine grains have been altered to serpentine. Thin bands of ultramafic rock neighbouring the reaction zone contain a significant amount of phlogopite, which often exhibit a planar fabric (e.g. RU 9310A in Fig 4.1). The width of this zone is about 10-50 cm. These rocks are composed of predominantly olivine with about ~12% of phlogopite modal, and traces of spinel and diopside (<1%)(Fig 4.4b).

Phlogopite- spinel-sapphirine zone (zone A)

The contact between the ultramafic country rock and the Phl + Spl + Spr bearing zone A is sharp but lobate. Aligned phlogopites are interlocked with spinel and sapphirine (Fig. 4.4c). Sapphirine replaces phlogopite in this zone.

Spinel-sapphirine-corundum zone (zone B)

Corundum + spinel + sapphirine mineral assemblages are common in zone B. First appearance of corundum marks this zone. Corundum coexists with spinel and sapphirine. Sapphirine grains are colourless, and anhedral (Fig. 4.4d). Phlogopite occurs in this zone only as rounded grains or as relicts in sapphirine. In contrast to the neighbouring zone, the

rocks occurring in the zone B are usually massive and lack any preferred mineral orientation.

Corundum- biotite-plagioclase zone (zone C)

Zone c is characterized by an abundance of samples containing plagioclase + corundum + biotite (Fig. 4.4e). Sapphirine is absent within this zone. Biotite is iron rich because biotite is in dark coloured in hand specimen. Plagioclase is commonly twinned. Biotite, corundum and plagioclase have subequal modes (~30% each).

Corundum- gneiss zone (zone D)

Zone D is the same as zone C in terms of the mineral assemblages, but the mineral modes and the degree of alteration is quite different. Plagioclase is volumetrically dominant over corundum and biotite (mode Pl ~80%, Crn ~5%, Bt ~10%). The zone is usually wider than other mineralogical zones and characterized by barrel-shaped corundum crystals (2mm-1cm), embedded in white coloured plagioclase matrix. Corundum crystals are not of gem quality. They are often surrounded by biotite flakes. Secondary chlorite is present as fine-grained, un-oriented crystals, as well as intergrowths with fine-grained muscovite, which appears to replace corundum. Here, diaspore occurs as vein fillings in corundum. Fibrolitization of biotite is advanced in many specimens within the zone D.

Siliceous granulites

Garnet-biotite-clinopyroxene-bearing gneisses (sample No.9708 in Fig. 4.1) are coarse-grained, dark coloured and display a strong schistosity (see Fig. 2.2a in chapter 2). Assemblages are typically Grt + Bt + Pl ± Ilm; Grt + Bt + Cpx + Pl ± Qtz ± Ilm; Grt + Cpx + Pl ± Qtz ± Ilm. Sillimanite-biotite gneisses in this zone are intercalated in thin bands (Fig. 4.4e). See chapter 1 for more details.

MINERAL CHEMISTRY

Compositions of the minerals in the reaction bands are presented in Table 4.1. The site distribution of cations in sapphirine, spinel, corundum, plagioclase and biotite was calculated assuming perfect stoichiometry.

Sapphirine

Sapphirines are fairly rich in X_{Mg} [=Mg/(Mg+Fe)] content, ranging 0.978-0.986. Along the traverse, X_{Mg} content is slightly higher in zone A than zone B. The colourless nature of sapphirine is due to high Mg content. Along the traverse from zone A to zone B, the Al content increases slightly (Table 4.1a). In general, actual sapphirines are more aluminous than the theoretical end-member $Mg_4Al_8Si_2O_{20}$ (2:2:1), due to $Si^{[4]}Mg^{[6]} = Al^{[6]}Al^{[4]}$ substitution. This substitution allows the composition of $Mg_7Al_{18}Si_3O_{40}$ (7:9:3) for sapphirine at Rupaha.

Spinel

The analysed spinel composition belongs to spinel-hercynite solid solution with X_{Mg} varying from 0.962-0.965 (Fig.4.1.a). Al content in spinel is always high, which ranges from 15.95-16.07pfu. No systematic variation in elements was observed across the reaction zones.

Corundum

Corundum is found in zone B, C and D are nearly pure phases, but contain few amounts of Fe (0.0015-0.0025 pfu) (Table 4.1b). Ti and Cr contents are insignificant in all zones.

Plagioclase

Plagioclase in zone C is more anorthitic (An_{86-91}) than that of zone D (An_{31-37}) (Table 4.1c). Si and Al contents of plagioclase have reciprocal variations between both zones because the high Al and low Si content were measured from zone C.

GROWTH OF THE MINERAL ZONES

Forsterite + spinel in the ultramafic zone, together with the presence of sapphirine + spinel in the neighbouring zone A suggest that forsterite is replaced by sapphirine, which was in turn replaced by corundum in zones B and C. Formation of sapphirine from ultramafic rocks obviously requires the addition of SiO_2 and the removal of MgO. The relative decreases of Mg-bearing minerals from ultramafic-bearing rocks to siliceous granulites through zone A to D mark the lateral variation of bulk chemistry across the reaction zones.

Several textural features of the reaction zones examined give evidence for metasomatic transport. Among those that place constraints on metasomatic development are, the sharp contacts that exist between mineral zones and the presence of relatively few mineral phases in each zone (e.g. Thompson 1959; Korzhinskii 1970; Fischer 1973, 1977; Braddy 1977; Joesten 1977).

The purpose of the following part is to present the physical conditions, the nature of metasomatism and its quantitative estimate of mass transfer. Quantitative chemical potential diagrams illustrate differences in chemical potential between siliceous granulites and ultramafic rocks. Quantitative mass transfer of elements is calculated from mass balances using isocon technique. The variation of some elements in biotites including halogens from siliceous granulites to ultramafic rocks across the reaction zones were studied in order to find further constraints of fluids composition. The biotite chemistry can also be used as monitors of fluid composition during metasomatic processes.

PHYSICAL CONDITIONS OF METASOMATISM -TEMPERATURE ESTIMATES

The empirically derived Fe-Mg exchange thermometer for co-existing spinel-sapphirine assemblages (Owen and Greenough 1991) was used to evaluate the temperatures during the formation of reaction bands. The geothermometer yields a temperature of $820 \pm 40^\circ\text{C}$, assuming a pressure of 9kbar. This pressure corresponds to the peak pressure recorded by the Grt-Cpx-Pl-Qtz barometry in the surrounding granulites (Chapter 2). The temperature obtained agrees well with the maximum temperature recorded in these granulites of $875 \pm 20^\circ\text{C}$ (Chapter 2). Ultramafic rocks yielded a temperature of $842 \pm 68^\circ\text{C}$ (Chapter 3). The mineral chemistry data used for the temperature estimates are presented in Table 4.1a.

The stability field of sapphirine-spinel-corundum assemblages is shown in a chemical potential diagram of MgO (μMgO)(Fig. 4.5). The activity corrected T- μMgO diagram is calculated for the system MgO-Al₂O₃-SiO₂-H₂O-CO₂ at 9kbar condition and assuming $X_{\text{CO}_2} = 0$, using the thermodynamic database of Holland and Powell (1998). The activity models for spinel and sapphirine are those of Holland and Powell (1998). The shaded area marks the stability field of sapphirine. The assemblage spinel-sapphirine-corundum occurs together at temperatures above 780°C . The grey area in Fig.4.5 was calculated for the $X_{\text{CO}_2} = 0.5$. The stability field of sapphirine extends towards the lower temperatures (725°C).

Nevertheless, the phase petrology agrees with reaction bands forming at high temperatures close to peak, granulite facies conditions.

Thermometry and T- μ MgO diagrams provide a reasonable estimate of 850°C for co-existing spinel-sapphirine-corundum assemblages at reaction zones. The pressure estimates of 9kbar in the surrounding siliceous granulite are taken as the reference pressure for the following calculations.

CHEMICAL POTENTIAL DIAGRAMS

Equilibrium phase relations among pertinent minerals are shown in the Fig. 4.6 for the system Al_2O_3 - SiO_2 - MgO - H_2O at 850°C, 9kbar fluid and solid pressure, and $a_{\text{H}_2\text{O}}$ of 1. The univariant boundaries and saturation limits were calculated with the thermodynamic database of Holland and Powell (1998). The activities of sapphirine and spinel were also calculated from the same database.

It can be seen in Fig 4.6 that spinel and forsterite are stable at high potential of MgO at low SiO_2 potential. Note that the enstatite-spinel stability field terminates against the spinel-sapphirine with increasing SiO_2 potential. The further increase in potential of SiO_2 is marked by the appearance of corundum and sapphirine. Sillimanite and quartz occupy a relatively high SiO_2 potential with low MgO potential. This latter assemblage is seen in the siliceous granulites. It is obvious from the Fig 4.6 that the two contrasting rock types show strong chemical potential gradients in MgO and SiO_2 . The components MgO and SiO_2 will start migrating to eliminate these gradients. As a result, the new minerals corundum and sapphirine are formed in the intermediate zones. The gradient of the chemical potential of MgO and SiO_2 changes abruptly at the boundaries of all the mineral zones. The dark line was drawn in the Fig. 4.6 to approximately a steady-state diffusional transfer of material to and from the parent rocks. The mass transfer of components across lithological boundaries at Rupaha can be accomplished through diffusion (Korzhinskii 1970; Braddy 1977; Rumble 1982).

MASS BALANCE CALCULATIONS

Methods and assumptions

The extent to which components were added to, or removed from a zone during the formation of the metasomatic zones can be assessed with the aid of mass balance calculations (Gresens 1967; Grant 1986; Baumgartner and Olsen 1995). The interpretation of mass balance calculations has been a major problem in many recent studies (e.g. Grant 1986; Baumgartner and Olsen 1995). Possible reference frames have to be assumed, e.g. one can assume constant volume or one can assume immobility of one (or more) components. The isocon method (Grant 1986) is a graphical representation of Gresens' method (1967), which was originally developed to determine the mobility of elements in the metasomatized rocks. Grant (1986) expressed the composition–volume equation as a linear relationship. Hence, for immobile components, the ratio of the concentrations in the original to altered rock concentration is constant, yielding a straight line, the isocon line. Baumgartner and Olsen (1995) introduced a statistically more rigorous least-square approach to the isocon method. An algorithm was presented to identify the immobile elements, with uncertainties, as does in our calculations. For a further discussion of the mathematical treatments and problems of mass balances see Gresens (1967), Grant (1986) and Baumgartner and Olsen (1995).

Elements with low-solubility are typically assumed to be immobile during an alteration process (Ague 1991; 1994; MacLean and Barrett 1993; Roser and Nathan 1997). This argument is based on experimental determination of solubility of such elements (Baumgartner and Eugster 1988; Ayers and Watson 1991, 1993). For summary see Eugster and Baumgartner (1987). Elements commonly assumed to have low mobility in rocks during the alteration and deformations include Al, Ti and high field strength elements (HFSE) such as Y, Zr, Nb, Hf and Ta (Grant 1986; Kerrich et al. 1987; Glazner and Bartley 1991; Marquer and Burkhard 1992). Although Al and Ti are widely believed to be relatively immobile in many geologic environments, there are many cases where one or both were mobile in the tectonic environments (Yardley 1977; Kerrick 1988; O'Hara 1989; Gieré 1990a, 1990b; Selverstone et al. 1991). The proven mobility of these elements under the appropriate fluid composition and PT conditions show that no element can be considered as immobile. Nevertheless, if several elements considered being immobile define on isocon line, this lends support for their respective immobility. The composition

of original protoliths is also a problem, because the true protolith no longer exists. However, the petrologic and field evidence presented earlier suggests that the siliceous granulite were the protolith for the reaction zones. Mass balance calculations have been done for alteration of this parent to; (a) corundum gneiss (5% Crn) (zone D), (b) corundum-biotite gneiss (30% Crn) (zone C) and (c). spinel-sapphirine-phlogopite gneiss (zone A). The compositional data in Tables 4.2a, b, c and d were used to evaluate mass transfer. A one-sigma confidence interval was chosen to account for a reasonable uncertainty in the element concentrations. By identifying all combinations of overlapping cone areas in the isocon plot, all possible compatible element combinations were obtained with the Program 'ISOCON 4.2' (Baumgartner and Olsen, 1995). At this point, geochemical considerations are introduced for the modelling. The mobility of Al and Ti deserves special attention when selecting the best-fit immobile element combination. It should be noted that neither Al nor Ti would fit into the same isocon in any of three alterations. This indicates either Ti or Al is mobile during the formation of reaction bands. The isocon combination that includes Al has more elements immobile. The light rare earth elements (LREE) of La, Ce, Pr, Sm and Nd are also colinear with Al in many combinations. On the other hand, the LREE results are less systematic than those for major and minor elements. The wide variations of LREE are probably due to analytical uncertainties due to limited sample size.

We selected isocon (65), which includes the elements Al, Nb, Hf, Ta, Pr, Nd and Sm, all considered to be relatively immobile (Table 4.3a). Isocons in Figs. 4.7b and c are mainly based on Ti, Zr and Hf, which show excellent linear arrays (Tables 4.3b, c). Lanthanum, Ce and Sm are also considered to be as immobile. Similar immobility of the combination of Ti, Zr and Hf in these environments has also been suggested by Kerrich et al. 1987. Therefore, the element combination (61) would be the best-fit isocons for the alteration to zone C and zone A. (Tables 4.3b, c). It is interesting to note that all isocon diagrams show similar geochemical trends in Si, Mg, LREE, U, and Th, reflecting systematic element mobility of these elements (Figs. 4.7a, b, c).

Mass balance- interpretation

The geochemical trend for the mass transfer of major and minor elements is illustrated in Fig. 4.8a and 4.8b. Mass losses, particularly the depletion in Si, LIL elements (Ba, Na, K,

Rb, Pb etc.) are inferred. In each of the zone, the materials gained gneisses include Mg, Al, U, Th and volatiles. In particular, a substantial loss of Si during the formation of reaction promoted the formation of silica-undersaturated minerals like corundum and spinel. Zones that consist corundum are characterized by absolute gains of 30 to 50 weight percent of Al (Fig. 4.8a). The mass gain of Al in the zone A is comparatively lower than those of zone C. This is because of the presence of sapphirine and spinel in the expense of corundum in zone A. The enrichment of Mg in the Zone A and C correlates with the presence of Mg-bearing minerals such as spinel and sapphirine. The fact, that elements like U, Pb are extremely enriched during the alteration, could be due to enrichments of some accessory minerals like monazite or alternatively, since these minerals have very low concentrations, this might reflect the sample volumes. The alteration to zone D from gneisses is accounted for a weight loss of $27 \pm 7\%$ while alteration to zone C and A have minor overall mass changes (~5-10%).

In summary, all rocks were metasomatically altered under conditions of volume reduction. The increase of Al requires introduction of aluminum from outside the system, since ultramafic rocks cannot provide it. Such additions may have occurred by local redistribution from neighbouring lithologies and/or introduction as a hydrothermal solute.

HALIDE COMPOSITION OF FLUIDS

Fluorine and chlorine are ubiquitous in fluids from all crustal levels, because they are incorporated into main common rock forming minerals such as amphiboles, micas or apatite. The presence of halogen-bearing fluids can easily be monitored and their abundance in metamorphic fluids can quantitatively be estimated (see also Munoz and Ludington 1974; Munoz and Swenson 1981; Munoz 1984; Zhu and Sverjenski 1991, 1992; Finch 1995; Finch et al. 1995; Markl and Bucher 1998). As fluids are involved in most magmatic and metamorphic events, the halogens are rendered powerful tools for the understanding of fluid evolution (Boudreau and McCallum 1989; Kullerud 1995, 1996; Markl and Schumacher 1996). Mineral-fluid equilibria used for models of any crustal processes depend on the composition of co-existing fluid. Results of the various studies show that (e.g. Touret 1985; Mora and Valley 1989), in some high-grade metamorphic terranes chlorine species should be taken into account in addition to typically modelling

H₂O-CO₂ binary mixture. Chlorine species have a profound effect on the H₂O activity. Hence, detailed knowledge of the abundance of the chlorine in fluids is necessary to allow precise modeling and it can help to decipher the progress of metamorphic reactions as well as the sources of fluids encountered in regionally metamorphosed terranes.

The fluid evaluation from the composition of halogen-bearing minerals in high-temperature metasomatic systems is less well studied. This part reports chemical analyses of F and Cl-bearing biotites in the reaction zones at Rupaha with its neighbouring siliceous granulites and ultramafic rocks. The focus of this part is placed on the changes of composition of biotite and the effect of halides in fluids contemporaneous with the high-temperature metasomatism.

Samples were chosen to provide a representative selection of each zone. Approximately 170 biotite grains, ranging along the profile ultramafic rocks, through the reaction zones to the siliceous granulites were analysed. Nearly all biotite grains show no alteration to chlorite. Error bars for biotite analyses, which represent the 1 σ standard deviations, are presented for each analytical point. The chemical compositions of biotites from the siliceous granulites to ultramafic rocks studied are given in Table 4.4. The biotite formula was calculated on the basis of 22 oxygens. The chemistry of biotite was plotted against the distance from the rock in order to demonstrate the variation with the different rock types (Fig 4.9). Average values (given as stars in Fig.4.9) and 1 σ standard deviation are given for each set of analysis from a section or zone. The chemical compositions of biotites are given in Tables C6 to C11 in Appendix. Biotite formulas were calculated on the basis of 22 oxygens, excluding H₂O.

Element variations in biotite

The element variation pattern in the tetrahedral position of biotite from siliceous granulites shows a trend of decreasing of Si towards the reaction zones, and subsequently increasing towards the ultramafic rocks (Fig 4.9a). Aluminum replaces it there, showing reciprocal relationship with Si (Fig. 4.9b). Note that biotites in the silica undersaturated reaction zones have excess Al to put into octahedral position while no excess Al is observed either in siliceous granulites or ultramafic rocks (Appendices C6-C11). (The site allocation method assumes complete filling of tetrahedral site by Si, then Al - theoretically 8 atoms

per 22 oxygens- The rest of Al atoms are assigned to octahedral positions). The dashed lines in each diagram denote the polynomial fits for chemistry of the particular elements.

The Mg and Fe concentrations in mica are a strong function of location. Biotites in ultramafic rocks are nearly pure phlogopites. X_{Mg} systematically decreases towards the siliceous granulites (Fig. 4.9c). The majority of the variation in biotite in the octahedral position comes from differences on the Fe and Mg contents (Fig. 4.9d). Ti decreases, while Mg increases (Fig. 4.9e). The evaluation of the biotite stoichiometry indicates that the substitutions preferably take place by the Tschermaks or Ti- Tschermaks substitution (Guidotti et al. 1977; Dymek 1983; Spear 1993).

The F-content of biotite first decreases and then increases towards the ultramafic rocks (Fig. 4.9f). In all cases, except siliceous granulites, biotite shows strong Fe-F avoidance. The extremely high F content at the ultramafic-reaction band interface is due to characteristic heterogeneous F- activity in fluids. The thin section evidences also support the idea for the formation of biotites from forsterite and spinel at the contacts with sufficient fluid activity (Fig. 4.4e see also Chapter 3). This suggests that the F contents of biotites of the present study have two controls: (1) strong structural control which is responsible for Fe-F avoidance, and (2). The activity of F in the fluid with, which the biotite last equilibrated.

The chlorine content of biotite is low and insignificant when compared to Fluorine. However, the high chlorine content is observed in the granulites (Fig. 4.9f). It ranges from 0.08-0.12 atoms pfu in the granulites while 0.03-0.06 atoms pfu is measured in the ultramafics.

Estimate of chloride content in fluid

The chlorine content of biotite can be used to calculate the composition of the chlorine content of the fluid phase, if assumed, that it is in local equilibrium with the aqueous fluids (e.g. Munoz 1984; Zhu and Sverjensky 1991; Robert et al. 1993; Kullerud 1995, 1996). Experimental studies on the partitioning of halogens between mica and fluids show that the amount of Cl in biotite is a strong function of fluid composition, temperature and pressure and Fe, Mg concentrations (e.g. Munoz and Ludington 1974; Munoz and Swenson 1981;

Munoz 1984; Aksyuk and Zhukovskaya 1994). Zhu and Sverjensky (1991, 1992) developed a method to calculate the activity of HCl° in aqueous fluids. Assuming unit activity of water in the system, one can calculate the activity of HCl° of the fluids during biotite crystallization. Once the HCl° concentration of aqueous fluids is known, the speciation and metal ion concentration of the supercritical fluids can be calculated at the temperature and pressure of interest (Wolery 1979, 1983; Eugster and Baumgartner 1987).

The Gibbs free energy for the reaction involving a partitioning of OH-biotite to Cl-biotite were calculated using thermodynamic properties for OH end member components from Berman (1988, 1990) with adjustment of free energies according to Sverjenski et al. (1991), and for Cl end member components from Zhu and Sverjenski (1991). Heat capacities, molar volume and entropy are taken from Zhu and Sverjenski (1991) and references therein (Table 4.4). The thermodynamic database are said to be internally consistent and therefore used for our calculations (for more details see Zhu and Sverjenski 1992).

The total of 21 analyses of biotite from siliceous gneisses and 58 from ultramafic equivalents was used for calculations (Appendix Tables C6, C11). The number of cations in the biotite formula was calculated on the basis of 22 oxygens. We assumed ideal mixing of F, Cl and OH in the hydroxyl site in mole fraction calculations.

Zhu and Sverjensky (1992) used experimental results of previous studies to calculate the slopes of the reaction (1) for different temperatures.

$$\log\left(\frac{X_{Cl}}{X_{OH}}\right) = \frac{1}{2} \left(\frac{\Delta G_R^{\circ}}{2.303RT} \right) X_{Mg} + \frac{1}{2} \log K - \log\left(\frac{a_{H_2O}}{a_{HCl}}\right) \quad (1)$$

The calculated average slope of -0.46 at 850°C for the Rupaha rocks matches well with the predicted value of Zhu and Sverjensky (1992) at 850°C (see Fig.10b of Zhu and Sverjensky 1992). The plot of $\log(X_{Cl}/X_{OH})$ against the X_{Mg} from biotites at Rupaha is shown in Fig. 4.10. The dotted lines denote the slope of -0.46, which is calculated at 850°C. The diagram shows that the fluid compositions at the grain boundaries of the reaction zones are in equilibrium with the neighbouring precursor rocks. For example, biotites at the boundary of zone D record fluid compositions similar to that of the siliceous

granulites while boundary of zone A is similar to that of ultramafic rocks. The average $\log(X_{\text{Cl}}/X_{\text{OH}})$ and X_{Mg} values of biotites from pelitic and ultramafic equivalents are provided in Table 4.5. The logarithms of the activity of HCl for the siliceous granulite are calculated as -3.6 while an activity of a_{HCl} of -3.5 was calculated for the ultramafic rocks. It shows that the HCl activities in fluids in the two rock types are equal within the error of determination.

SUMMARY AND CONCLUSIONS

Conditions of metamorphism and metasomatism

The field and petrologic observations suggest that the reaction bands associated with siliceous granulites and ultramafic rocks at Rupaha formed by diffusional transport between the two chemically different rock types. The reaction bands are comprised of silica undersaturated corundum, sapphirine and spinel assemblages. The ion-exchange thermometry provides an estimate of $820 \pm 40^\circ\text{C}$ for coexisting spinel and sapphirine at 9 kbar. This observation, together with T- μMgO diagrams suggest that reaction bands too are formed during high temperature granulite facies metamorphism. Mg contents and low X_{Fe} , together with low SiO_2 and high Al_2O_3 , in the Rupaha reaction zones provide appropriate geochemical conditions for sapphirine formation.

Mechanism of metasomatism

The zoned sequence can be well illustrated by an activity diagram of SiO_2 vs MgO . The reaction bands formed primarily due to Mg and Si metasomatism. Chemical potential of Mg generated continuous monotonic gradient across the profile, allowing steady state diffusion. This agrees with a dominant transport by diffusion.

Major and trace element concentrations provide quantitative constraints on element mobility. Mass gains, particularly the enrichment in Al, and the considerable loss of Si, during the formation of reaction bands are inferred from isocon diagrams. Ti, Zr and Hf behaved isochemically in most zones. The diffusional transport of elements over more than centimetre distances is permitted with the presence of fluids in the system. It is most likely that a fluid phase pervaded the grain boundaries sufficiently to provide an interconnected network through which diffusion could occur. The concentration of the fluids in the system

is known from the biotite chemistry. High temperature supercritical fluids are responsible for carrying U and Th to and LIL elements from the rocks. The absence of a pervasive fluid flux during the formation of reaction bands was probably the most important condition for development of these textures and geometry, allowing them to be controlled by diffusive transport. The idea is also supported by the presence of element variation in biotite across the profile. The reciprocal relationship of Si and Al in the reaction zones are illustrated. The gain of Al and losses of Si at the reaction zones do not fit with the simple bi-metasomatic process. It is most likely that the introduction of Al-rich fluids into these rocks and leaking of Si along sub parallel channels, most likely along the foliation planes, while Mg is diffused across the layers resulted, in metasomatic reactions bands.

This study uses the reaction zones formed in the granulite-ultramafic contact at Rupaha to derive information about mass transport in high-grade granulites. These reaction zones are formed by diffusion-controlled reaction mechanisms that develop during peak metamorphism. This study has shown that not only pressure and temperature conditions but most importantly P_{H_2O} and the concentration of the aqueous fluids also control the diffusion of the elements in different geological environments. Therefore, nature and reaction kinetics of supercritical fluids during the high-temperature metasomatism should take into account in mass transfer calculations.

REFERENCES

- Ague JJ* (1991). Evidence for major mass transfer and volume strain during regional metamorphism of pelites. *Geol.* 19: 855-858
- Ague JJ* (1994). Mass transfer during Barrovian metamorphism of pelites, south-central Connecticut. I: Evidence for changes in composition and volume. *Am. J. Sci.* 294: 989-1057
- Aksyuk AM, Zhukovskaya TN* (1994). Experimental calibration of the phlogopite fluorimeter at 500-700°C and 1-4 kbar, and estimated HF concentrations of fluids associated with marbles: some examples. *Geochim. Cosmochim. Acta.* 58: 4305-4315
- Armstrong JT* (1988). Quantitative analyses of silicate and oxide minerals: comparisons of Monte Carlo, ZAF and Phi-rho-z procedures. In: *Microbeam analysis* (*Newbury DE* ed). -1988, San Francisco Press, San Francisco, 239-246
- Armstrong JT* (1989). CITZAF: combined ZAF and phi-rho (Z) electron beam correction programs. California Institute of Technology, Pasadena, CA
- Ayers JC, Watson EB* (1991). Solubility of apatite, monazite, zircon and rutile in supercritical aqueous fluids with implications for subduction zone geochemistry. *Royal Soc. (Lond) Phil. Trans.* 335: 365-375
- Ayers JC, Watson EB* (1993). Rutile solubility and mobility in supercritical aqueous fluids. *Contrib. Mineral. Petrol.* 114: 321-330
- Bauer N, Kröner A, Todt W, Liew TC, Hofmann AW* (1991). U-Pb isotope systematics of zircons from prograde and retrograde transition zones in high-grade orthogneisses, Sri Lanka. *J. Geol.* 99: 527-545
- Baumgartner LP, Eugster HP* (1988): Experimental determination of corundum solubility and Al-speciation in supercritical H₂O-H solutions [abs.]. *Geol. Soc. Am. Abs. with Prog.* 20:191
- Baumgartner LP, Olsen SN* (1995). A Least-Squares approach to mass transport calculations using the Isocon method. *Econ. Geol.* 90: 1261-1270
- Berger AR, Jayasinghe NR* (1976). Precambrian structure and chronology in the Highland Series of Sri Lanka. *Precam. Res.* 3: 559-576
- Berman, RG* (1988). Internally consistent thermodynamic data for minerals in system Na₂O - K₂O - CaO - MgO - FeO - Fe₂O₃ - Al₂O₃ - SiO₂ - TiO₂ - H₂O - CO₂: representation, estimation, and high temperature extrapolation, *J. Petrol.* 29: 445-522

- Berman RG* (1990). Mixing properties of Ca-Mg-Fe-Mn in garnets. *Am. Mineral.* 75: 328-344
- Boudreau AE, McCallum IS* (1989). Investigations of the Stillwater complex V. Apatites as indicators of evolving fluid composition. *Contrib. Mineral. Petrol.* 102: 138-153
- Braddy JB* (1977). Metasomatic zoning in metamorphic rocks. *Geochem. Cosmochim. Acta* 41: 113-125
- Cooray PG* (1994) The Precambrian of Sri Lanka: a historic review. *Precam. Res.* 66: 3-18
- Dunkley DJ, Clarke GL, Harley SL* (1999). Diffusion metasomatism in silica-undersaturated sapphirine-bearing granulite from Rumdoole Peak, Framnes Mountains, East Antarctica. *Contrib. Mineral. Petrol.* 134: 264-276
- Dymek RF* (1983). Titanium, aluminium and interlayer cation substitutions in biotite from high-grade gneisses, west Greenland. *Am. Mineral.* 68: 880-899
- Eugster HP, Baumgartner LP* (1987). Mineral solubilities and speciation in supercritical metamorphic fluids. In: (*Carmichael ISE, Eugster HP* eds), *Thermodynamic modeling of geological materials: minerals, fluids and melts.* Mineral. Soc. Am., Reviews of Mineral. 17: 367-403
- Faulhaber S, Raith M* (1991). Geothermometry and geobarometry of high-grade rocks: a case study on garnet-pyroxene granulites in southern Sri Lanka, *Min. Mag.* 55: 17-40
- Ferry JM, Dipple GM* (1991). Fluid flow, mineral reactions and metasomatism. *Geol.* 19: 211-214
- Finch A* (1995). Metasomatic overprinting by juvenile igneous fluids, Igdlarfisalik, South Greenland, *Contrib. Mineral. Petrol.* 122: 11-24
- Finch A, Parsons I, Mingard SC* (1995). Biotites as indicators of fluorine fugacities in late-stage magmatic fluids: the Garder Province of South Greenland. *J. Petrol.* 36: 1701-1728
- Fischer GW* (1973). Non-equilibrium thermodynamics as a model for diffusion controlled metamorphic processes. *Am. J. Sci.* 273: 897-924
- Fischer GW* (1977). Non-equilibrium thermodynamics in metamorphism. In: *Thermodynamic in Geology.* (*Fraser DG* ed). Reidel Publ Co, Boston, 381-403
- Frisch CJ, Helgeson HC* (1984). Metasomatic phase relations in dolomites of the Adamello Alps. *Am. J. Sci.* 284: 121-185
- Fyfe WS, Price NJ, Thompson AB* (1978). *Fluids in the earth's crust:* Elsevier Publ, Amsterdam, pp383

- Gieré R* (1990a). Quantification of element mobility at a tonalite/dolomite contact. PhD dissertation, University of Zürich, Switzerland, pp92
- Gieré R* (1990b). Hydrothermal mobility of Ti, Zr and REE; examples from the Bergell and Adamello contact aureoles (Italy). *Terra Nova* 2: 60-67
- Glazner AF, Bartley JM* (1991) Volume loss, fluid flow and state of strain in extensional mylonites from central Mojave Desert, California. *J. Structural Geol.* 13:587-594
- Grant JA* (1986) The isocon diagram-a simple solution to Gresens equation to metasomatic alteration. *Econ. Geol.* 81: 1976-1982
- Gresens RL* (1967) Composition-volume relationships of metasomatism. *Chem. Geol.* 2: 47-55
- Guidotti, CV* (1984). Micas in metamorphic rock. In: *Micas.* (*Bailey SW* ed), Mineral. Soc. Am., *Reviews in Mineral.* 13: 357-456
- Guidotti, CV, Cheney JT, Guggenheim S* (1977). Distribution of Ti between coexisting muscovite and biotite in pelitic schists from northwestern Maine. *Am. Mineral.* 62: 438-448
- Hokada T, Osanai Y, Toyoshima T, Owada M, Tsunogae T, Crowe WA* (1999). Petrology and metamorphism of sapphirine-bearing aluminous gneisses from Tonagh Island in the Napier Complex, East Antarctica, *Polar Geosci.* 12: 49-70
- Holland TJB, Powell R* (1998) An internally consistent thermodynamic data set for phases of petrological interest. *J. metamorphic Geol.* 16: 309-343
- Hözl S, Hofmann AW, Todt W, Köhler H* (1994). U-Pb geochronology of the Sri Lankan basement, *Precam. Res.* 66: 123-149
- Joesten R* (1977). Evolution of mineral assemblage zoning in diffusion metasomatism. *Geochem. Cosmochim. Acta* 41: 649-670
- Kerrick R, Fyfe WS, Barnett RL, Blair BB, Willmore LM* (1987). Corundum, Cr-muscovite rocks at O'Briens, Zimbabwe: the conjunctions of hydrothermal desilicification and LIL-element enrichment- geochemical and isotope evidences. *Contrib. Mineral. Petrol.* 95: 481-498
- Kerrick DM* (1988): Al₂O₅-bearing segregations in the Lepontine Alps, Switzerland; aluminium mobility in metapelites. *Geol.* 16: 636-640
- Korzhinskii DS* (1970). *Theory of metasomatic zoning.* Clarendon Press, Oxford, 111-146
- Kretz R* (1983) Symbols for rock forming minerals. *Am. Mineral.* 68: 277-279

- Kriegsman LM* (1991). Sapphirine-bearing granulite from central Sri Lanka-outcrop description and mineral chemistry. In: the crystalline crust of Sri Lanka, part 1, summary of research of Sri Lankan-German Consortium (*Kröner A* ed), Geol. Surv. Dept. of Sri Lanka, Prof Pap 5: 178-187
- Kriegsman LM* (1993). Geodynamic evolution of the Pan-African lower crust in Sri Lanka- Structural and petrological investigations into a high-grade gneiss terrain. PhD thesis, University of Utrecht, The Netherlands, pp207
- Kriesman LM, Schumacher JC* (2000). Petrology of sapphirine-bearing and associated granulites from central Sri Lanka. *J. Petrol.* 40: 1211-1239
- Kröner A, Cooray PG, Vitanage PW* (1991). Lithotectonic subdivision of the Precambrian basement in Sri Lanka. In: The crystalline crust of Sri Lanka, Part -1. Summary of research of the German-Sri Lankan Consortium *Kröner A* (Ed), Geol. Surv. Dept. Sri Lanka, Prof. Pap. 5: 5-21
- Kullerud K* (1995). Chlorine, titanium and barium-rich biotites: factors controlling biotite composition and implication for garnet-biotite geothermometry, *Contrib. Mineral. Petrol.* 120: 42-59
- Kullerud K* (1996). Chlorine-rich amphiboles: interplay between amphibole composition and evolving fluid, *Eu. J. Mineral.* 8: 355-370
- MacLean WH, Barrett TJ* (1993). Lithogeochemical techniques using immobile elements. *J. Geochem. Explor.* 48: 109-133
- Markl G, Bucher K* (1998). Metamorphic salt in granulite; implications for the presence and composition of fluid in the Lower crust. *Nature*, 391: 781-783
- Markl G, Schumacher JC* (1996). Spatial variations in temperature and composition of greisen-forming fluids: an example from the Variscan Triberg granite complex, Germany. *Econ. Geol.* 91: 576-589
- Marquer D, Burkhard M* (1992) Fluid circulation, progressive deformation and mass transfer processes in the upper crust: the example of basement-cover relationships in the External Crystalline Massifs, Switzerland. *J. Structural Geol.* 14: 1047-1057
- Milicenda CC, Liew TC, Hofmann AW* (1994) Nd isotopic mapping of the Sri Lanka basement: update and additional constraints from Sr isotopes. *Precam. Res.* 66: 95-110
- Mora C, Valley JW* (1989). Halogen-rich scapolite and biotite: implications for metamorphic fluid-rock interaction. *Am. Mineral.* 74: 721-737

- Munoz JL* (1984). F-OH and Cl-OH exchange in micas with applications to hydrothermal ore deposits. In: *Micas*. (*Bailey SW* ed), Mineral. Soc. Am., Reviews in Mineral. 13: 469-494
- Munoz JL, Ludington S* (1974). Fluoride-hydroxyl exchange in biotite. *Am. J. Sci.* 274: 396-413
- Munoz JL, Swenzen A* (1981). Chloride-hydroxyl exchange in biotite and estimation of relative HCl/HF activities in hydrothermal fluids. *Econ. Geol.* 76: 2212-2221
- O'Hara K, Blackburn WH* (1989) Volume loss model for trace elements enrichments in mylonites. *Geol.* 17: 524-527
- Osanai Y* (1989). A preliminary report on sapphirine/kornerupine granulite from Highland Series, Sri Lanka (extended abstract), Seminar on recent advances in Precambrian geology in Sri Lanka
- Osanai Y, Owada M, Kagami H, Hamamoto T, Hensen J* (1996). Sapphirine granulite and related high-P-T metamorphic rocks from Highland Complex, Sri Lanka, Gondwana Research Group Misc. Publ. No. 4, (*Santosh M, Yoshida M* eds), 107-108
- Owen VJ, Greenough JD* (1991). An empirical sapphirine-spinel Fe-Mg exchange thermometer and its application to high-grade xenoliths in the Popes Harbour dyke, Nova Scotia, Canada. *Lithos* 26:317-322
- Robert JL, Beny JM, Della Ventura J, Hardy M* (1993). Fluorine in micas: crystal chemical control of OH-F distribution between trioctahedral and dioctaheral sites. *Eu. J. Mineral.* 5: 7-18
- Roser BP, Nathan S* (1997). An evaluation of elemental mobility during metamorphism of a turbidite sequence (Greenland Group, New Zealand). *Geol. Mag.* 134: 219-234
- Rumble D III* (1982). The role of perfectly mobile components metamorphism. *Ann. Rev. Earth. Planet. Sci.* 10: 221-233.
- Schenk V, Raase P, Schumacher R* (1988) Very high temperatures and isobaric cooling before tectonic uplift in the Highland Series. *Terra Cognita* 8: 265
- Schumacher JC, Robinson P* (1987). Mineral chemistry and metasomatic growth of aluminous enclaves in gedrite-cordierite-gneiss from southwestern New Hampshire, USA. *J. Petrol.* 28: 1033-1073
- Schumacher R, Faulhaber S* (1994). Summary and discussion of P-T estimates from garnet-pyroxene-plagioclase-quartz-bearing granulite- facies rocks from Sri Lanka. *Precam. Res.* 66: 295-308

- Selverstone J, Morteani G, Staude JM* (1991) Fluid channelling during ductile shearing transformation of granodiorite into aluminous schist in the Tauren Window, eastern Alps. *J. Metamorphic Geol.* 9: 419-431
- Spear FS* (1993) Metamorphic phase equilibria and pressure-temperature-time paths Monograph series, Mineral. Soc. Am., Washinton D.C., pp799
- Thompson JB* (1959). Local equilibrium in metasomatic processes. In: *Researches in geochemistry (Abelson, PH ed)*, John Willey & Sons, New York, 437-457
- Touret JLR* (1985). Fluid regime in southern Norway: the record of fluid inclusions. In: *The deep Proterozoic crust in the North Atlantic Provinces (Tobi AC, Touret JLR eds)*. Reidel, Dordrecht, 517-550
- Voll G, Evangelakakis C, Kroll H* (1994) Revised two-feldspar geothermometry applied to Sri Lankan feldspars. *Precam. Res.* 66: 351-377
- Wolery TJ* (1979). Calculation of chemical equilibria between aqueous solutions and minerals: the EQ3/6 software package. Lawrence Livermore National Laboratory, URCL-52658
- Wolrey TJ, Sherwood DJ, Jackson KJ, Delany JM, Puigdomenech I* (1983). EQ3/6: Status and applications, Lawrence Livermore National Lab, Livermore, CA, UCRL-91884, pp.12
- Yardley BWD* (1977). The nature and significance of the mechanism of suillimanite growth in the Conemara schist, Ireland. *Contrib. Mineral. Petrol.* 65: 53-58
- Zhu C, Sverjensky DA* (1991). Partitioning of F-Cl-OH between minerals and hydrothermal fluids. *Geochim. Cosmochim. Acta* 55: 1837-1858
- Zhu C, Sverjensky DA* (1992). F-Cl-OH partitioning between biotite and apatite. *Geochim. Cosmochim. Acta* 56: 3435-3467

Table 4.1b Corundum composition of reaction zones										Table 4.1c Representative plagioclase composition of reaction zones									
Location analyses Zone	9805		9805		9805		9805		9806		Sample analyses zone	9805		9805		9806		9804	
	D	D	D	D	C	C	C	C	B	D		D	D	D	C	C	C		
SiO ₂	0.03	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.05	SiO ₂	59.34	59.90	45.36	44.68				
TiO ₂	0.05	0.04	0.03	0.13	0.05	0.05	0.02	0.02	0.02	0.01	TiO ₂	0.00	0.00	0.01	0.01				
Al ₂ O ₃	98.88	99.19	99.75	99.71	99.17	99.17	98.83	98.83	98.83	98.83	Al ₂ O ₃	25.21	24.79	34.48	34.87				
FeO	0.14	0.12	0.23	0.18	0.12	0.12	0.10	0.10	0.10	0.10	FeO	0.09	0.00	0.00	0.02				
Cr ₂ O ₃	0.01	0.00	0.01	0.00	0.02	0.02	0.01	0.01	0.01	0.01	Cr ₂ O ₃	0.00	0.05	0.00	0.01				
MnO	0.00	0.01	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00	MnO	0.06	0.01	0.00	0.03				
MgO	0.02	0.02	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.01	MgO	0.09	0.00	0.00	0.00				
CaO	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	CaO	6.35	6.46	18.29	18.55				
GeO ₂	0.00	0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	Na ₂ O	7.57	7.94	1.16	1.04				
Sc ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	K ₂ O	0.58	0.26	0.03	0.00				
V ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	BaO	0.09	0.02	0.00	0.00				
Gr ₂ O ₃	0.02	0.01	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.00	F	0.14	0.00	0.12	0.05				
Total	99.15	99.45	100.08	100.09	99.44	99.44	99.04	99.04	99.04	99.04	Cl	0.01	0.00	0.00	0.01				
Si	0.0005	0.0007	0.0005	0.0006	0.0005	0.0005	0.0008	0.0008	0.0008	0.0008	Total	99.52	99.42	99.45	99.27				
Ti	0.0006	0.0005	0.0003	0.0016	0.0006	0.0006	0.0003	0.0003	0.0003	0.0003	Si	10.652	10.740	8.409	8.311				
Al	1.9945	1.9944	1.9941	1.9928	1.9944	1.9944	1.9950	1.9950	1.9950	1.9950	Ti	0.000	0.000	0.001	0.001				
Fe	0.0020	0.0018	0.0032	0.0025	0.0017	0.0017	0.0015	0.0015	0.0015	0.0015	Al	5.333	5.238	7.533	7.644				
Cr	0.0001	0.0000	0.0001	0.0000	0.0002	0.0002	0.0001	0.0001	0.0001	0.0001	Fe	0.013	0.000	0.000	0.003				
Mn	0.0000	0.0001	0.0001	0.0000	0.0002	0.0002	0.0000	0.0000	0.0000	0.0000	Cr	0.000	0.007	0.000	0.002				
Mg	0.0006	0.0006	0.0003	0.0004	0.0005	0.0005	0.0003	0.0003	0.0003	0.0003	Mn	0.009	0.002	0.000	0.005				
Ca	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0002	0.0002	0.0002	0.0002	Mg	0.023	0.000	0.000	0.000				
Ge	0.0000	0.0001	0.0000	0.0001	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	Ca	1.221	1.241	3.633	3.696				
Sc	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	Na	2.634	2.760	0.415	0.376				
V	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	K	0.132	0.059	0.008	0.000				
Ga	0.0002	0.0001	0.0002	0.0001	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	Ba	0.007	0.001	0.000	0.000				
Cations all iron as FeO	1.9985	1.9983	1.9988	1.9981	1.9985	1.9985	1.9985	1.9985	1.9985	1.9985	F	0.079	0.000	0.070	0.029				
											Cl	0.003	0.000	0.000	0.002				
											X _{An}	0.31	0.31	0.90	0.91				
											An	30.63	30.57	89.57	90.76				
											Ab	66.07	67.99	10.24	9.24				
											Or	3.30	1.45	0.20	0.00				
											X _{an} = [(Ca/(Ca+Na+K))								

Table 4.2a Whole rock analyses of siliceous granulites (parent rock)

Sample No.	RU 9708 L	RU 9708 M	RU 9708 N	RU 9707 L	RU 9707 M	RU 9707 N	RU 9804	RU 9708 A *	RU 9708 B *	Average	1s
SiO ₂ %	61.77	61.72	62.14	58.84	59.33	58.84	63.80	65.57	64.82	61.871	2.526
Al ₂ O ₃ %	18.92	19.03	19.28	19.22	18.68	19.36	18.80	16.71	18.11	18.679	0.830
Fe ₂ O ₃ %	2.29	2.25	2.13	5.56	5.58	5.21	4.48	4.59	2.35	3.827	1.536
MnO %	0.14	0.14	0.12	0.05	0.05	0.05	0.02	0.03	0.03	0.071	0.050
MgO %	0.89	0.84	0.80	0.98	0.87	0.85	0.44	0.45	0.85	0.775	0.195
CaO %	2.05	2.13	2.11	4.53	4.55	4.80	2.65	2.59	2.85	3.139	1.150
Na ₂ O %	3.96	4.04	4.01	4.77	4.80	5.02	4.86	5.03	2.48	4.331	0.820
K ₂ O %	8.17	8.26	7.85	3.69	3.67	3.50	3.51	3.47	7.03	5.460	2.274
TiO ₂ %	0.31	0.19	0.22	0.50	0.54	0.60	0.36	0.26	0.31	0.365	0.149
P ₂ O ₅ %	0.05	0.04	0.05	0.06	0.05	0.04	0.05	0.08	0.01	0.048	0.019
LOI %	1.06	0.97	0.91	1.45	1.51	1.36	0.72	0.88	0.82	1.076	0.291
Total	99.61	99.61	99.62	99.64	99.64	99.64	99.68	99.66	99.67		
(ppm)											
Sc ₂ O ₃	3.1	3.2	6.1	20.0	18.5	21.5	4.6	3.1	3.1	9.2	8.2
V ₂ O ₅	79.4	75.7	72.8	84.0	87.2	76.7	80.9	80.5	92.9	81.1	6.2
Cr ₂ O ₃	22.3	19.5	17.4	54.2	47.0	42.5	16.1	17.8	22.0	28.7	14.8
CeO	51.8	41.8	49.1	47.1	35.8	34.4	59.7	52.8	57.3	47.8	8.9
NiO	20.7	19.6	17.6	33.1	32.0	29.3	2.5	5.2	7.6	18.6	11.6
CuO	12.8	12.9	16.1	1.3	1.3	2.5	7.5	6.3	3.8	7.2	5.6
ZnO	50.7	48.6	45.6	37.4	40.0	36.2	42.3	34.1	61.1	44.0	8.5
Ga ₂ O ₃	28.8	29.0	28.0	32.3	33.8	31.0	28.2	27.2	18.9	28.6	4.2
Rb ₂ O	286.3	286.8	274.0	317.6	317.6	293.8	260.2	260.4	241.0	282.0	26.0
SrO	468.6	471.9	461.4	394.4	398.1	404.2	435.0	448.2	375.6	428.6	36.2
Y ₂ O ₃	13.5	10.6	10.2	13.3	8.9	8.9	5.9	6.0	4.4	9.1	3.2
ZrO ₂	216.0	214.0	184.6	247.5	236.2	245.1	160.7	266.9	239.5	223.4	33.5
Nb ₂ O ₅	6.4	6.5	7.5	12.6	12.6	12.6	11.3	7.7	8.8	9.6	2.7
BaO	2462.5	2509.1	2433.3	2085.2	2075.8	2106.1	1901.7	2079.4	1996.7	2183.3	223.2
U ₂ O ₃	1.1	1.1	1.1	7.7	8.9	7.7	1.1	1.1	1.1	3.4	3.5
Th ₂ O ₃	5.6	3.4	3.3	7.7	6.7	7.7	3.3	3.4	3.3	4.9	2.0
PbO	46.1	46.5	44.8	69.0	70.4	69.1	29.1	29.5	36.7	49.0	16.7
HfO ₂	14.4	4.9	4.7	11.8	11.9	11.8	3.5	8.4	3.5	8.3	4.3
Ta ₂ O ₅	3.5	2.3	3.4	3.4	3.4	3.4	2.3	2.3	2.3	2.9	0.6
La ₂ O ₃	41.8	39.8	38.3	49.3	57.8	54.1	41.0	34.5	20.0	41.8	11.2
Ce ₂ O ₃	40.6	38.5	34.8	49.3	56.5	57.5	39.8	39.2	45.8	44.7	8.2
Pr ₂ O ₃	4.8	3.6	4.6	8.2	9.4	8.2	5.8	4.7	2.3	5.8	2.4
Nd ₂ O ₃	16.6	13.2	15.0	21.0	19.9	19.9	14.0	15.4	5.8	15.7	4.6
Sm ₂ O ₃	2.4	2.4	2.3	7.0	4.7	7.0	3.5	2.3	2.3	3.8	2.0

Table 4.2b Whole rock analyses of zone D
(corundum-biotite-plagioclase gneiss)

Sample No.	RU 9805 AL	RU 9805 AM	RU 9805 AN	RU 9805 L	RU 9805 M	RU 9805 N	average	1s
SiO ₂ %	60.25	60.82	60.77	57.05	55.57	56.18	58.44	2.436
Al ₂ O ₃ %	24.33	23.64	23.72	27.18	28.50	27.70	25.84	2.189
Fe ₂ O ₃ %	0.34	0.26	0.26	0.30	0.42	0.43	0.33	0.075
MnO %	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.004
MgO %	0.40	0.45	0.41	0.48	0.63	0.70	0.51	0.123
CaO %	2.37	2.34	2.33	5.53	5.42	5.46	3.91	1.714
Na ₂ O %	6.61	6.68	6.71	6.75	6.52	6.59	6.64	0.084
K ₂ O %	3.84	4.02	3.82	1.20	1.25	1.21	2.56	1.468
TiO ₂ %	0.09	0.06	0.01	0.10	0.13	0.12	0.08	0.044
P ₂ O ₅ %	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.000
LOI %	1.42	1.37	1.61	1.04	1.17	1.18	1.30	0.206
Total (ppm)	99.66	99.65	99.66	99.64	99.63	99.61		
Se ₂ O ₃	3.1	4.6	1.5	4.6	4.6	7.6	4.3	2.0
V ₂ O ₃	7.3	5.9	7.3	8.8	13.2	11.7	9.0	2.8
Cr ₂ O ₃	2.9	2.9	2.9	2.9	2.9	4.4	3.2	0.6
CoO	126.9	139.6	185.4	153.4	208.0	205.0	169.7	34.5
NiO	3.8	1.3	1.3	5.1	5.1	3.8	3.4	1.7
Zn								
Ga ₂ O ₃	30.9	29.5	29.5	28.1	29.5	28.1	29.3	1.0
Rb ₂ O	60.0	63.3	68.8	50.2	55.6	54.4	58.7	6.7
SrO	777.8	793.3	787.7	1096.5	1055.8	1057.1	928.0	156.1
Y ₂ O ₃	30.9	26.5	27.9	32.3	33.8	33.7	30.8	3.1
ZrO ₂	84.9	80.9	87.7	113.1	124.0	135.8	104.4	23.0
Nb ₂ O ₃	12.6	7.5	7.5	10.0	13.8	13.8	10.9	2.9
BaO	2038.1	2134.3	2045.9	1781.0	1841.1	1996.0	1972.7	134.4
U ₂ O ₃	13.2	9.9	9.9	48.3	73.6	69.0	37.3	30.1
Th ₂ O ₃	18.7	16.5	16.5	30.8	46.2	45.0	29.0	14.0
PbO	58.1	60.2	57.0	89.1	89.2	89.0	73.8	16.8
HfO ₂	4.7	5.9	3.5	5.9	5.9	8.2	5.7	1.6
Ta ₂ O ₃	3.4	3.4	3.4	4.5	4.5	4.5	4.0	0.6
La ₂ O ₃	22.2	22.2	22.3	33.9	33.9	33.9	28.1	6.4
Ce ₂ O ₃	28.1	18.7	23.4	54.9	47.9	50.1	37.2	15.6
Pr ₂ O ₃	5.8	4.7	3.5	7.0	5.8	5.8	5.4	1.2
Nd ₂ O ₃	21.0	15.1	17.5	24.4	25.6	26.7	21.7	4.7
Sm ₂ O ₃	3.5	2.3	2.3	5.8	6.9	4.6	4.2	1.9

Table 4.2c Whole rock analyses of (Zone C) (corundum-plagioclase-biotite-bearing gneiss)				Table 4.2d Whole rock analyses of Zone A (phlogopite-spinel-sapphirine-bearing gneiss)							
Sample No.	RU 9806 CL	RU 9806 CM	RU 9806 CN	Average	1s	Sample No.	RU 9806 SL	RU 9806 SM	RU 9806 SN	Average	1s
SiO ₂ %	24.41	24.05	24.39	24.28	0.162	SiO ₂ %	16.87	16.86	17.18	16.969	0.147
Al ₂ O ₃ %	56.92	57.44	56.94	57.10	0.241	Al ₂ O ₃ %	52.15	51.62	52.35	52.042	0.309
Fe ₂ O ₃ %	0.57	0.53	0.50	0.54	0.029	Fe ₂ O ₃ %	1.02	1.10	1.08	1.066	0.030
MnO %	0.01	0.01	0.01	0.01	0.000	MnO %	0.02	0.02	0.02	0.020	0.000
MgO %	4.47	4.44	4.26	4.39	0.093	MgO %	21.11	21.47	20.20	20.927	0.534
CaO %	5.21	5.19	5.37	5.26	0.081	CaO %	1.33	1.29	1.56	1.391	0.119
Na ₂ O %	0.64	0.63	0.68	0.65	0.023	Na ₂ O %	0.39	0.32	0.33	0.349	0.031
K ₂ O %	2.70	2.64	2.58	2.64	0.052	K ₂ O %	3.24	3.28	3.18	3.234	0.044
TiO ₂ %	0.39	0.38	0.37	0.38	0.009	TiO ₂ %	0.35	0.35	0.36	0.355	0.005
P ₂ O ₅ %	0.03	0.04	0.03	0.03	0.005	P ₂ O ₅ %	0.33	0.33	0.30	0.322	0.014
LOI %	4.25	4.25	4.47	4.32	0.104	LOI %	2.81	2.97	3.07	2.949	0.104
Total	99.60	99.60	99.59			Total	99.63	99.62	99.62		
(ppm)						(ppm)					
Se ₂ O ₃	12.3	10.8	12.3	11.8	0.7	Se ₂ O ₃	6.2	3.1	7.7	5.7	1.9
V ₂ O ₅	47.3	44.5	44.2	45.3	1.4	V ₂ O ₅	81.3	84.4	81.3	82.3	1.5
Cr ₂ O ₃	22.0	13.3	20.5	18.6	3.8	Cr ₂ O ₃	13.2	11.8	13.2	12.7	0.7
CoO	316.7	236.1	359.3	304.0	51.1	CoO	90.7	124.2	111.2	108.7	13.8
NiO	5.1	3.9	6.4	5.1	1.0	NiO	8.9	7.7	7.7	8.1	0.6
CuO	7.5	6.3	8.8	7.5	1.0	CuO	7.5	7.6	10.1	8.4	1.2
ZnO	28.8	35.2	32.4	32.1	2.6	ZnO	949.1	998.7	908.3	952.0	37.0
Ga ₂ O ₃	40.2	41.4	42.1	41.2	0.8	Ga ₂ O ₃	101.5	105.7	99.5	102.2	2.6
Rb ₂ O	180.1	177.6	172.0	176.6	3.4	Rb ₂ O	251.6	256.5	250.6	252.9	2.6
SrO	668.7	668.2	716.9	684.6	22.8	SrO	211.5	219.1	246.0	225.5	14.8
Y ₂ O ₃	34.0	41.6	36.9	37.5	3.1	Y ₂ O ₃	37.0	38.5	38.5	38.0	0.7
ZrO ₂	177.7	203.1	204.4	195.1	12.3	ZrO ₂	267.3	252.9	255.2	258.5	6.3
Nb ₂ O ₅	32.9	33.0	34.0	33.3	0.5	Nb ₂ O ₅	31.6	30.4	32.9	31.6	1.0
BaO	1973.7	1984.9	1945.4	1968.0	16.6	BaO	1340.4	1347.6	1381.4	1356.5	17.9
U ₂ O ₅	48.6	66.6	56.3	57.2	7.4	U ₂ O ₅	64.1	63.2	62.0	63.1	0.9
Th ₂ O ₃	46.5	57.9	47.5	50.7	5.1	Th ₂ O ₃	37.7	36.7	34.4	36.2	1.4
PbO	16.2	17.4	16.2	16.6	0.6	PbO	8.7	8.7	8.7	8.7	0.0
HfO ₂	4.7	7.1	5.9	5.9	1.0	HfO ₂	8.3	8.3	9.5	8.7	0.6
Ta ₂ O ₅	8.0	6.9	10.2	8.3	1.4	Ta ₂ O ₅	5.7	6.8	6.8	6.5	0.5
La ₂ O ₃	84.8	91.1	82.3	86.1	3.7	La ₂ O ₃	54.2	49.6	54.2	52.7	2.2
Ce ₂ O ₃	122.3	131.2	125.6	126.4	3.6	Ce ₂ O ₃	88.3	89.6	91.8	89.9	1.5
Pr ₂ O ₃	15.3	17.7	14.1	15.7	1.5	Pr ₂ O ₃	12.9	13.0	10.6	12.2	1.1
Nd ₂ O ₃	46.9	51.8	46.7	48.5	2.3	Nd ₂ O ₃	35.2	35.2	35.2	35.2	0.0
Sm ₂ O ₃	11.6	7.0	11.6	10.1	2.2	Sm ₂ O ₃	7.0	4.7	4.7	5.4	1.1

Table 4.3a. complete list of all possible Isocon compatible element combinations obtained from overlapping cone method (siliceous granulite to zone D alteration) The element combination 65 has taken as best fit-i socon (Baumgartner and Jensen 1995)

	Si	Al	Ti	Fe	Mn	Mg	Ch	K	Na	P	LOI	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Ba	U	Th	Pb	Hf	Ta	La	Ce	Pr	Nd	Su				
1				X																																	X		
2																											X	X									X		
3				X	X																																X		
4												X						X					X																
5																							X					X	X								X		
6				X	X									X				X										X									X		
7												X						X					X														X		
8												X						X					X					X										X	
9												X						X					X					X											
10																							X					X											
11																							X					X											
12				X	X																		X					X							X	X			
13				X									X																							X	X		
14													X					X																	X	X			
15												X						X					X						X									X	
16												X						X					X					X										X	
17												X						X					X				X												
18																		X					X				X												
19				X	X								X	X				X					X				X	X								X	X		
20				X									X	X			X																		X	X			
21				X									X	X			X																		X	X			
22			X										X	X			X																		X	X			
23			X										X	X			X					X													X	X			
24			X										X	X			X																			X	X		
25			X					X					X	X			X								X														
26								X					X	X			X							X															
27							X						X	X			X					X							X									X	
28				X									X	X			X																			X	X		
29													X	X			X					X														X	X		
30													X	X			X					X														X	X		
31			X										X	X			X					X														X	X		
32			X					X					X	X			X							X													X	X	
33			X					X					X	X			X							X												X	X		
34			X					X					X	X			X							X												X	X		
35								X					X	X			X							X															
36						X		X					X	X			X							X														X	X
37						X		X	X				X	X			X												X								X	X	
38						X		X					X	X			X					X							X								X	X	
39			X					X					X	X	X		X				X													X				X	X
40						X		X					X	X			X							X												X	X		
41						X		X					X	X			X							X												X	X		
42						X		X					X	X			X							X												X	X		
43						X		X					X	X			X							X													X	X	
44						X		X	X				X	X			X					X							X									X	X
45						X	X	X					X	X			X						X						X									X	X
46						X	X	X	X				X	X			X							X				X		X							X	X	
47						X	X	X	X				X	X			X							X				X		X							X	X	
48						X	X	X	X		X		X	X			X							X				X		X							X	X	
49						X	X	X	X				X	X			X							X	X			X		X							X	X	
50						X	X	X	X				X	X			X							X	X			X		X							X	X	
51						X	X	X	X				X	X			X							X	X			X		X							X	X	
52						X	X	X	X				X	X			X							X	X			X		X							X	X	
53						X	X	X	X				X	X			X							X	X			X		X							X	X	
54						X	X	X	X				X	X			X							X	X			X		X							X	X	
55	X					X	X	X	X				X	X			X							X	X			X		X							X	X	
56	X					X	X	X	X				X	X			X							X	X			X		X							X	X	
57						X	X	X	X				X	X			X							X	X			X		X							X	X	
58						X	X	X	X				X	X			X							X	X			X		X							X	X	
59						X	X	X	X				X	X			X							X	X			X		X							X	X	
60			X			X	X	X	X				X	X			X							X	X			X		X							X	X	
61			X			X	X	X	X				X	X			X							X	X			X		X							X	X	
62	X					X	X	X	X				X	X			X							X	X			X		X							X	X	
63	X					X	X	X	X				X	X			X							X	X			X		X							X	X	
64						X	X	X	X				X	X			X							X	X			X		X							X	X	
65	X					X	X	X	X				X	X			X							X	X			X		X							X	X	

Table 4.4 Gibbs free energies and log K values of mineral and aqueous species calculated for the ion exchange reaction; $\text{KFe}_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2 + 2\text{HCl} = \text{KFe}_3[\text{AlSi}_3\text{O}_{10}](\text{Cl})_2 + 2\text{H}_2\text{O}$

Mineral/Aqueous Species	ΔG (850°C/9kbar) (Jmol^{-1})	Reference
Cl- annite [$\text{KFe}_3(\text{AlSi}_3\text{O}_{10})\text{Cl}_2$]	-5093652.10	Zhu and Sverjensky (1991, 1992)
Annite [$\text{KFe}_3(\text{AlSi}_3\text{O}_{10})\text{OH}_2$]	-5301270.00	Zhu and Sverjensky (1991, 1992)
$\text{HCl}_{(\text{aq})}$.186614.13	Sverjensky et al. (1991)
H_2O	-319351.89	Berman (1988)
$\Delta G^{\text{reaction}}$	-57857.62	
Log K	2.6906	

Table 4.5 Average values of $\log(X_{\text{Cl}}/X_{\text{OH}})$ and X_{Mg} in biotites and the calculated activity of HCl of the respective aqueous fluids

Rock type	$\log(X_{\text{Cl}}/X_{\text{OH}})$	X_{Mg}	$\log a_{\text{HCl}}$
ultramafic rocks	-1.720 ± 0.062	0.991 ± 0.001	-3.50
ultramafic rocks neighbour to physical contact)	-1.650 ± 0.032	0.991 ± 0.001	-3.51
siliceous granulites	-1.551 ± 0.043	0.634 ± 0.009	-3.56

FIGURE CAPTIONS

Fig. 4.1 Simplified Geological map of Sri Lanka (after Cooray 1994; Kröner et al. 1991) and location map of the area. Ultramafic-siliceous granulitic rock units are exposed at the ‘*Garandu Kandura*’ at Rupaha.

Fig. 4.2 Cross section showing the lithological bands along the lines A-B-C in Fig. 4.1. Note the repetition of the ultramafic-siliceous granulite contact, which consist zoning in many places.

Fig. 4.3 (a) Schematic diagram showing the complete sequence of reaction bands formed between the siliceous granulites and the ultramafic rocks. This section is based on the samples RU 9805 and RU 9806. Zone A- phlogopite-spinel-sapphirine gneiss; Zone B- corundum-sapphirine-spinel gneiss; Zone C- corundum-biotite-plagioclase gneiss (30% Crn); Zone D- corundum-biotite-plagioclase gneiss (5% Crn); See text for further details; (b) a hand specimen showing the reaction zones (9805-9806).

Fig. 4.4. Photomicrographs show the mineral assemblages of complete profile 9805-9806: (a). forsterite-diopside-enstatite in ultramafic rock, (b). forsterite-spinel at the contact of ultramafic rock and the reaction zones. Note the formation of phlogopite from spinel and forsterite, (c). phlogopite-spinel-sapphirine gneiss in zone A, (d). corundum-sapphirine-spinel gneiss in zone B, (e). corundum biotite plagioclase gneiss (zone C), (f) sillimanite, biotite, quartz and plagioclase in sillimanite-biotite gneiss.

Fig. 4.5 Chemical potential (μ_{MgO})-temperature diagram for the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ at 9kbar and $X_{\text{CO}_2} = 0$, computed with the thermodynamic data of Holland and Powell (1998). The light shaded area is the stability limit of sapphirine. The dark shaded area demonstrates the increase of the spinel-sapphirine-corundum stability field toward the lower temperatures at 725°C, for a X_{CO_2} of 0.5.

Fig 4.6 Quantitative chemical potential diagram of μ_{SiO_2} Vs μ_{MgO} for the system SiO_2 - MgO - Al_2O_3 at 850°C and 9kbar and $X_{\text{CO}_2}=0$. Phase field boundaries were constructed by balancing the mineral reactions with Al_2O_3 using thermodynamic data of Holland and Powell (1998). The dark line represents the shift of chemical potential from siliceous granulites to ultramafic rock through the reaction zones as inferred by co-existing minerals. Along this path, an increase in μ_{MgO} involves the reduction of μ_{SiO_2} towards the ultramafic zone.

Fig 4.7 Double-logarithmic ‘isocn diagrams’ showing Major, minor and LREE element transfer during the alteration of siliceous granulite to: (a). corundum biotite gneiss (zone D), (b). corundum-biotite-plagioclase gneiss (zone C), (c). phlogopite-spinel-sapphirine gneiss (zone A). Elements bolded are considered as immobile components, which are aligned on the isocn line. See text for details on isocn method.

Fig. 4.8 Histograms summarise the: (a). Major (b) minor element enrichment and depletion during the alteration to reaction bands with respect to siliceous granulites.

Fig. 4.9 Cation distribution of biotite from siliceous granulites to ultramafic rocks through reaction zones: (a). distribution of Si, (b). distribution of Al, (c). distribution of X_{Mg} [$\text{Mg}/(\text{Fe}+\text{Mg})$], (d). distribution of Fe and Mg, (e). distribution of Ti, (f). distribution of Cl and F. All cations per formula unit in biotite were calculated on the basis of 22 oxygens. Average values and standard deviation of 1σ for each analytical point were also calculated.

Fig. 4.10 The chemical data for biotites from the siliceous granulites, reaction zones and ultramafic rocks at Rupaha. The lines are calculations of the gradient for 850°C . The biotites from zone D are partly equilibrated from the siliceous granulites while some biotite analyses from zone A are equivalent with ultramafic rocks.

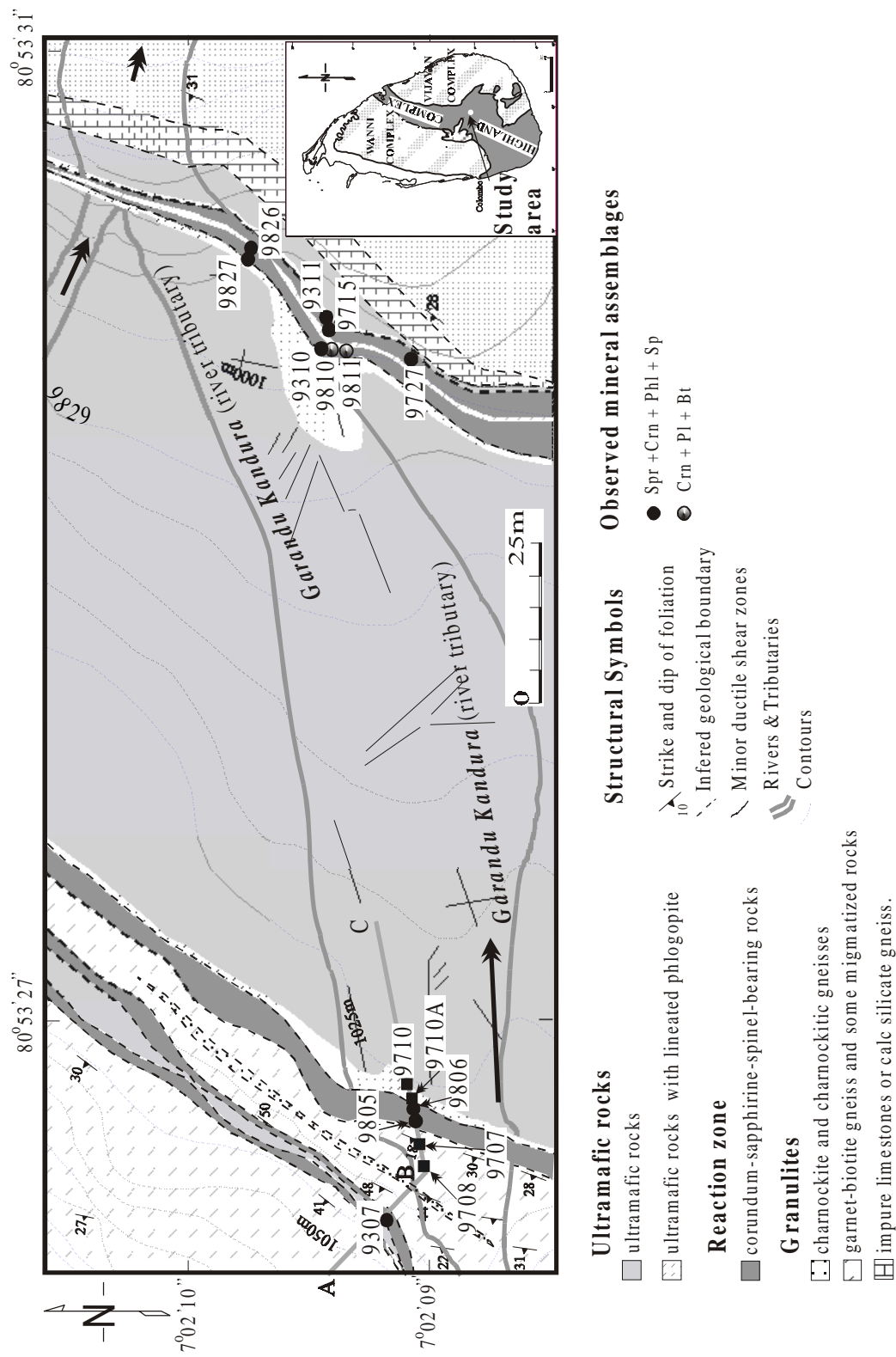


Fig. 4.1

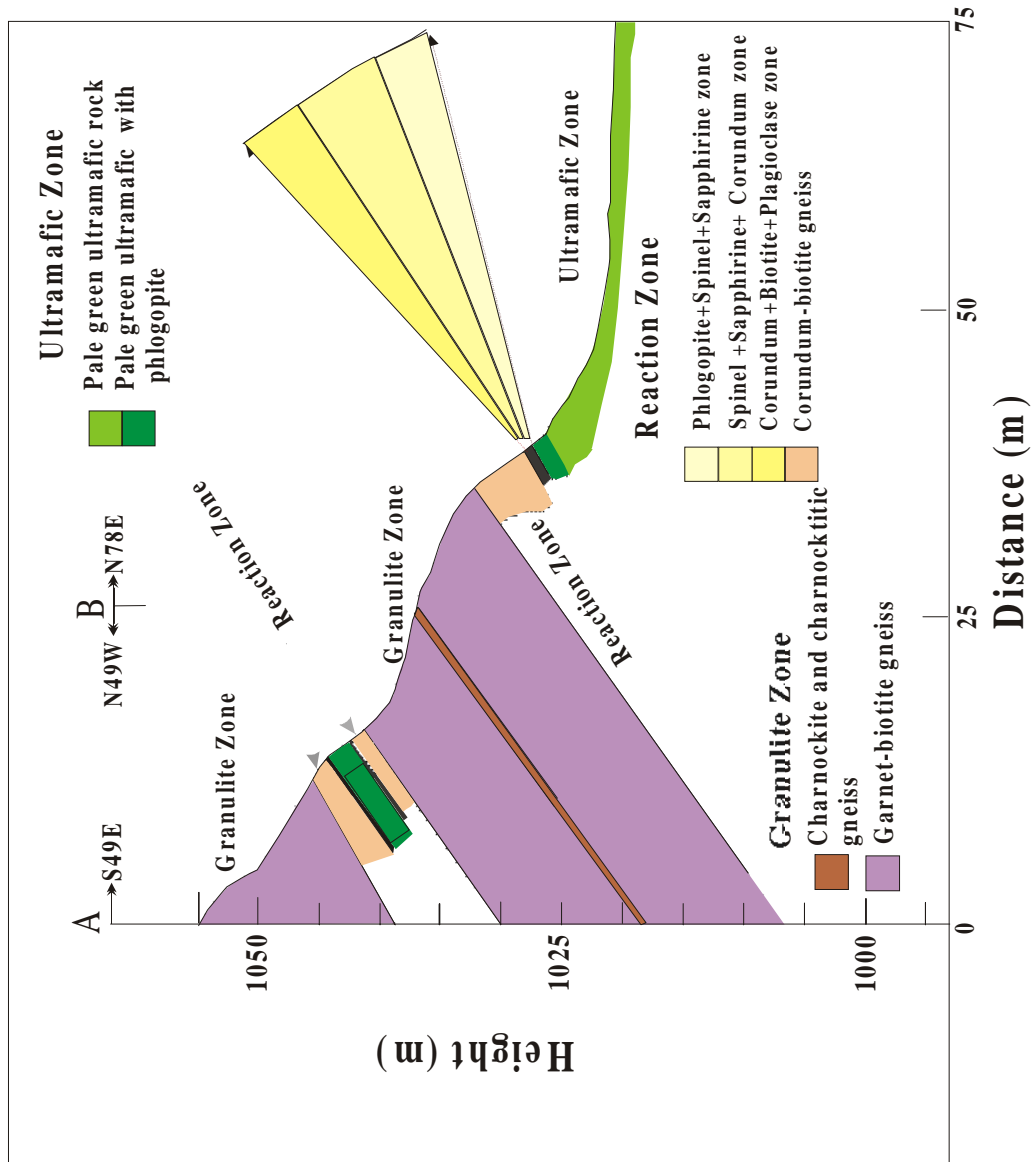


Fig. 4.2

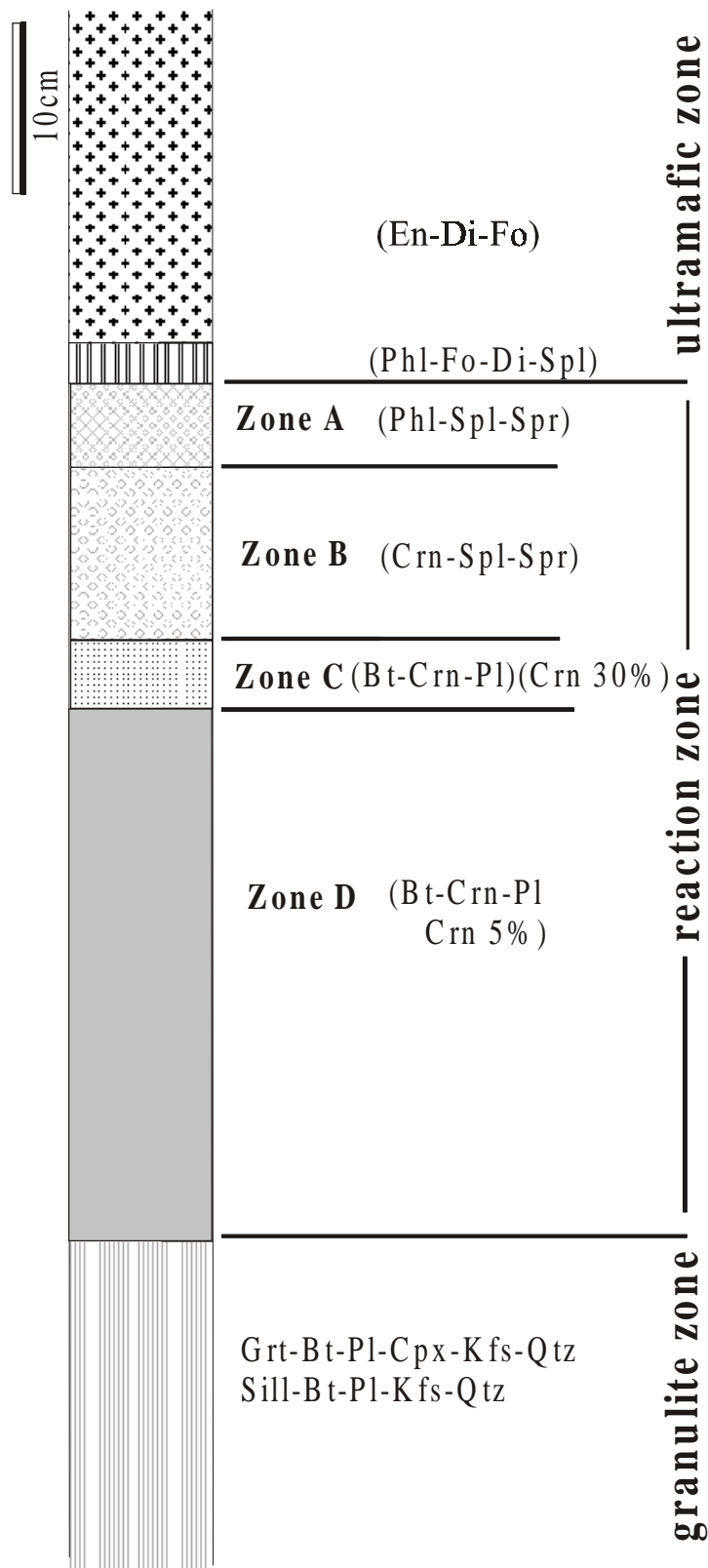


Fig. 4.3a

Fig.4.3(b)

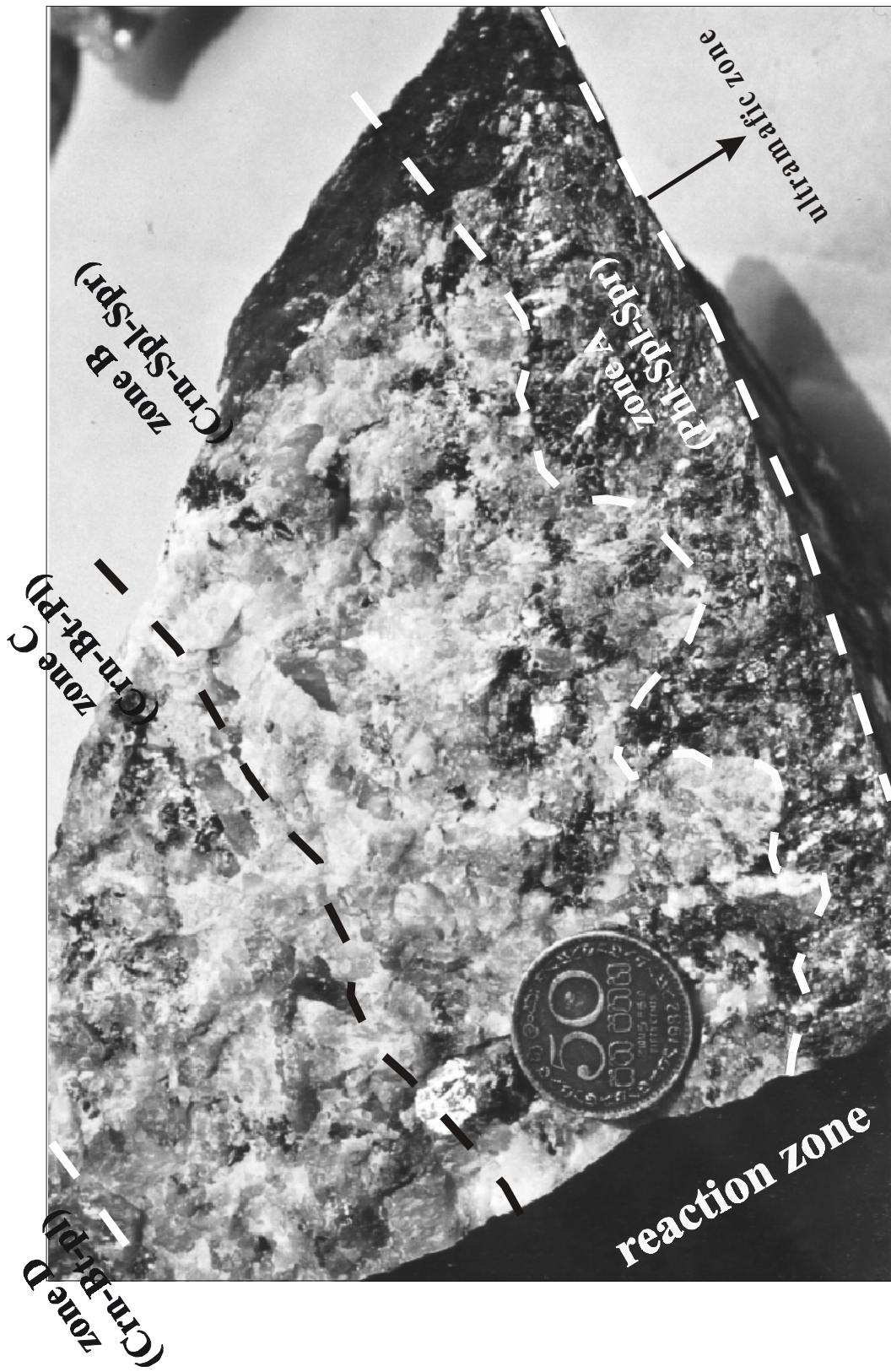


Fig. 4.3b

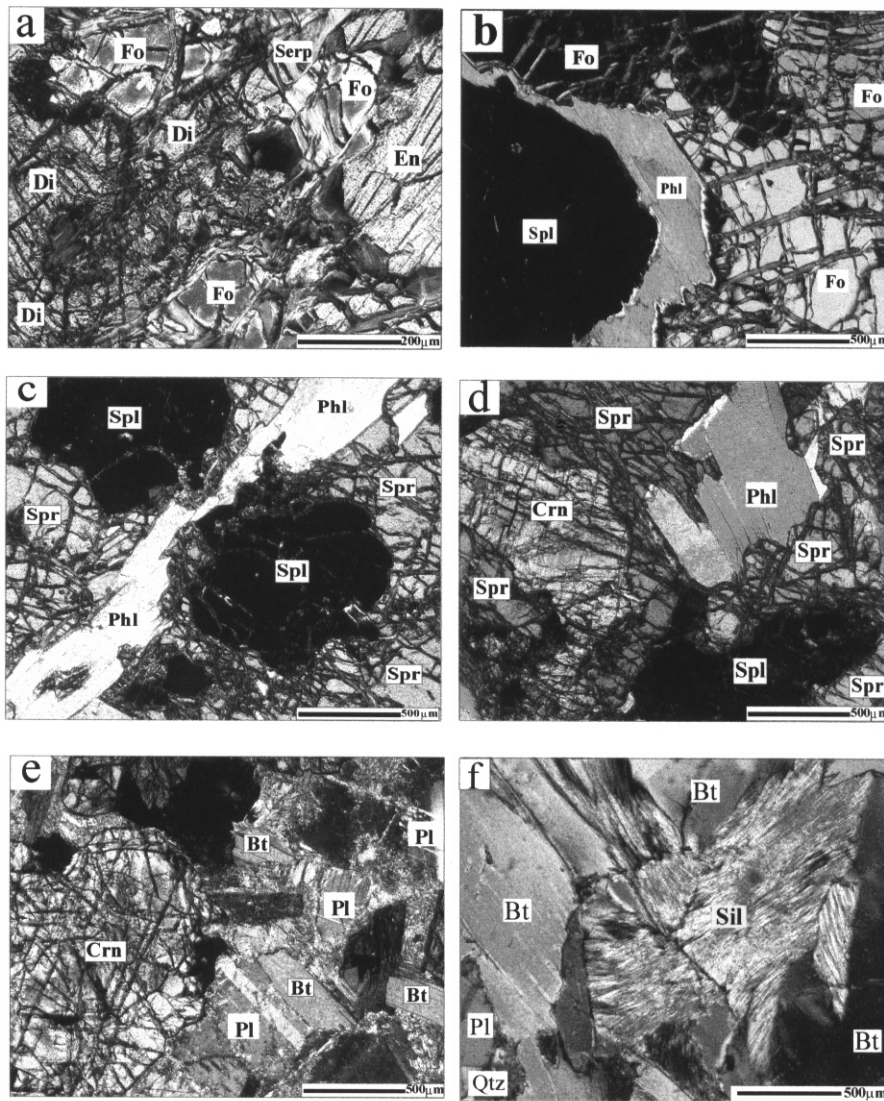


Fig. 4.4

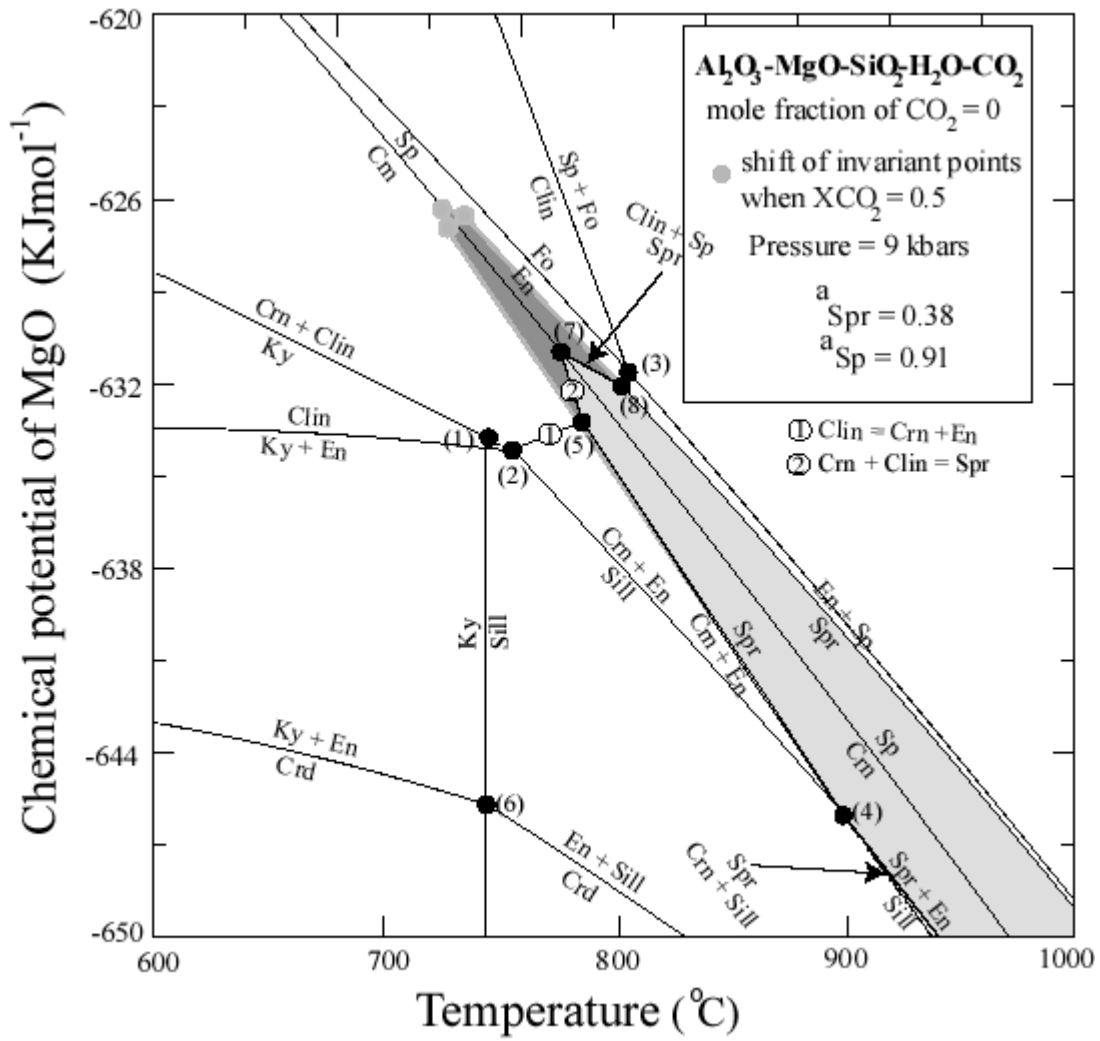


Fig.4.5

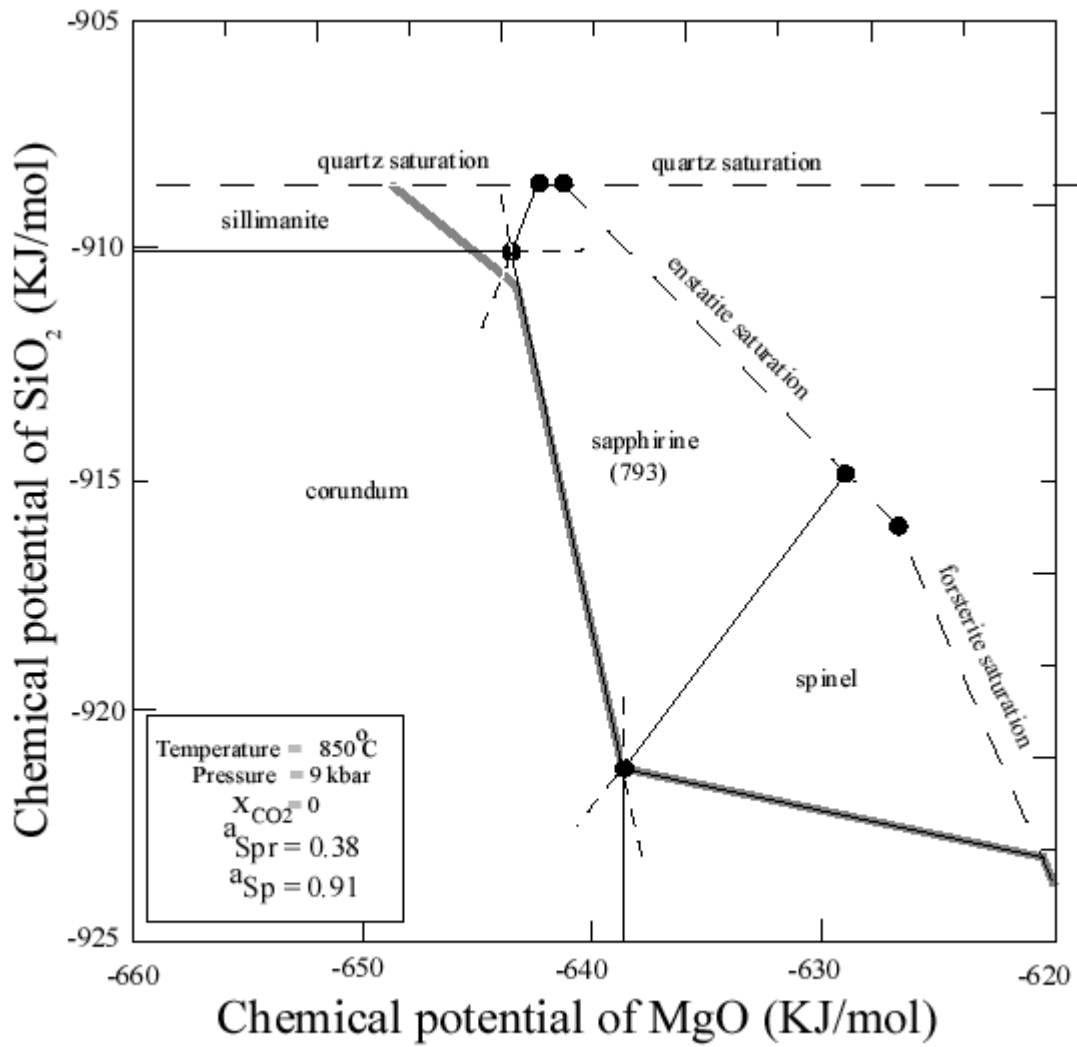


Fig. 4.6

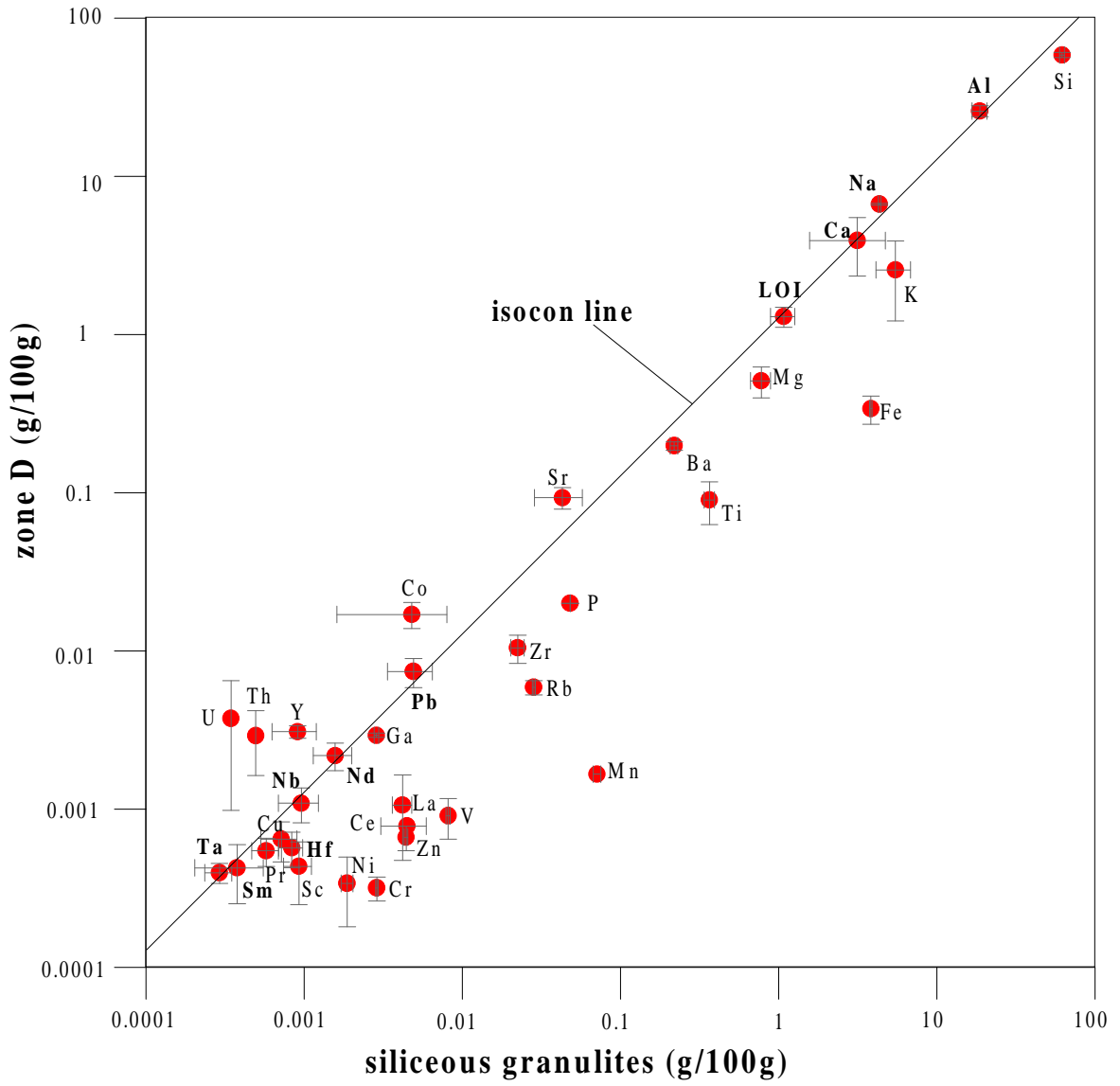


Fig. 4.7(a)

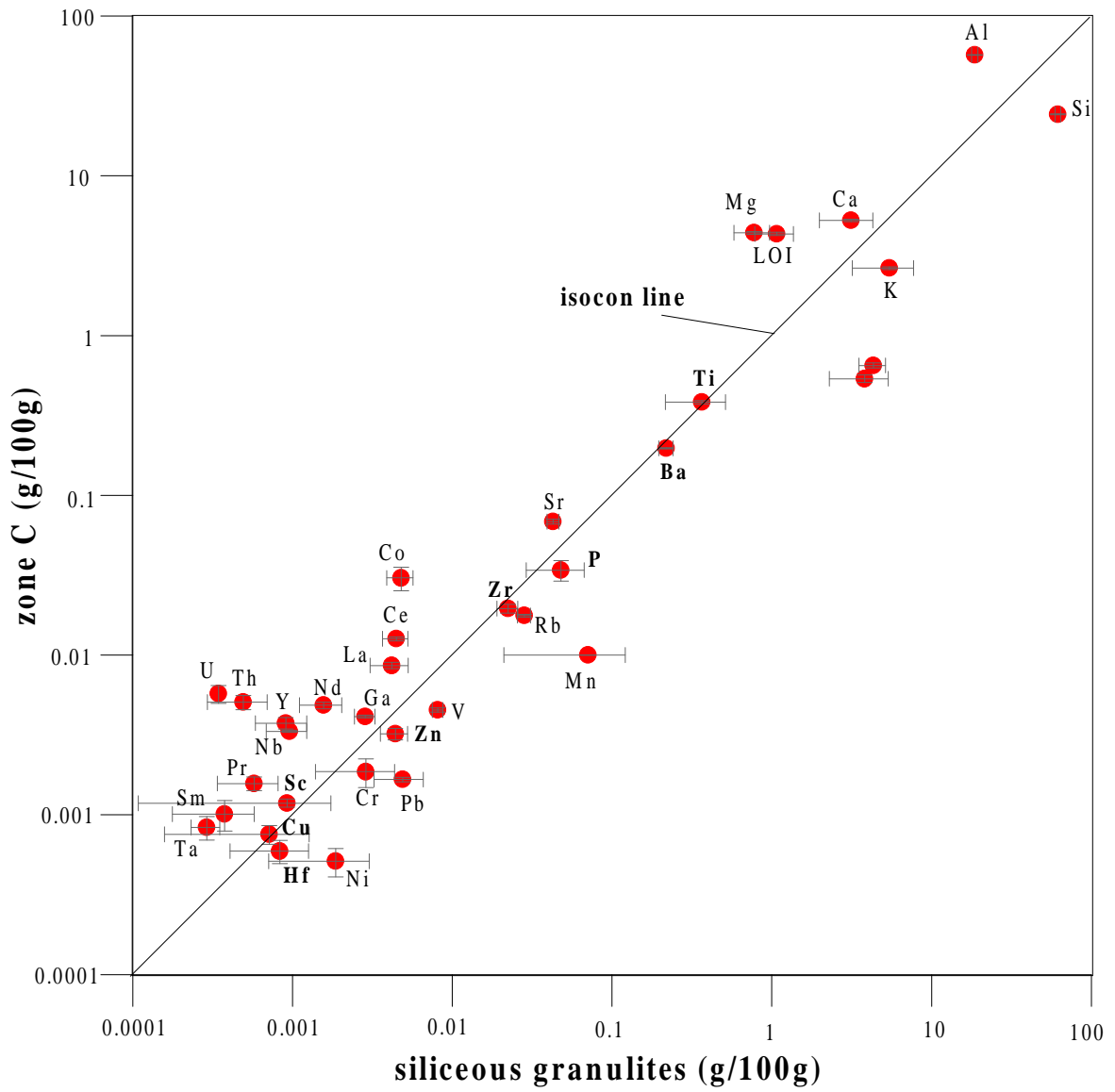


Fig. 4.7(b)

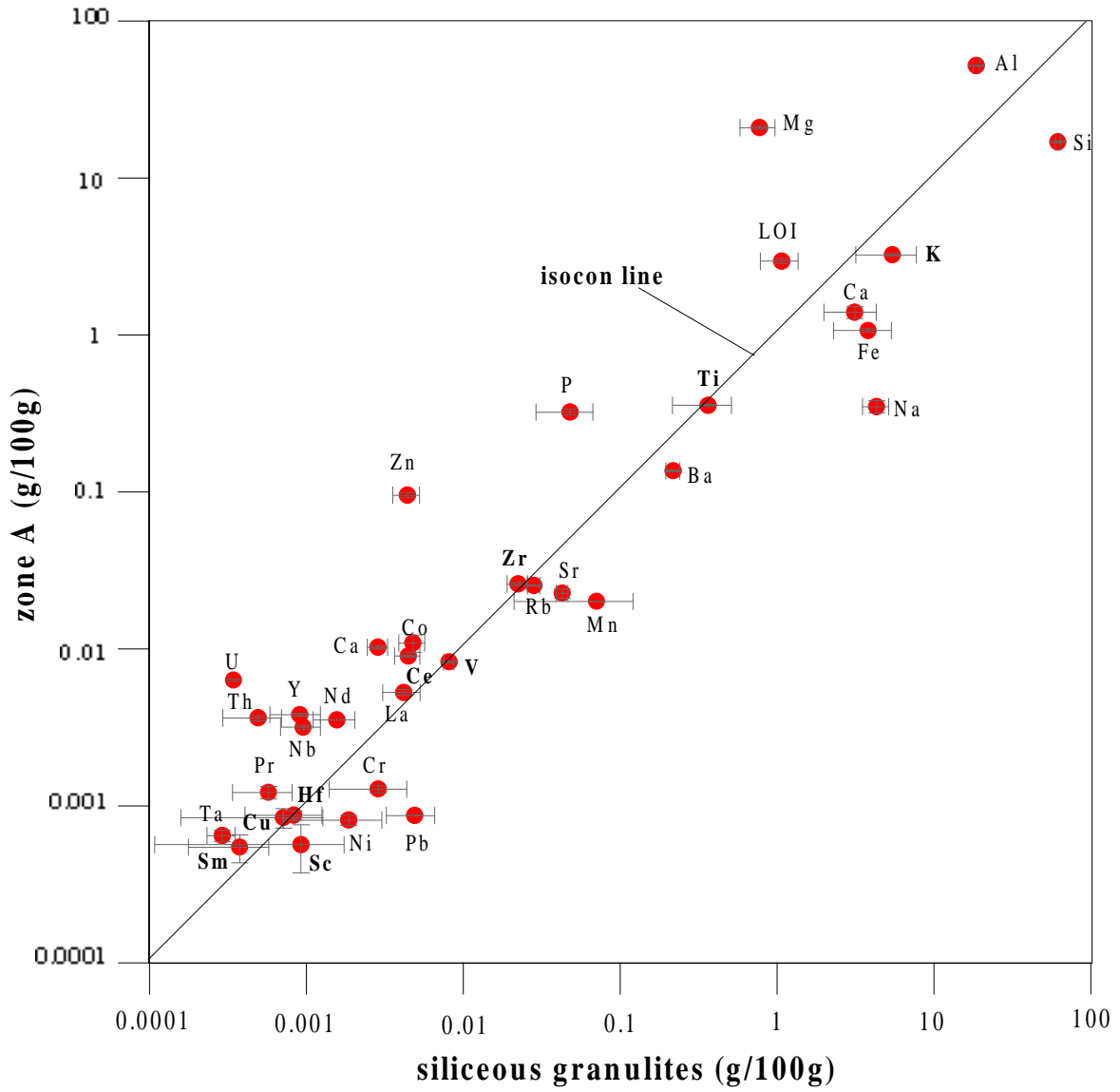


Fig. 4.7(c)

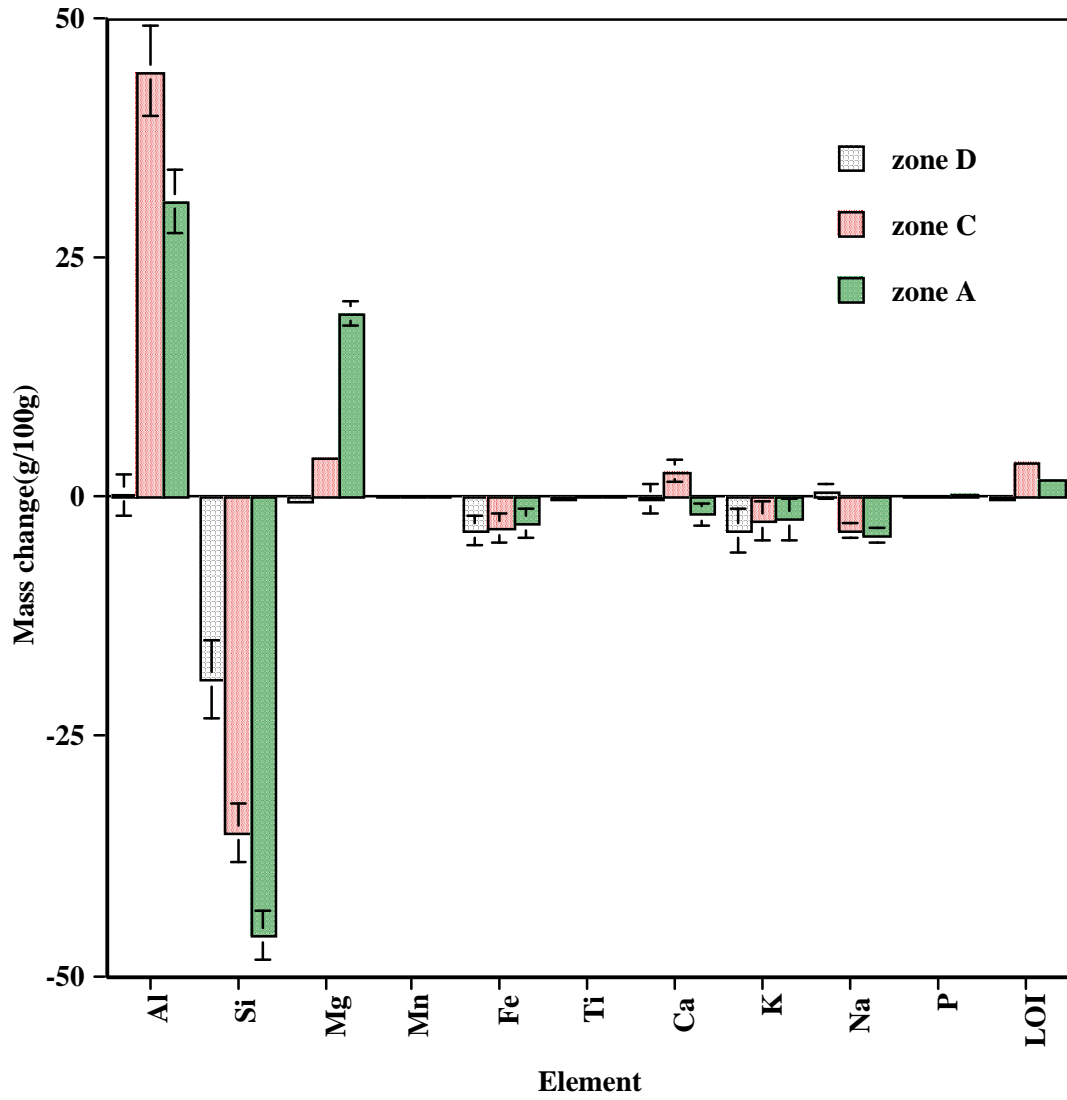


Fig. 4.8a

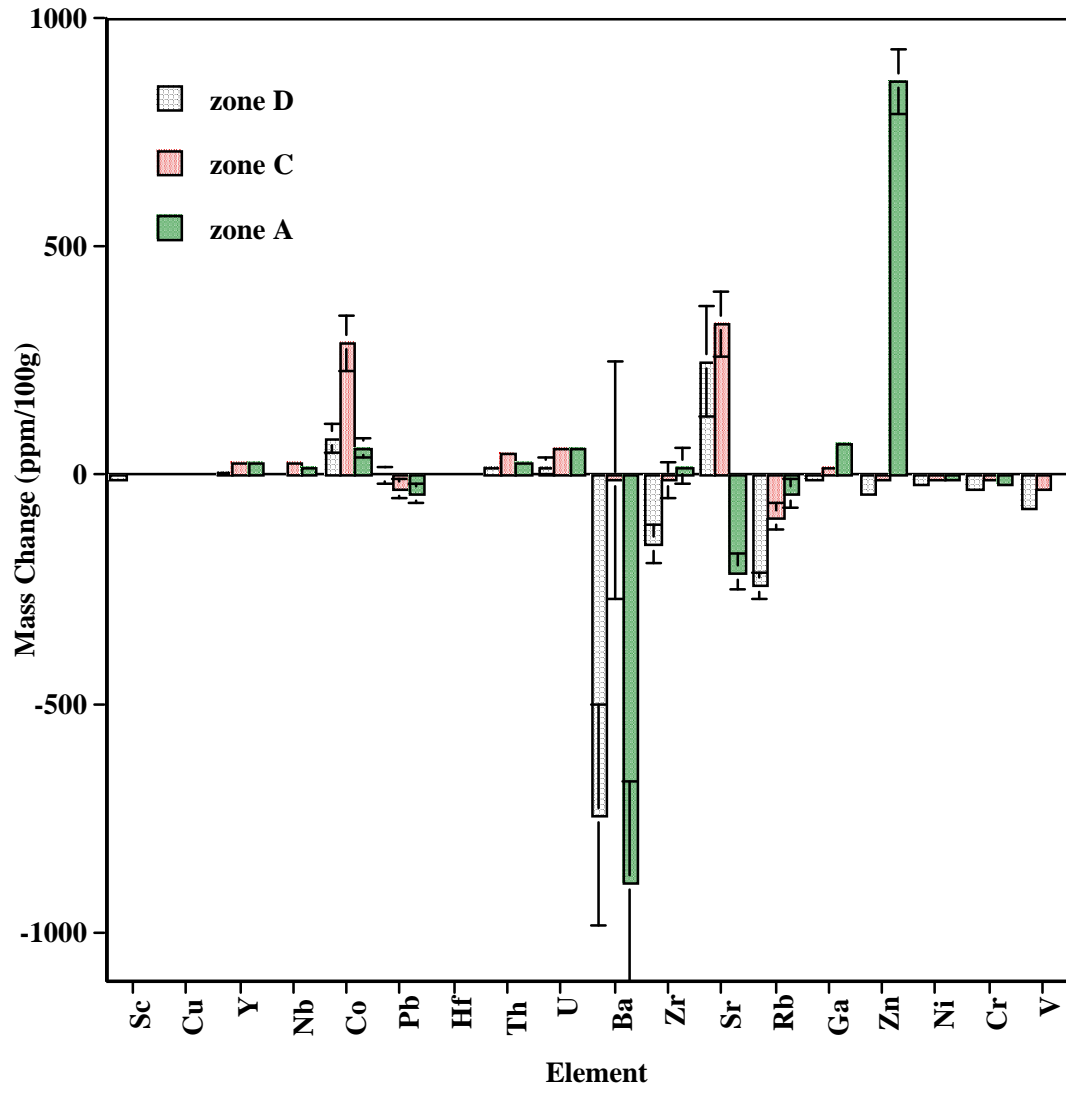


Fig. 4.8b

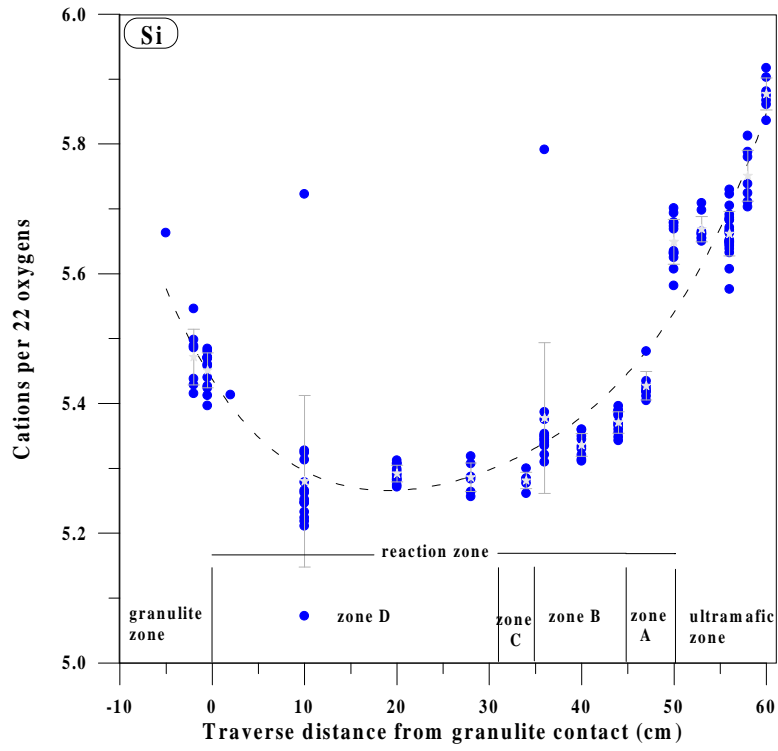


Fig. 4.9a

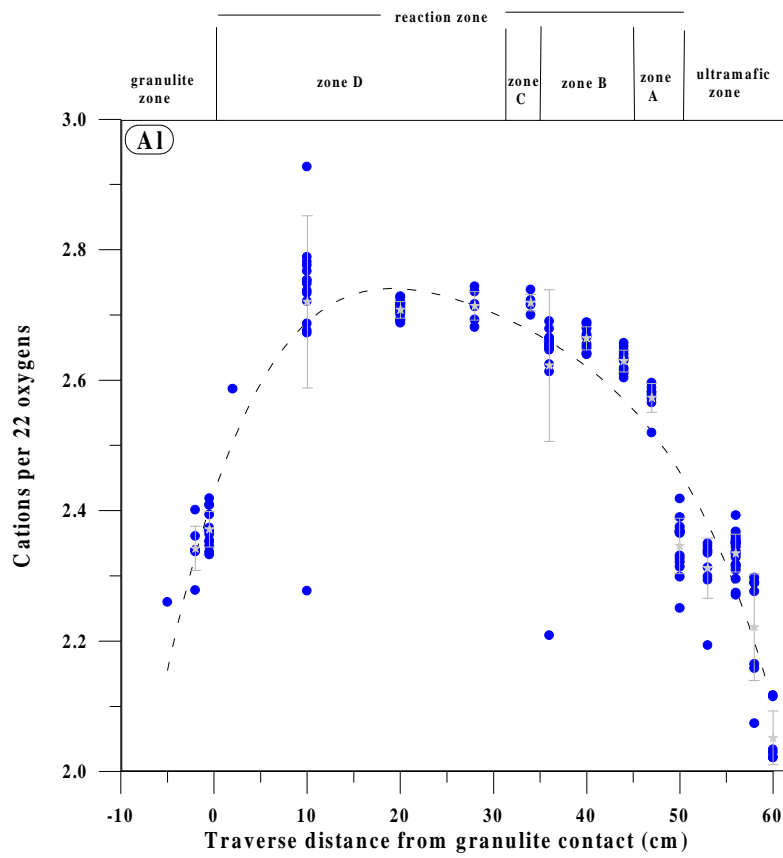


Fig. 4.9b

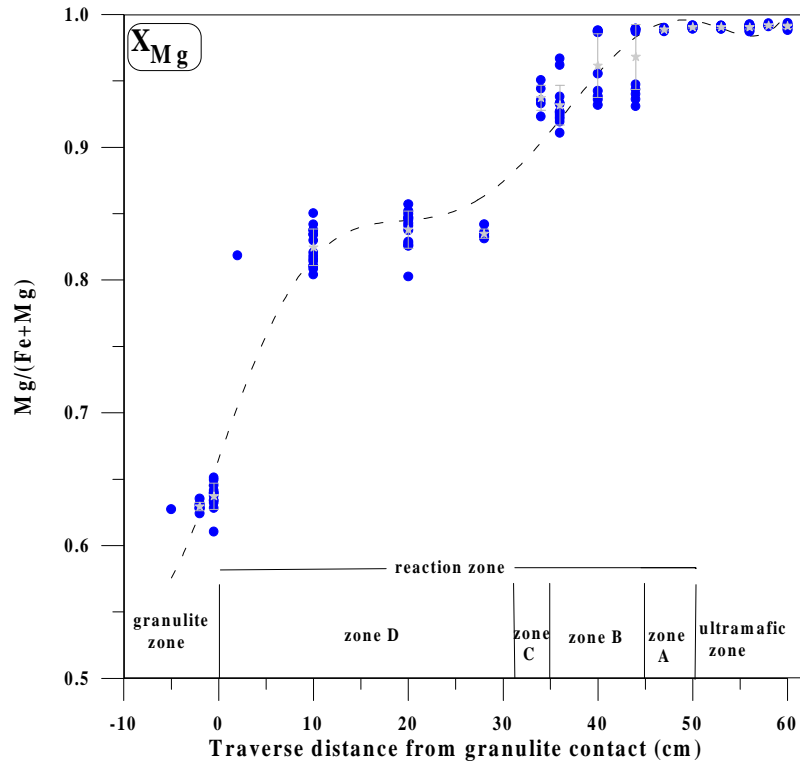


Fig. 4.9c

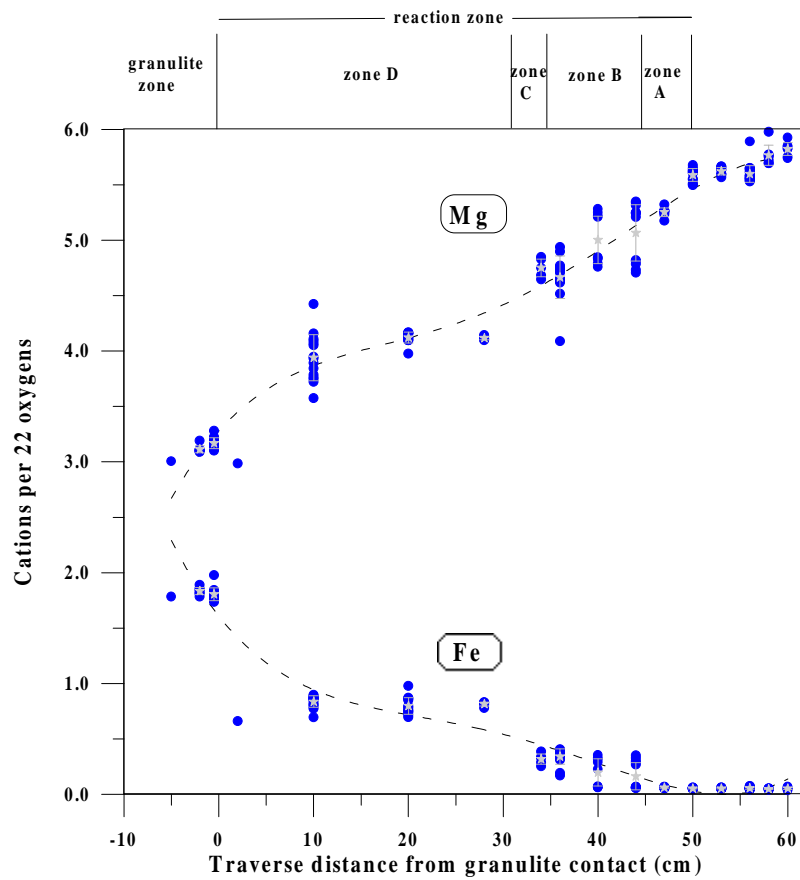


Fig. 4.9d

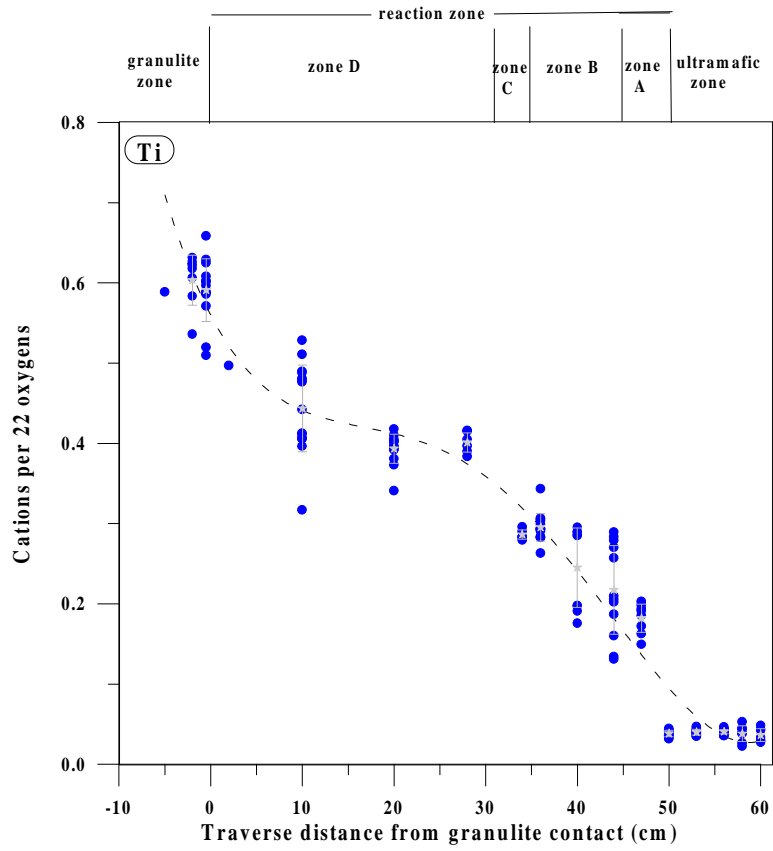


Fig. 4.9e

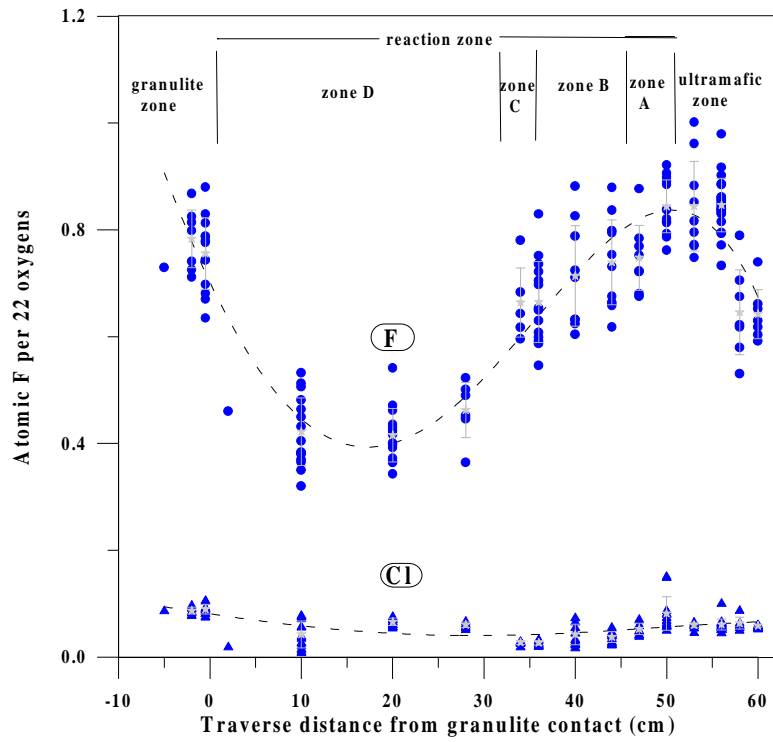


Fig. 4.9f

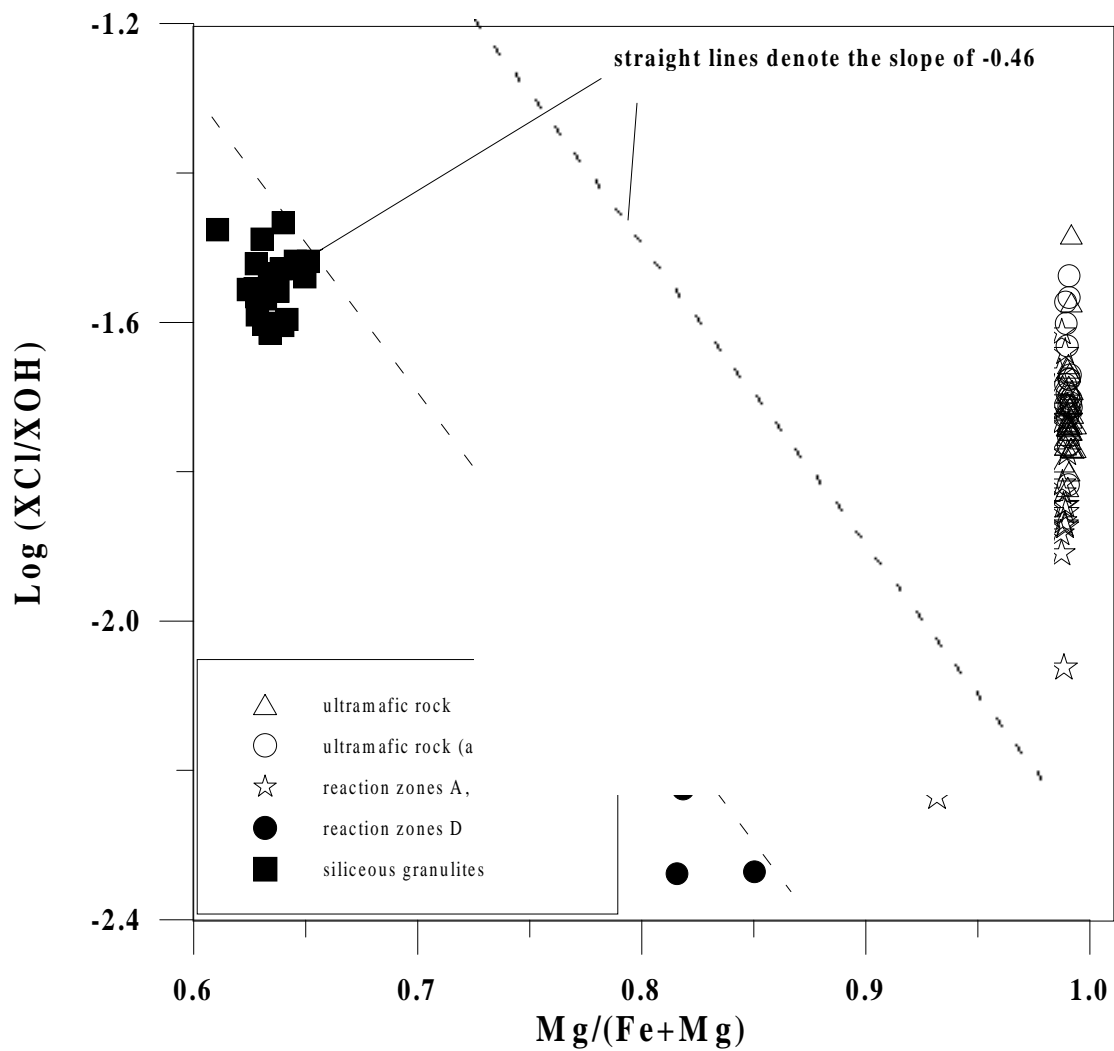


Fig. 4.10

Appendix

Appendix A - List of abbreviations

A.1 Minerals and phases after Kretz (1983)

Ab	albite	En	enstatite	Pl	plagioclase
Alm	almandine	Fo	forsterite	Prp	pyrope
Ann	annite	Fs	ferrosilite	Qtz	quartz
An	anorthite	Grt	garnet	San	sanidine
Atg	antigorite	Grs	grossular	Sil	sillimanite
Ap	apatite	Hed	hedenbergite	Spr	sapphirine
Bt	biotite	Ilm	ilmenite	Spl	spinel
Cal	calcite	Kfs	K-feldspar	Srp	serpentine
Chl	chlorite	Ol	olivine	Tlc	talc
Crn	corundum	Opx	orthopyroxene	Tr	tremolite
Di	diopside	Per	periclase		
Dol	dolomite	Phl	phlogopite		

A.2 Thermodynamic and mathematical symbols

For chemical elements and compounds, the standard symbols are used (H₂O, CO₂ etc.)

R	universal gas constant (1.987 cal K ⁻¹ mol ⁻¹)
P	pressure
T	temperature
t	time
a	activity
ΔG	Gibbs free energy
ln	natural logarithm (base e)
log	logarithm to the base 10
σ	standard deviation
exp	exponent

Appendix B – Analytical procedures

(1) X-Ray Fluorescence Spectroscopy

Overview

In X-Ray fluorescence (XRF) spectroscopy a continuous spectrum of X-Rays is used to cause emission of characteristic X-Rays (secondary fluorescence) in a sample by excitation of inner shell electrons. Intensity and wavelength of the emitted X-Rays are characteristic for the elements and their concentration present in the sample. The spectrum is then diffracted by suitable monochromator crystals, and characteristic element peaks are measured at source-sample-detector angles given for a specific wavelength by Bragg equation $n\lambda = 2d \sin\theta$. The X-Ray source is an evacuated tube where electrons, emitted from a heated W cathode are accelerated towards a metal anode by as much as 100kV, producing a continuous spectrum of X-Rays by collision with the metal. The characteristic X-Rays of the metal anode are superimposed on the continuous spectrum. Analytical work is performed in the Institute of Geosciences at the University of Mainz using fully automated Philips PW-1404 wavelength dispersive X-Ray fluorescence spectrometer operating with Rh-tube (see table B1 for standard operating conditions) with automated sample changer (72 positions). All major and trace element concentrations are determined by comparing the fluorescence intensities of the sample with calibration curve obtained from international standards, which closely match the sample matrix in overall composition. Remote control and data processing, including matrix correction procedures, was done with Philips software running on 486 PC.

Preparation methods

Major and trace element analysis performed in XRF spectrometer require different techniques of rock powder preparation.

- (a) Major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, Cr, Ni) are diluted with an excess of a substance that absorbs X-Rays only weakly (i.e. has a low atomic number) and are fused to a glass tablet. This reduces matrix effects and makes them essentially constant in both, the unknown sample and the reference standards (Skoog and Leary 1992). Additionally, better homogeneity of the sample improves the quality in analysing the light elements (Na, Mg), which can significantly suffer from surface effects.

- (b) Trace elements (Sc, Y, Rb, Sr, Ba, Zn, Cu, Ni, Co, Cr, V, Ga, Nb, Zr, Pb, Th, U, Hf, Ta) and light rare earth elements (La, Ce, Pr, Nd, Sm) are analysed on pressed powder pellets.

Glass tablet preparation

Rock powder ($< 63\mu\text{m}$) was dried for 24h at 105°C to adhesive water. The glass tablet was produced by thoroughly mixing of 0.8g of the sample with a 4.80g charge of lithium tetraborate (Merck Spectromelt A10) in a platinum crucible and subsequent melting at 1100°C using a semi-automated melting apparatus. The molten mixture was shaken carefully for 10 minutes and then automatically poured into platinum mold.

Powder Pellet Preparation

Pressed powder pellets were produced by homogenizing of 6g of sample powder and two-component SCANDIPLEX epoxy resin and hardener (ratio 3:2) in a agate mortar and subsequent compression of the mixture at pressures of $7.0\text{ metric ton/cm}^2$ for 40 seconds. The pellets were then dried at 60°C for 4-5 hours.

Determination of Loss of Ignition (LOI)

The amount of volatile elements in the samples (H_2O , CO_2 , S, F, Cl etc.) was determined by heating if 1g rock powder, dried at 105°C , in a muffle furnace to more than 1000°C for about 4 hours. The weight loss reported in percent (of the original weight) as loss of ignition (LOI). The LOI is an essential term for the correction of the major element analysis because it considers the loss of volatiles during glass tablet preparation. However, errors can be introduced if ferrous ion is oxidized to a different extent in the furnace compared to fusion of the glass tablet, which takes significantly less time.

Analyses of ferrous/ ferric ion contents

The amount of ferrous and ferric ion present in a sample cannot be distinguished by XRF analyses. Thus, the iron content is reported as total ferric ion (Fe_2O_3).

International Standards

The following international standards were used for analysing of major, minor and LREE elements. The different standards were used for different rock types.

Standards for basaltic and ultramafic rocks:

AN-G, BCR-1, BE-N, BHVO-1, BIR-1, BM, BR, DNC-1, DR-N, DZE-2, GSS-4, GSS-5, GSS-6, JA-2, JB-1, JB-3, JGB-1, JP-1, MRG-1, NBS688, NIM-D, NIM-N, NIM-P, PACS-1, S-18, SDU-1, W-1, W-2

Standards for granitic rocks:

G-2, GA, GH, GM, GSD-02, GSD-08, GSD-09, GSD-12, GSP-1, GSR-1, GSR-4, GSS-3, JA-1, JF-1, JF-2, JG-1, JG-1a, JR-2, MA-N, NBS278, NBS2704, NIM-G, RGM-1, SDC-1, STM-1, SY-2, T-1, TB, TS,

Standards for carbonate rocks:

BCS368, BCS393, GSR-6, KH-2, NBS88A

Standards for trace elements (Routine):

AGV-1, AN-G, BCR-1, BE-N, BHVO-1, BIR-1, BR, DNC-1, DR-N, DZE-2, G-2, GSD-02, GSD-06, GSD-08, GSD-09, GSD-12, GSN, GSP-1, GSR-1, GSR-6, GSS-2, GSS-3, GSS-4, GSS-5, JB-2, JG-2, MAG-1, MY-4, NIM-G, NIM-S, QLO-1, RGM-1, SCO-1, SDC-1, SDU-1, SGR-1, SO-4, STM-1, SY-2, W-1, W-2 ,

Discussion of analytical quality

The major element analyses sum up to 99 and 100.2 wt% with all Fe calculated as Fe_2O_3 . In order to determine the precision of the measurements, ten replicate analyses of the same glass and powder tablets were performed in sequence (Tables B2 and B3). The resulting standard deviations (1σ error) from the mean are less than 0.6% for the major elements except for Na, where it is > 0.6% and for Mn with 0.88%. The smaller precision of Mn is due to its low concentration.

Table B1. Operating condition for major- and trace elements analyses with a Philips PW 1404 XRF spectrometer using Rh-anode at Institute of Geosciences, University of Mainz

Element Line	Accl. kV	Current mA	Collimator	Crystal	Detector
TRACE ELEMENTS					
Sc	K α	40	60 Fine	LIF200	FL
V	K α	40	60 Fine	LIF220	FL
Cr	K α	40	60 Fine	LIF220	FL
Co	K α	60	40 Fine	LIF220	FS
Ni	K α	60	40 Fine	LIF220	FS
Cu	K α	60	40 Fine	LIF220	FS
Zn	K α	80	30 Fine	LIF220	FS
Ga	K α	80	30 Fine	LIF200	FS
As	K α	80	35 Fine	LIF200	FS
Rb	K α	80	30 Fine	LIF220	SC
Sr	K α	80	30 Fine	LIF220	SC
Y	K α	80	30 Fine	LIF220	SC
Zr	K α	80	30 Fine	LIF220	SC
Nb	K α	80	30 Fine	LIF220	SC
Cd	K α *	80	35 Coarse	LIF200	SC
Sn	K α	80	35 Coarse	LIF200	SC
Sb	K α	80	35 Coarse	LIF200	SC
Ba	L α	40	60 Fine	LIF200	FL
La	L α	40	70 Coarse	LIF220	FL
Ce	L α	40	70 Coarse	LIF220	FL
Pr	L α	40	70 Coarse	LIF220	FL
Nd	L α	40	70 Coarse	LIF220	FL
Sm	L α	40	70 Coarse	LIF220	FL
Hf	L α	60	40 Fine	LIF200	FS
Ta	L α	60	40 Fine	LIF200	FS
Pb	L β	80	30 Fine	LIF200	SC
Th	L α	80	30 Fine	LIF200	SC
U	L α	80	30 Fine	LIF200	SC
Rh	Compton	80	30 Fine	LIF220	SC
MAJOR ELEMENTS					
Na	K α	40	60 Coarse	PX1	FL
Mg	K α	40	60 Coarse	PX1	FL
Al	K α	40	60 Coarse	PE	FL
Si	K α	40	60 Coarse	PE	FL
P	K α	40	60 Coarse	PE	FL
K	K α	40	60 Coarse	GE	FL
Ca	K α	40	60 Fine	LIF200	FL
Ti	K α	40	60 Fine	LIF200	FL
Cr	K α	40	60 Fine	LIF200	FL
Mn	K α	60	40 Fine	LIF220	FL
Fe	K α	60	40 Fine	LIF220	FS
Ni		60	40 Fine	LIF220	FS
K α		60	40 Fine	LIF200	FS
* with Messing-Filte					

LIF lithium fluoride PE pentaerythrite PX1 multilayer crystal GE germanium

Table B2. Reproducibility of major elements

Reproducibility of major elements from 10 replicate analyses of same glass tablets			
Oxide	Average (Wt%)	Standard Deviation (s)	s (% rel)
SiO ₂	44.2	0.060	0.13
TiO ₂	2.17	0.003	0.16
Al ₂ O ₃	12.33	0.031	0.25
Fe ₂ O ₃	12.27	0.014	0.11
MnO	0.19	0.002	0.88
MgO	12.23	0.029	0.23
CaO	10.06	0.016	0.16
Na ₂ O	2.70	0.016	0.61
K ₂ O	1.08	0.005	0.45
P ₂ O ₅	0.62	0.003	0.48
Cr ₂ O ₃	0.063	0.000	0.54
NiO	0.043	0.000	0.56

For the trace elements, precision is better than 3%, except for Co (3.9%), Cu (3.7%), Ga (3.9%), Pr (4.9%), Nd (5.1%), Sm (6.9%), Hf (5.0%), Ta (4.3%), Th (3.1%), U (6.0%). The large standard deviation (1σ error) of these elements is caused by their low concentration, which is close to the detection limit.

Accuracy of all major elements, determined from relative deviations to USGS standards, measured together with samples, is less than 1% (Table B2). Trace element analyses generally have accuracy within 6% (Table B3) of the working value of the measured standard (Govindaraju 1989).

Table B3. Reproducibility and detection limits of minor elements

Reproducibility of major elements from 10 replicate analyses of same glass tablets				
Element	average (ppm)	Standard deviation (s)	s (%rel)	Detection limit (ppm)
V	220	1.8	0.8	1.1
Cr	435	5.1	1.2	2.1
Co	57	2.3	3.9	1.9
Ni	345	2.9	0.8	1.1
Cu	60	2.2	3.7	0.4
Zn	105	1.5	1.3	1.8
Ga	18	0.7	3.9	1.4
Rb	44	1.0	2.4	1.3
Sr	755	2.5	0.3	1.4
Y	26	0.6	2.4	1.6
Zr	223	1.5	0.7	1.1
Nb	77	0.3	0.4	1.0
Ba	585	3.6	0.6	6.6
La	278	1.9	0.7	3.6
Ce	406	3.7	0.9	9.1
Pr	39	1.9	4.9	2.5
Nd	109	2.1	2.0	5.1
Sm	8	1.8	2.2	6.9
Hf	24	1.2	5.0	2.5
Ta	23	1.0	4.3	3.2
Pb	30	0.6	2.0	2.0
Th	13	0.4	3.1	1.0
U	5	0.3	6.0	1.6

(2) Electron Probe Microanalyser (EPMA)

Overview

The electron microprobe (EMP) is used for the quantitative chemical analysis of small areas (typically 1-10 μ m in diameter) on a polished surface (e.g. polished thin sections). The concentration of elements from Be to U can be measured in minerals and glasses at levels as low as 100ppm, and their lateral distribution can be determined by mapping. When an electron beam is focussed on a sample surface, emission of characteristic X-Rays is one of the numerous effects caused by interaction of energetic electrons (normally 10 to 30 keV) with sample material. Wavelength and intensity of the characteristic X-Rays reflect the specific elements and their concentration in the excited area. All emitted X-Rays are diffracted by suitable monochromator crystals arranged together with the detector and the sample in a setting (configuration) to satisfy the Bragg equation $n\lambda = 2d \sin\theta$.

All mineral compositions were analysed using the electron microprobe in the Institute for Geosciences, University of Mainz. The EMP in Mainz is fully automated JEOL JXA 8900 RL with five wavelength dispersive diffractometers, which is operated from a windows-based menu running on a HP-UX workstation (software from JEOL). Spectrometers with fixed monochromator crystals allow off-peak measurement of the background. Mean atomic number and background correction are then iteratively calculated in combination with ZAF X-Ray absorption correction (Amstrong 1988, 1989).

Standard operating conditions listed in Table B4 was used. The following Table B5 contain information on the spectrometer configuration and standards used for electron microprobe analyses at the University of Mainz, Germany. X-Ray intensities were automatically corrected for probe current drift, dead time, background and matrix effects by the built-in software.

Discussion of Analytical quality

Accurate determination of mineral compositions is indispensable for accurate estimates of metamorphic temperatures, pressures and some other applications as well. The quality of microprobe data was evaluated on the basis of stoichiometry of minerals. It can be generally concluded that for element oxides with concentrations greater than 5% wt the standard deviation is smaller than 2%, and that for concentrations between 5 and 0.5 wt%

it is smaller than 10%. Accuracy is better than 1% of the working value from major elements (Govindraju 1989).

Table B4. Normal operating conditions for the electron probe microanalyser in Institute for Geosciences, University of Mainz

Acceleration voltage	15 kV
Probe current	12 nA (Ba 8nA)
Probe diameter	2µm
Take off angle	40°
Absorption correction	ZAF
Background correction	Off-peak

Table B5. Spectrometer configuration and standards used for calibration in electron microprobe analyses in Institute for Geosciences, University of Mainz

Element peak intensity (cps)	X-Ray line	Spectro meter	Crystal	Standard	element concen- (wt%)	peak-counting time (s)	
Na	Kα	2	TAP	albite	11.7409	15	694.6
K	Kα	3	PET	orthoclase	14.6721	15	36.0
Fe	Kα	5	LIF	Fe₂O₃	89.9765	15	4417.6
Si	Kα	1	TAP	wollastonite	51.5118	15	6917.7
Mg	Kα	2	TAP	MgO	99.9874	15	10834.1
Ca	Kα	3	PET	wollastonite	47.7408	15	2968.2
Ti	Kα	4	PET	TiO₂	100.0001	15	5758.5
Mn	Kα	5	LIF	rhodocrosite	43.4885	15	1990.3
Al	Kα	1	TAP	Al₂O₃	99.9949	15	14128.6
Cr	Kα	4	PET	Cr₂O₃	99.9985	30	7172.6
Ba	Lα	2	LIF	BaSO₄	65.6948	15	745.1
Cl	Kα	5	PET	tugtupit	7.5800	15	564.5
F	Kα	1	TAP	F-phlogopite	9.2000	15	36.0

TAP thallium acide phtalate

LIF lithium fluoride

PET pentaerythrite

References

- Amstrong JT* (1988). Quantitative analyses of silicate and oxide minerals: comparisons of Monte Carlo, ZAF and Phi-rho-z procedures. In: *Newbury DE* (eds) Microbeam analysis-1988. San Francisco Press, San Francisco, 239-246
- Amstrong JT* (1989). CITZAF: combined ZAF and phi-rho (Z) electron beam correction programs. California Institute of Technology, Pasadena, CA
- Govindraju K* (1989). Compiltatoin of working values and sample descriptions for 272 geostandards. Special Issue of Geostandards Newsletter (sp. Issue), 1-113
- Kretz R* (1983). Symbols for rock forming minerals. *Am. Mineral.* 68: 277-279
- Skoog DA, Leary JJ* (1992). Principles of instrumental analysis, Saunders College publishing

Appendix C- Mineral Chemistry

The following tables contain detailed list of mineral analyses referenced in this dissertation.

Table C1. Chemistry of orthopyroxene used for Opx-Cpx ion exchange thermometry						Table C1. Chemistry of clinopyroxene used for Opx-Cpx ion exchange thermometry						
Sample No.	RU 9817A	RU 9817A	RU 9817A	RU 9817A	RU 9817A	Sample No.	RU 9817A	RU 9817A	RU 9817A	RU 9817A	RU 9817A	
Analysis No.	63	65	84	108	119	60	64	66	87	106	121	
Mineral pair	1	2	3	4	5	6	1	2	3	4	5	
SiO ₂	48.83	48.33	48.56	48.28	49.17	49.22	49.73	50.65	50.58	49.58	49.69	49.93
TiO ₂	0.10	0.08	0.05	0.10	0.07	0.06	0.13	0.09	0.10	0.19	0.19	0.15
Al ₂ O ₃	0.70	0.68	0.54	0.52	0.54	0.77	1.57	1.22	1.28	1.49	1.91	1.88
FeO	37.61	38.03	38.40	38.02	37.99	38.03	18.15	18.44	18.17	18.22	19.46	18.91
Cr ₂ O ₃	0.02	0.05	0.04	0.01	0.00	0.00	0.03	0.05	0.11	0.04	0.04	0.07
MnO	0.90	0.89	0.87	0.89	0.89	0.83	0.44	0.38	0.45	0.38	0.45	0.38
MgO	10.78	10.66	10.95	11.20	11.27	10.64	8.20	8.45	8.55	8.42	7.97	8.03
CaO	0.96	0.87	0.89	0.87	0.87	0.92	20.99	20.75	20.68	20.39	19.91	20.41
Na ₂ O	0.06	0.01	0.00	0.04	0.00	0.03	0.63	0.51	0.55	0.58	0.72	0.64
K ₂ O	0.02	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.03	0.00
Total	99.97	99.61	100.31	99.93	100.80	100.51	99.87	100.55	100.48	99.28	100.37	100.40
formula	formula for 6 oxygens						formula for 6 oxygens					
Si	1.974	1.967	1.964	1.959	1.971	1.978	1.946	1.964	1.961	1.949	1.940	1.944
Ti	0.003	0.002	0.001	0.003	0.002	0.002	0.004	0.003	0.003	0.005	0.006	0.004
Al	0.033	0.033	0.026	0.025	0.026	0.036	0.072	0.056	0.059	0.069	0.088	0.086
Fe	1.271	1.294	1.299	1.290	1.274	1.278	0.594	0.598	0.589	0.599	0.635	0.616
Cr	0.001	0.002	0.001	0.000	0.000	0.000	0.001	0.002	0.003	0.001	0.001	0.002
Mn	0.031	0.031	0.030	0.030	0.030	0.028	0.015	0.012	0.015	0.013	0.015	0.013
Mg	0.650	0.647	0.660	0.678	0.674	0.638	0.478	0.488	0.494	0.493	0.464	0.466
Ca	0.041	0.038	0.039	0.038	0.037	0.040	0.880	0.862	0.859	0.859	0.833	0.852
Na	0.005	0.001	0.000	0.003	0.000	0.002	0.048	0.038	0.041	0.044	0.054	0.048
K	0.001	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000
Total cations	4.010	4.015	4.020	4.027	4.014	4.002	4.038	4.023	4.024	4.032	4.038	4.031
Fe ²⁺ as total iron												
mineral pairs concerned:	63-64, 65-66, 84-87, 106-108, 119-121, 60-122											
Temperature pressure estimates												
Combined Opx-Cpx / GADS												
Brev and Köhler (1990) and Eckert et al. (1991)												
	Analysis No.	Pair No.	Temperature(°C)	Pressure(kbar)								
	63-64	1	873	8.7								
	65-66	2	870	8.6								
	84-87	3	872	8.6								
	106-108	4	875	8.1								
	119-121	5	882	9.1								
	60-122	6	871	9.0								
	Average			874 ± 4								

Table C2. Chemistry of gamet used for Grt-Cpx ion exchange thermom:										Table C2. Chemistry of clinopyroxene used for Grt-Cpx ion exchange thermom:											
Sample No.	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	RU 9708	
Analysis No	64	66	68	70	74	76	78	78	78	78	78	78	78	78	78	78	78	78	78	78	
Mineral pair:	1	2	3	4	5	6	7	7	7	7	7	7	7	7	7	7	7	7	7	7	
SiO ₂	38.79	38.46	38.22	38.58	38.92	38.63	38.65	38.65	38.65	38.65	38.65	38.65	38.65	38.65	38.65	38.65	38.65	38.65	38.65	38.65	
TiO ₂	0.05	0.02	0.05	0.05	0.08	0.07	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	
Al ₂ O ₃	20.99	21.23	20.94	21.03	21.37	21.03	21.15	21.15	21.15	21.15	21.15	21.15	21.15	21.15	21.15	21.15	21.15	21.15	21.15	21.15	
FeO	22.74	23.02	23.24	22.94	22.31	22.94	23.30	23.30	23.30	23.30	23.30	23.30	23.30	23.30	23.30	23.30	23.30	23.30	23.30	23.30	
Cr ₂ O ₃	0.09	0.08	0.03	0.08	0.02	0.14	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	
MnO	6.39	6.35	6.50	6.42	7.12	6.39	6.25	6.25	6.25	6.25	6.25	6.25	6.25	6.25	6.25	6.25	6.25	6.25	6.25	6.25	
MgO	5.71	5.50	5.42	5.55	5.10	5.41	5.44	5.44	5.44	5.44	5.44	5.44	5.44	5.44	5.44	5.44	5.44	5.44	5.44	5.44	
CaO	5.95	6.03	6.06	6.01	6.19	5.93	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	6.05	
Na ₂ O	0.16	0.02	0.09	0.05	0.07	0.05	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Total	100.87	100.72	100.55	100.72	101.17	100.59	101.21	101.21	101.21	101.21	101.21	101.21	101.21	101.21	101.21	101.21	101.21	101.21	101.21	101.21	
formula for 24 oxygens																					
Si	6.012	5.981	5.959	5.999	6.034	6.020	5.978	5.978	5.978	5.978	5.978	5.978	5.978	5.978	5.978	5.978	5.978	5.978	5.978	5.978	
Al	3.831	3.889	3.845	3.852	3.902	3.860	3.853	3.853	3.853	3.853	3.853	3.853	3.853	3.853	3.853	3.853	3.853	3.853	3.853	3.853	
Ti	0.006	0.003	0.006	0.006	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	
Fe	2.947	2.994	3.030	2.983	2.892	2.990	3.014	3.014	3.014	3.014	3.014	3.014	3.014	3.014	3.014	3.014	3.014	3.014	3.014	3.014	
Cr	0.011	0.010	0.004	0.010	0.002	0.017	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	
Mg	1.319	1.275	1.260	1.287	1.179	1.257	1.254	1.254	1.254	1.254	1.254	1.254	1.254	1.254	1.254	1.254	1.254	1.254	1.254	1.254	
Mn	0.839	0.836	0.858	0.846	0.935	0.844	0.819	0.819	0.819	0.819	0.819	0.819	0.819	0.819	0.819	0.819	0.819	0.819	0.819	0.819	
Ca	0.988	1.005	1.012	1.001	1.028	0.990	1.003	1.003	1.003	1.003	1.003	1.003	1.003	1.003	1.003	1.003	1.003	1.003	1.003	1.003	
Na	0.048	0.007	0.026	0.016	0.020	0.014	0.058	0.058	0.058	0.058	0.058	0.058	0.058	0.058	0.058	0.058	0.058	0.058	0.058	0.058	
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Total cations	16.001	16.000	16.000	16.000	16.001	16.001	16.000	16.000	16.000	16.001	16.001	16.000	16.000	16.000	16.000	16.000	16.000	16.000	16.000	16.000	
Fe ²⁺ as total iron																					
mineral pairs concerned: 64-106, 66-88, 68-90, 70-82, 74-98, 76-93, 78-79																					
Temperature pressure estimates																					
Combined Grt-Cpx / GADS																					
Sengupta et al. (1989) and Eckert et al. (1991)																					
Analysis No/Pair No / Temperature ^o C / Pressure(kbar)																					
64-106 / 1 / 738 / 7.24																					
66-88 / 2 / 728 / 7.14																					
68-90 / 3 / 714 / 7.08																					
70-82 / 4 / 724 / 7.10																					
74-98 / 5 / 728 / 7.14																					
76-93 / 6 / 727 / 7.13																					
78-79 / 7 / 706 / 6.91																					
Average / 724 ± 10 / 7.1 ± 0.1																					

Table C3. Chemistry of biotite used for Grt-Bt ion exchange thermometry.

Sample No.	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	
Analysis No	28	30	31	35	37	39	43	45	47	57	70	74	78	88	82	171									
Mineral Pair	12	13	14	15	16	17	18	19	20	21	22	23	24	26	25	27									
SiO ₂	36.76	37.48	37.62	37.92	36.84	37.23	36.28	37.67	37.52	36.68	38.07	37.28	37.51	36.29	37.18	36.43									
TiO ₂	5.1	4.65	4.74	5.4	5.4	5.73	5.36	5.57	5.47	5.37	5.51	5.49	3.89	5.41	5.67	5.28									
Al ₂ O ₃	13.65	14.03	13.77	13.8	13.97	14.1	13.24	13.87	13.75	13.26	13.76	13.51	13.73	12.84	13.18	13.34									
Cr ₂ O ₃	0.058	0.102	0.059	0.083	0.105	0.028	0.059	0.056	0.046	0.068	0.067	0.073	0.076	0.052	0.096	0.054									
FeO	13.93	14.54	14.42	14.81	14.69	14.89	15.82	14.98	15.08	14.99	14.55	14.67	13.55	14.01	14.63	14.49									
MnO	0.19	0.134	0.207	0.121	0.159	0.128	0.181	0.118	0.182	0.122	0.201	0.135	0.106	0.163	0.207	0.197									
MgO	14.48	14.84	15.1	14.76	14.49	14.45	13.91	14.43	14.3	14.12	13.67	14.47	16	13.89	14.12	13.92									
CaO	0.038	0.09	0	0	0	0.026	0.058	0	0	0.067	0.027	0	0	0.03	0.049										
Na ₂ O	0.225	0.14	0.228	0.292	0.172	0.177	0.377	0.198	0.132	0.229	0.183	0.097	0.108	0.216	0.21	0.169									
K ₂ O	9.23	9.43	9.51	9.52	9.39	9.55	9.04	9.44	9.36	8.53	9.43	9.29	9.44	8.99	9.08	9.21									
BaO	0.247	0.384	0.451	0.393	0.302	0.431	0.301	0.37	0.303	0.215	0.296	0.256	0.281	0.104	0.305	0									
F	1.58	1.91	1.71	1.71	1.6	1.81	1.44	1.52	1.45	1.52	1.416	1.76	1.87	1.51	1.63	1.51									
Cl	0.363	0.372	0.383	0.435	0.352	0.366	0.424	0.353	0.337	0.342	0.332	0.336	0.355	0.308	0.305	0.308									
Total	95.851	98.102	98.198	99.244	97.47	98.916	96.49	98.575	97.93	95.513	97.512	97.367	96.916	93.813	96.664	94.957									
O F Cl	0.747	0.888	0.806	0.818	0.753	0.845	0.702	0.72	0.687	0.717	0.671	0.817	0.867	0.705	0.755	0.705									
CTotal	95.104	97.214	97.392	98.426	96.717	98.071	95.788	97.855	97.243	94.796	96.841	96.55	96.049	93.108	95.909	94.252									
Si	5.576	5.583	5.592	5.581	5.516	5.512	5.522	5.569	5.58	5.585	5.663	5.584	5.623	5.62	5.605	5.582									
Ti	0.582	0.521	0.53	0.598	0.608	0.638	0.614	0.619	0.612	0.615	0.617	0.619	0.439	0.63	0.643	0.609									
Al	2.438	2.461	2.411	2.392	2.463	2.458	2.373	2.415	2.408	2.378	2.411	2.383	2.424	2.342	2.34	2.409									
Fe	1.767	1.811	1.793	1.823	1.84	1.843	2.014	1.852	1.875	1.909	1.81	1.838	1.699	1.814	1.844	1.857									
Cr	0.007	0.012	0.007	0.01	0.012	0.003	0.007	0.007	0.005	0.008	0.008	0.009	0.009	0.006	0.011	0.007									
Mn	0.024	0.017	0.026	0.015	0.02	0.016	0.023	0.015	0.023	0.016	0.025	0.017	0.013	0.021	0.026	0.026									
Mg	3.274	3.296	3.346	3.239	3.234	3.189	3.156	3.18	3.17	3.205	3.031	3.231	3.576	3.207	3.173	3.180									
Ba	0.015	0.022	0.026	0.023	0.018	0.025	0.018	0.021	0.018	0.013	0.017	0.015	0.017	0.006	0.018	0									
Ca	0.006	0.014	0	0	0	0.004	0.009	0	0	0.011	0.004	0	0	0.005	0.008	0.008									
Na	0.066	0.04	0.066	0.083	0.05	0.051	0.111	0.057	0.038	0.068	0.053	0.028	0.031	0.065	0.061	0.050									
K	1.786	1.792	1.803	1.788	1.794	1.804	1.755	1.78	1.776	1.657	1.79	1.775	1.805	1.776	1.746	1.800									
Total cations	15.541	15.569	15.6	15.552	15.555	15.543	15.602	15.515	15.505	15.465	15.429	15.499	15.636	15.492	15.475	15.527									
F	1.516	1.8	1.608	1.592	1.515	1.695	1.386	1.421	1.364	1.464	1.332	1.667	1.773	1.479	1.554	0									
Cl	0.187	0.188	0.193	0.217	0.179	0.184	0.219	0.177	0.17	0.177	0.167	0.171	0.18	0.162	0.156	0									
Fe ^[2] as total iron																									

formula for 22 oxygens

Table C3. Temperature-pressure estimates							
From combined Grt-Bt / GADS							
Dasgupta et al. (1990) and Eckert et al. (1991)							
for garnet core/biotite				for garnet rim/biotite			
Analysis No.	Pair No	T	P	Analysis No.	Pair No	T	P
33-30	13A	807	7.96	32-28	12C	780	7.68
36-35	15A	803	7.92	34-31	14C	783	7.71
40-37	16A	826	8.16	44-45	19C	793	7.82
41-39	17A	823	8.13	56-57	21C	814	8.04
42-43	18A	834	8.25	71-70	22C	804	7.93
46-47	20A	819	8.09	75-74	23C	794	7.83
54-57	21A	829	8.19	79-78	24C	757	7.44
55-57	21B	820	8.10	83-82	25C	821	8.11
73-70	22A	834	8.25	169-171	27C	685	6.17
72-70	22B	839	8.30		average	781	7.6
77-74	23A	812	8.02		standard	41	0.6
76-74	23B	817	8.07		deviation		
81-78	24A	787	7.76				
80-78	24B	774	7.62				
84-82	25B	840	8.31				
85-88	26A	832	8.22				
86-88	26B	833	8.24				
85-171	27A	818	7.52				
	average	819	8.1				
	standard	18	0.2				
	deviation						

Table C4 Representative mineral pairs used for Grt-Cpx-Pl-Qtz barometry (Eckert et al. 1991)																	
Garnet			Quartz			Clinopyroxene			Plagioclase								
Sample No	9708	9708	Sample No	9708	9708	Sample No	9708	9708	Sample No	9708	9708						
Analysis No.	62	66	Analysis No.	136	137	Analysis No.	63	67	Analysis No.	64	68						
Pair No.	1	2	Pair No.	1	2	Pair No.	1	2	Pair No.	1	2						
SiO ₂	38.52	39.12	SiO ₂	99.69	100.05	SiO ₂	51.49	52.04	SiO ₂	38.44	60.51						
TiO ₂	0.042	0.064	TiO ₂	0.00	0.00	TiO ₂	0.217	0.219	TiO ₂	0.08	0.00						
Al ₂ O ₃	21.32	21.72	Al ₂ O ₃	0.00	0.06	Al ₂ O ₃	2.12	2	Al ₂ O ₃	21.22	23.54						
Cr ₂ O ₃	0.045	0.063	Cr ₂ O ₃	0.02	0.00	FeO	9.82	10.2	Cr ₂ O ₃	0.10	0.02						
FeO	23.5	22.58	FeO	0.02	0.00	Cr ₂ O ₃	0	0.061	FeO	23.25	0.09						
MnO	6.27	6.24	MnO	0.03	0.00	MnO	1.126	1.225	MnO	6.10	0.01						
MgO	5.59	5.22	MgO	0.00	0.00	MgO	12.86	13.14	MgO	5.54	0.01						
CaO	5.99	6.11	CaO	0.01	0.03	CaO	20.92	21.09	CaO	6.00	6.19						
Na ₂ O	0.011	0.093	Na ₂ O	0.04	0.09	Na ₂ O	0.527	0.515	Na ₂ O	0.01	8.37						
F	0	0	K ₂ O	0.05	0.10	K ₂ O	0.011	0.017	K ₂ O	0.03	0.21						
Cl	0.016	0.033	BaO	0.00	0.01	Total	99.091	100.507	BaO	0.00	0.00						
Total	101.26	101.18	F	0.00	0.00	formula for 6 oxygens						F	0.00	0.12			
formula for 24 oxygens												Cl			Cl	0.02	0.01
Si	5.959	6.049	Total	99.89	100.41	formula for 2 oxygens						Total	100.78	99.09			
Al	3.884	3.955	formula for 2 oxygens			Si	1.951	1.948	formula for 32 oxygens			Si	7.990	10.888			
Cr	0.005	0.009	Si	0.999	0.998	Al	0.095	0.088	Al	5.198	4.992						
Ti	0.005	0.007	Al	0.000	0.001	Fe	0.311	0.319	Cr	0.016	0.003						
Fe	3.040	2.920	Cr	0.000	0.000	Ti	0.006	0.006	Ti	0.012	0.000						
Mg	1.289	1.203	Ti	0.000	0.000	Cr	0	0.002	Fe	4.041	0.013						
Mn	0.822	0.817	Fe	0.000	0.000	Mg	0.727	0.733	Mg	1.717	0.004						
Ca	0.993	1.012	Mg	0.000	0.000	Mn	0.036	0.039	Mn	1.074	0.002						
Na	0.003	0.028	Mn	0.000	0.000	Ca	0.849	0.846	Ca	1.336	1.193						
Total Cation	16.000	16.000	Ca	0.000	0.000	Na	0.039	0.037	Na	0.003	2.920						
F	0	0	Na	0.001	0.002	K	0.001	0.001	K	0.007	0.049						
Cl	0.004	0.009	K	0.001	0.001	Ba	0.001	0.001	Ba	0.000	0.000						
			Ba	0.000	0.000	Total Cation	4.015	4.019	Total Cation	21.392	20.063						
			Total Cations	1.001	1.002												
			F	0.000	0.000							F	0.000	0.069			
			Cl	0.001	0.001							Cl	0.008	0.003			

Table C5. Chemical composition of garnet along the drawn line AB in Fig. 2.3

part 1	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Analysed distance (micro meter)	0.00	3.97	7.94	11.90	15.87	19.84	23.81	27.78	31.75	35.71	39.68	43.65	47.62	51.59	55.56	59.52	63.49	67.46	71.43	75.40	79.37	83.33	87.30	91.27	95.24	99.21	103.17	107.14
SiO ₂	38.44	38.35	38.77	38.65	38.43	38.50	38.68	38.77	38.58	38.38	38.69	38.67	37.90	38.26	38.68	38.76	38.73	38.57	38.66	38.30	38.34	38.45	38.32	38.34	38.34	38.49	38.61	38.22
TiO ₂	0.14	0.07	0.11	0.05	0.05	0.01	0.11	0.05	0.02	0.08	0.05	0.07	0.06	0.06	0.08	0.02	0.07	0.06	0.07	0.04	0.11	0.12	0.04	0.04	0.05	0.05	0.07	0.05
Al ₂ O ₃	21.81	21.49	21.63	21.90	21.63	21.83	21.95	21.76	21.89	22.00	21.86	21.45	21.64	21.75	21.89	21.79	21.69	21.85	21.98	21.68	21.58	21.71	21.74	21.84	21.96	22.04	22.05	
FeO	24.62	24.11	23.88	23.74	24.03	24.07	23.82	23.78	23.63	24.11	23.51	23.57	22.87	23.42	23.70	23.65	23.59	23.42	23.36	23.60	23.29	23.37	23.18	23.67	23.55	23.48	23.49	23.53
Cr ₂ O ₃	0.06	0.13	0.05	0.04	0.02	0.09	0.03	0.04	0.08	0.11	0.05	0.05	0.07	0.07	0.07	0.07	0.06	0.13	0.08	0.00	0.08	0.07	0.10	0.12	0.09	0.10	0.03	0.02
MnO	6.31	6.22	5.92	5.85	6.18	5.95	5.99	5.89	5.81	5.84	6.06	5.86	5.60	5.81	6.05	5.95	5.95	5.77	5.88	5.77	5.81	5.79	5.88	5.86	5.71	5.81	5.82	5.84
MgO	4.44	4.70	4.82	5.10	5.03	5.11	5.21	5.25	5.12	5.36	5.35	5.23	5.37	5.39	5.37	5.51	5.48	5.50	5.45	5.45	5.48	5.56	5.43	5.51	5.67	5.61	5.60	
CaO	6.04	6.02	6.14	6.12	6.00	6.02	5.97	6.02	6.10	6.05	6.10	6.02	5.99	5.99	6.09	5.83	5.99	5.93	6.03	6.01	6.08	5.88	5.97	5.99	5.98	5.89	6.00	5.85
Na ₂ O	0.00	0.05	0.02	0.03	0.05	0.08	0.04	0.00	0.02	0.03	0.07	0.22	0.03	0.07	0.16	0.04	0.04	0.05	0.04	0.16	0.04	0.32	0.07	0.07	0.12	0.03	0.00	0.03
K ₂ O	0.04	0.00	0.04	0.01	0.02	0.01	0.00	0.00	0.02	0.02	0.00	0.01	0.37	0.03	0.02	0.01	0.03	0.01	0.05	0.02	0.24	0.03	0.00	0.03	0.02	0.02	0.00	0.02
Total	101.90	101.25	101.37	101.32	101.44	101.78	101.58	101.82	101.18	101.80	101.87	101.59	100.65	101.81	101.87	101.58	101.77	101.11	101.64	101.57	101.36	100.73	100.96	101.33	101.12	101.47	101.72	101.20
Si	5.961	5.981	6.011	5.991	5.969	5.953	5.982	5.976	5.986	5.934	5.961	5.972	5.922	5.961	5.967	5.985	5.973	5.981	5.966	5.943	5.972	5.970	5.946	5.949	5.947	5.950	5.926	
Ti	0.016	0.008	0.013	0.006	0.006	0.001	0.012	0.006	0.003	0.009	0.006	0.008	0.007	0.010	0.010	0.002	0.008	0.007	0.008	0.005	0.013	0.014	0.005	0.005	0.006	0.005	0.008	0.006
Al	3.986	3.950	3.952	3.968	3.959	3.991	3.978	3.987	3.979	3.988	3.994	3.978	3.961	3.973	3.954	3.983	3.960	3.964	3.974	3.999	3.964	3.961	3.972	3.975	3.994	3.999	4.003	4.029
Fe	3.193	3.144	3.096	3.077	3.121	3.112	3.080	3.065	3.066	3.117	3.029	3.044	2.996	3.051	3.057	3.033	3.042	3.037	3.015	3.046	3.022	3.044	3.009	3.071	3.056	3.054	3.027	3.051
Cr	0.007	0.016	0.006	0.005	0.003	0.011	0.004	0.005	0.010	0.014	0.006	0.006	0.008	0.009	0.008	0.007	0.016	0.010	0.010	0.010	0.009	0.012	0.015	0.011	0.012	0.003	0.002	
Mn	0.829	0.822	0.777	0.768	0.813	0.779	0.785	0.769	0.763	0.765	0.791	0.766	0.745	0.767	0.790	0.778	0.777	0.758	0.769	0.754	0.763	0.773	0.770	0.750	0.760	0.760	0.767	
Mg	1.026	1.093	1.114	1.179	1.165	1.178	1.201	1.206	1.184	1.235	1.229	1.250	1.222	1.247	1.240	1.236	1.267	1.265	1.254	1.261	1.272	1.283	1.256	1.275	1.306	1.289	1.294	
Ca	1.003	1.006	1.020	1.016	0.998	0.997	0.989	0.994	1.014	1.002	1.007	0.996	1.005	1.000	1.007	0.964	0.980	0.985	0.997	0.984	1.011	0.981	0.983	0.996	0.984	0.975	0.991	0.972
Na	0.000	0.016	0.007	0.010	0.015	0.022	0.012	0.000	0.005	0.007	0.009	0.022	0.372	0.050	0.011	0.011	0.016	0.013	0.047	0.011	0.095	0.022	0.022	0.037	0.010	0.000	0.015	0.008
K	0.009	0.000	0.007	0.003	0.004	0.003	0.000	0.002	0.006	0.004	0.000	0.002	0.075	0.006	0.004	0.002	0.006	0.003	0.010	0.005	0.048	0.000	0.007	0.003	0.004	0.000	0.000	0.005
Fe ²⁺ as total iron formula for 2.4 oxygens																												
part 2																												
Analysed distance (micro meter)	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57
SiO ₂	38.52	38.34	38.51	38.69	38.73	38.61	38.79	38.99	38.62	38.61	38.89	38.67	38.90	38.83	38.69	38.62	38.96	38.66	38.77	38.74	38.93	38.49	38.74	38.84	38.83	38.57	38.66	
TiO ₂	0.06	0.06	0.06	0.05	0.13	0.12	0.07	0.07	0.10	0.07	0.06	0.07	0.10	0.05	0.13	0.06	0.09	0.08	0.05	0.10	0.11	0.02	0.03	0.07	0.06	0.01	0.07	0.13
Al ₂ O ₃	21.72	21.96	21.94	21.82	21.87	21.84	21.73	21.81	21.72	21.99	21.77	21.73	21.76	22.10	21.83	21.80	22.03	21.81	22.06	21.83	21.75	22.05	21.93	21.77	22.02	21.84	21.82	21.87
FeO	23.48	23.29	23.58	23.39	23.45	23.38	23.66	23.79	23.42	23.31	23.64	23.41	23.80	23.59	23.75	23.35	23.68	23.74	23.34	23.40	23.53	23.26	23.38	23.39	23.60	23.15	23.45	23.57
Cr ₂ O ₃	0.11	0.01	0.09	0.04	0.13	0.08	0.07	0.09	0.12	0.13	0.04	0.05	0.08	0.06	0.09	0.07	0.11	0.04	0.02	0.15	0.01	0.08	0.02	0.07	0.07	0.10	0.07	0.04
MnO	5.82	5.88	5.83	5.74	5.77	5.75	5.93	5.83	5.83	5.74	5.83	5.93	6.01	5.77	5.83	5.73	5.86	5.74	5.67	5.80	5.87	5.71	5.80	5.82	5.70	5.75	5.71	5.64
MgO	5.54	5.51	5.60	5.61	5.77	5.60	5.73	5.52	5.53	5.62	5.65	5.58	5.54	5.60	5.54	5.72	5.55	5.57	5.59	5.68	5.64	5.60	5.67	5.72	5.70	5.63	5.77	
CaO	6.00	5.86	5.97	6.02	5.91	5.97	5.82	5.89	5.96	5.95	5.78	6.00	5.84	5.99	5.86	5.94	6.06	5.90	5.77	6.03	5.91	5.87	5.94	5.81	5.83	5.97	5.88	6.04
Na ₂ O	0.01	0.05	0.00	0.05	0.01	0.04	0.03	0.07	0.08	0.04	0.04	0.06	0.02	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.05	0.07	0.05	0.03	0.01	0.05	0.07	0.04
K ₂ O	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.05	0.03	0.01	0.04	0.01	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.02	0.03	0.01	0.07	0.05	0.03	0.00	0.03
Total	101.26	100.97	101.58	101.40	101.77	101.40	101.83	102.06	101.41	101.55	102.19	101.65	101.93	101.65	101.93	101.20	102.24	101.89	101.14	101.77	101.62	101.33	101.42	101.89	101.40	101.30	101.76	
Si	5.968	5.932	5.948	5.977	5.962	5.966	5.976	5.982	5.973	5.985	5.992	5.974	5.976	5.941	5.975	5.986	5.930	5.993	5.977	5.972	5.975	5.989	5.986	5.984	5.970	5.980	5.967	5.955
Ti	0.007	0.006	0.007	0.005	0.015	0.014	0.008	0.008	0.011	0.009	0.007	0.008	0.011	0.006	0.015	0.006	0.011	0.009	0.006	0.012	0.012	0.002	0.003	0.008	0.007	0.001	0.008	0.015
Al	3.966	4.018	3.993	3.973	3.988	3.977	3.945	3.950	3.959	3.944	3.953	3.956	3.939	3.944	3.953	3.986	3.975	3.986	4.020	3.963	3.953	3.989	3.963	3.989	3.999	3.971	3.979	3.970
Fe	3.042	3.023	3.045	3.029	3.019	3.021	3.048	3.057	3.029	3.022	3.046	3.024	3.057	3.044	3.056	3.021	3.040	3.054	3.018	3.014	3.035	2.992	3.02					

Table C5. contd...																														
part3																														
Analysed	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	
detained	230.16	234.13	238.10	242.06	246.03	250.00	253.97	257.94	261.90	265.87	269.84	273.81	277.78	281.75	285.72	289.68	293.65	297.62	301.59	305.56	309.52	313.49	317.46	321.43	325.40	329.37	333.33	337.30	341.27	
(nt cro meter)																														
SiO ₂	38.56	38.66	38.51	38.79	38.64	38.59	38.38	38.70	38.63	38.50	39.01	38.56	38.49	38.83	37.33	38.95	38.88	38.85	38.63	38.48	38.77	38.82	38.85	39.03	38.55	38.59	38.48	38.63	38.08	
TiO ₂	0.11	0.05	0.06	0.07	0.06	0.05	0.14	0.03	0.07	0.07	0.09	0.06	0.12	0.08	0.08	0.04	0.03	0.12	0.01	0.08	0.07	0.07	0.14	0.06	0.11	0.06	0.06	0.11	0.04	
Al ₂ O ₃	21.98	21.83	21.83	21.77	22.29	21.85	21.90	21.74	21.95	21.85	22.14	21.86	21.94	21.85	21.79	22.13	21.86	21.83	21.96	21.86	21.82	21.93	22.05	21.81	21.82	21.74	21.79	21.83	21.83	
FeO	23.35	23.53	23.84	23.29	23.70	23.45	23.28	23.53	23.77	23.48	23.58	23.45	23.48	23.63	23.48	23.87	23.48	23.52	23.30	23.26	23.35	23.43	23.45	23.45	23.42	23.63	23.68	24.03	24.35	
Cr ₂ O ₃	0.11	0.06	0.01	0.12	0.04	0.07	0.09	0.10	0.04	0.09	0.03	0.09	0.03	0.07	0.07	0.09	0.05	0.05	0.13	0.06	0.11	0.06	0.11	0.05	0.05	0.04	0.08	0.09	0.04	
MnO	5.75	5.69	5.85	5.74	5.89	5.82	5.80	5.80	5.77	5.84	5.94	5.70	5.72	5.71	4.09	5.64	5.67	5.58	5.78	5.74	5.67	5.62	5.73	5.86	5.68	5.68	5.79	5.72	5.74	
MgO	5.51	5.74	5.38	5.61	5.66	5.80	5.68	5.64	5.68	5.64	5.68	5.71	5.71	5.55	5.64	5.76	5.74	5.71	5.74	5.63	5.69	5.51	5.55	5.56	5.41	5.60	5.60	5.54	5.08	
CaO	5.97	5.79	5.96	5.92	6.00	5.88	5.80	5.85	6.08	6.01	5.92	6.11	5.95	5.92	4.47	6.02	5.96	6.00	6.04	6.03	6.02	6.05	6.02	5.81	5.87	5.97	5.90	5.94	5.98	
Na ₂ O	0.02	0.00	0.00	0.00	0.02	0.06	0.14	0.05	0.04	0.04	0.01	0.02	0.04	0.03	0.00	0.05	0.01	0.03	0.11	0.05	0.05	0.06	0.05	0.02	0.13	0.04	0.07	0.12		
K ₂ O	0.00	0.00	0.00	0.01	0.03	0.03	0.06	0.03	0.02	0.01	0.01	0.01	0.00	0.00	0.16	0.00	0.00	0.03	0.01	0.00	0.00	0.02	0.00	0.00	0.01	0.00	0.04	0.05		
Total	101.36	101.35	101.64	101.95	101.69	101.83	101.39	101.25	101.99	101.57	102.44	101.47	101.32	101.76	94.83	102.36	102.02	101.57	101.45	101.61	101.40	101.83	101.41	101.35	101.48	101.43	101.75	101.30		
Si	5.939	5.974	5.951	5.972	5.953	5.948	5.939	5.986	5.946	5.947	5.965	5.955	5.954	5.979	6.184	5.966	6.008	5.960	5.961	5.950	5.975	5.989	5.972	6.018	5.968	5.967	5.955	5.966	5.927	
Ti	0.012	0.005	0.007	0.008	0.007	0.006	0.016	0.003	0.008	0.009	0.011	0.007	0.014	0.010	0.010	0.005	0.003	0.013	0.001	0.008	0.008	0.017	0.007	0.013	0.007	0.007	0.012	0.004		
Al	4.003	3.976	3.976	3.950	4.005	3.966	3.984	3.963	3.981	3.978	3.990	3.979	4.000	3.963	3.294	3.964	3.957	4.001	3.976	3.983	3.965	3.987	3.991	3.983	3.981	3.962	3.974	3.966	4.004	
Fe	3.018	3.040	3.081	3.080	3.000	3.055	3.034	3.011	3.059	3.033	3.015	3.037	3.043	3.294	3.057	3.034	3.017	3.004	3.041	3.003	3.001	3.014	3.010	3.032	3.055	3.064	3.103	3.169		
Cr	0.013	0.008	0.001	0.015	0.005	0.009	0.010	0.012	0.005	0.011	0.003	0.011	0.004	0.008	0.009	0.011	0.006	0.006	0.002	0.002	0.016	0.007	0.013	0.003	0.006	0.005	0.010	0.011	0.005	
Mn	0.735	0.745	0.766	0.748	0.769	0.760	0.760	0.760	0.752	0.764	0.769	0.746	0.749	0.745	0.574	0.752	0.742	0.725	0.767	0.757	0.749	0.741	0.732	0.748	0.768	0.744	0.759	0.748	0.737	
Mg	1.270	1.322	1.286	1.288	1.300	1.333	1.301	1.310	1.294	1.308	1.302	1.315	1.280	1.291	1.269	1.306	1.321	1.298	1.307	1.272	1.278	1.249	1.291	1.292	1.249	1.291	1.292	1.279	1.179	
Ca	0.988	0.959	0.987	0.976	0.990	0.971	0.962	0.969	1.003	0.995	0.970	1.011	0.986	0.977	0.793	0.988	0.987	0.986	0.999	0.999	0.994	0.991	0.989	0.994	0.989	0.978	0.983	0.987		
Na	0.007	0.000	0.000	0.000	0.006	0.019	0.041	0.014	0.008	0.012	0.003	0.007	0.011	0.009	0.000	0.014	0.002	0.010	0.033	0.015	0.015	0.017	0.015	0.007	0.039	0.013	0.020	0.035		
K	0.000	0.000	0.000	0.002	0.006	0.005	0.011	0.006	0.003	0.002	0.000	0.000	0.000	0.000	0.033	0.000	0.000	0.000	0.003	0.000	0.004	0.000	0.000	0.002	0.011	0.007	0.003	0.008	0.010	
Fe ²⁺ as total iron																														
formula for 24 oxygens																														
part4																														
Analysed	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	
detained	345.24	349.21	353.17	357.14	361.11	365.08	369.05	373.02	376.98	380.95	384.92	388.89	392.86	396.83	400.79	404.76	408.73	412.70	416.67	420.63	424.60	428.57	432.54	436.51	440.48	444.44	448.41	452.38	456.35	
(nt cro meter)																														
SiO ₂	36.77	38.44	38.78	38.97	38.85	38.37	38.78	38.55	38.73	39.10	38.54	38.78	38.58	38.58	38.70	38.73	38.88	38.74	38.67	38.94	38.55	38.68	38.58	38.46	38.63	38.77	38.62	38.63	38.62	
TiO ₂	3.10	1.04	0.08	0.05	0.05	0.13	0.00	0.09	0.00	0.14	0.06	0.11	0.02	0.04	0.16	0.03	0.04	0.03	0.05	0.05	0.10	0.06	0.03	0.04	0.05	0.05	0.11	0.06		
Al ₂ O ₃	18.34	20.61	21.75	21.59	21.90	21.64	21.94	21.93	21.71	21.47	21.62	21.68	22.00	21.72	21.85	21.85	21.83	22.19	22.07	21.60	21.89	21.88	21.85	21.90	21.73	22.05	21.87	21.86	21.96	
FeO	20.29	23.27	24.30	23.88	23.83	24.08	23.68	23.37	23.64	23.79	23.12	23.54	23.43	23.67	23.78	23.51	23.70	23.37	23.61	23.28	23.45	23.43	23.78	23.51	23.46	23.71	23.57	23.71	23.36	
Cr ₂ O ₃	0.10	0.05	0.09	0.05	0.02	0.11	0.09	0.11	0.07	0.08	0.15	0.03	0.06	0.08	0.08	0.05	0.07	0.14	0.10	0.09	0.09	0.11	0.07	0.00	0.00	0.00	0.08	0.07	0.04	
MnO	3.78	5.17	5.70	5.87	6.03	5.85	5.93	5.75	5.79	5.63	5.75	5.69	5.90	5.85	5.69	5.72	5.90	5.78	5.80	5.70	5.58	5.70	5.58	5.78	5.70	5.87	5.78	5.83	5.86	
MgO	8.56	6.03	5.38	5.28	5.30	5.51	5.55	5.43	5.55	5.53	5.51	5.48	5.50	5.52	5.62	5.53	5.70	5.57	5.60	5.56	5.57	5.65	5.52	5.67	5.63	5.59	5.54	5.53	5.62	
CaO	3.65	5.21	5.91	5.78	5.92	5.92	5.92	5.97	5.95	5.98	6.19	6.02	6.13	6.01	6.03	5.96	6.07	6.09	6.03	6.06	6.15	6.00	5.97	6.02	5.97	5.92	5.94	5.92	5.98	
Na ₂ O	0.19	0.09	0.02	0.02	0.05	0.04	0.03	0.04	0.02	0.22	0.02	0.00	0.04	0.00	0.06	0.04	0.04	0.04	0.00	0.00	0.00	0.03	0.06	0.05	0.01	0.03	0.01	0.00	0.02	
K ₂ O	3.72	1.27	0.03	0.01	0.04	0.00	0.00	0.00	0.02	0.01	0.05	0.00	0.00	0.00	0.02	0.00	0.01	0.02	0.00	0.01	0.00	0.03	0.03	0.02	0.01	0.02	0.01	0.02	0.02	
Total	98.51	101.18	102.03	101.51	102.19	101.65	101.96	101.53	101.51	101.96	101.01	101.44	101.55																	

Table C5. cont'd...																														
part5																														
Aux/ye	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	
distance	460.32	464.29	468.25	472.22	476.19	480.16	484.13	488.10	492.06	496.03	500.00	503.97	507.94	511.90	515.87	519.84	523.81	527.78	531.75	535.71	539.68	543.65	547.62	551.59	555.56	559.52	563.49	567.46	571.43	
(micro meter)																														
SiO ₂	38.51	38.49	38.76	38.74	38.55	38.66	38.51	38.54	38.70	38.74	38.56	38.66	38.93	38.69	38.81	38.76	38.95	38.72	38.73	38.83	38.59	38.85	39.01	38.78	39.17	38.77	38.75	38.65	38.72	
TiO ₂	0.10	0.16	0.02	0.01	0.07	0.05	0.05	0.05	0.09	0.07	0.07	0.05	0.11	0.06	0.10	0.07	0.07	0.10	0.05	0.09	0.08	0.08	0.07	0.05	0.09	0.05	0.04	0.09	0.08	
Al ₂ O ₃	21.68	21.83	22.05	21.89	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82	21.82
FeO	25.42	23.52	23.59	23.62	23.53	23.40	23.66	23.84	23.49	23.51	23.67	23.77	23.77	23.52	23.56	23.65	23.66	23.81	23.68	23.71	23.69	23.63	23.73	23.75	23.35	23.36	23.63	23.36	23.45	
Cr ₂ O ₃	0.13	0.07	0.07	0.06	0.08	0.10	0.06	0.06	0.07	0.07	0.07	0.07	0.11	0.08	0.02	0.09	0.11	0.09	0.11	0.01	0.03	0.07	0.08	0.05	0.00	0.02	0.03	0.07	0.12	
MnO	5.81	5.75	5.93	5.88	5.72	5.74	5.66	5.92	5.68	5.83	5.83	5.74	5.68	5.95	5.77	5.68	5.95	5.77	5.90	5.68	5.76	5.88	5.66	5.91	5.86	5.84	5.86	5.78	5.80	
MgO	5.59	5.59	5.59	5.51	5.53	5.61	5.50	5.65	5.51	5.61	5.65	5.55	5.38	5.56	5.44	5.66	5.59	5.63	5.38	5.54	5.46	5.62	5.50	5.46	5.59	5.50	5.40	5.69	5.69	
CaO	6.08	6.05	6.09	6.07	5.96	5.98	5.93	6.11	6.18	5.99	6.04	6.05	6.01	6.12	6.01	6.02	6.04	6.02	6.05	5.90	6.02	6.05	5.99	5.88	6.03	6.03	6.06	5.98	5.94	
Na ₂ O	0.07	0.05	0.02	0.01	0.03	0.05	0.04	0.03	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	
K ₂ O	0.00	0.03	0.04	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.04	0.02	0.01	0.00	0.00	0.00	0.01	0.02	0.02	0.00	0.02	0.03	0.00	0.02	0.00	0.00	0.02	0.04	0.02	
Total	101.38	101.61	102.17	101.79	101.28	101.49	101.25	102.04	101.66	101.88	101.77	101.71	102.52	101.15	101.70	101.99	102.20	102.18	101.79	101.45	101.42	102.23	102.00	101.91	101.68	101.36	101.88	101.04	101.56	
Si	5.660	5.943	5.933	5.971	5.968	5.967	5.965	5.939	5.980	5.961	5.949	5.963	5.964	5.985	5.979	5.969	5.980	5.948	5.974	5.984	5.973	5.964	5.991	5.970	6.028	5.983	5.959	5.994	5.977	
Ti	0.011	0.018	0.002	0.001	0.008	0.005	0.006	0.005	0.011	0.008	0.008	0.006	0.013	0.007	0.011	0.008	0.008	0.012	0.006	0.011	0.009	0.009	0.009	0.009	0.006	0.010	0.006	0.004	0.010	0.009
Al	3.955	3.972	3.991	3.976	3.981	3.987	3.983	3.962	3.984	3.987	3.971	3.974	3.974	3.984	3.984	3.984	3.984	3.979	3.947	4.007	3.958	3.964	3.962	3.963	3.943	3.962	4.011	3.963	3.948	
Fe	3.031	3.037	3.029	3.044	3.046	3.020	3.065	3.072	3.028	3.025	3.054	3.066	3.064	3.012	3.035	3.041	3.037	3.058	3.054	3.001	3.066	3.033	3.047	3.057	3.005	3.019	3.039	3.029	3.027	
Cr	0.016	0.009	0.009	0.007	0.009	0.012	0.007	0.007	0.008	0.009	0.005	0.014	0.010	0.003	0.011	0.013	0.011	0.014	0.002	0.004	0.009	0.009	0.006	0.000	0.002	0.003	0.008	0.008	0.015	
Mn	0.762	0.749	0.771	0.768	0.750	0.750	0.743	0.773	0.742	0.760	0.758	0.737	0.775	0.765	0.789	0.740	0.774	0.751	0.771	0.741	0.755	0.777	0.756	0.770	0.764	0.763	0.759	0.758		
Mg	1.290	1.308	1.280	1.266	1.276	1.291	1.270	1.298	1.266	1.287	1.300	1.276	1.284	1.284	1.287	1.279	1.283	1.275	1.260	1.286	1.259	1.253	1.257	1.257	1.256	1.249	1.309	1.309		
Ca	1.008	1.001	1.002	1.002	0.988	0.989	0.984	1.009	1.021	0.987	0.988	1.000	0.986	1.016	0.992	1.001	0.990	0.978	1.000	0.974	0.985	0.970	0.984	0.989	0.988	0.994	0.982	0.982		
Na	0.020	0.016	0.007	0.000	0.002	0.010	0.016	0.010	0.009	0.018	0.010	0.000	0.013	0.005	0.010	0.011	0.025	0.013	0.010	0.008	0.000	0.012	0.013	0.010	0.010	0.010	0.011	0.000	0.009	
K	0.000	0.006	0.008	0.003	0.002	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.003	0.003	0.005	0.000	0.004	0.005	0.000	0.004	0.000	0.000	0.004	0.007	0.004	
Fe ²⁺ as total iron																														
formula for 24 oxygens																														
part6																														
Aux/ye	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169						
distance	575.40	579.37	583.33	587.30	591.27	595.24	599.21	603.17	607.14	611.11	615.08	619.05	623.02	626.98	630.95	634.92	638.89	642.86	646.83	650.79	654.76	658.73	662.70	666.67						
(micro meter)																														
SiO ₂	38.61	38.68	38.99	38.65	38.59	38.81	38.47	38.62	38.66	38.89	38.52	38.94	38.90	38.55	38.89	38.77	38.71	38.59	38.60	38.78	38.83	38.93	38.65	38.57						
TiO ₂	0.07	0.03	0.04	0.08	0.01	0.06	0.02	0.11	0.00	0.04	0.07	0.04	0.06	0.04	0.10	0.06	0.05	0.10	0.05	0.07	0.02	0.02	0.06	0.08	0.10					
Al ₂ O ₃	21.72	21.94	21.81	21.94	22.05	22.00	21.96	21.90	21.67	21.90	21.67	21.90	21.82	21.74	21.86	21.81	21.73	21.60	21.76	21.73	21.51	21.47	21.64	21.75						
FeO	25.66	23.53	23.48	23.56	23.75	23.48	23.61	23.57	23.67	23.65	23.61	23.16	23.50	23.36	23.80	24.02	23.96	23.55	24.01	23.88	24.20	24.34	24.60	24.72						
Cr ₂ O ₃	0.07	0.05	0.05	0.08	0.05	0.07	0.00	0.08	0.02	0.05	0.02	0.02	0.08	0.00	0.07	0.07	0.11	0.03	0.08	0.08	0.04	0.04	0.08	0.06						
MnO	5.90	6.02	5.93	5.86	5.90	5.95	6.04	6.01	5.79	6.06	5.87	5.98	5.75	6.09	6.05	5.91	6.08	5.90	6.08	6.10	6.26	6.27	6.30	6.50						
MgO	5.59	5.44	5.48	5.58	5.46	5.48	5.46	5.35	5.33	5.38	5.19	5.41	5.34	5.22	5.34	5.15	5.22	5.04	5.17	4.93	4.78	4.72	4.43	4.14						
CaO	5.98	6.00	6.03	6.02	6.09	5.96	5.98	5.87	5.98	5.97	6.15	6.16	6.15	6.03	6.05	6.01	6.04	6.18	6.16	6.17	6.06	6.28	6.09	5.99						
Na ₂ O	0.05	0.08	0.00	0.10	0.03	0.00	0.07	0.00	0.07	0.00	0.05	0.11	0.06	0.05	0.03	0.01	0.04	0.05	0.05	0.01	0.06	0.00	0.08	0.00						
K ₂ O	0.01	0.02	0.03	0.00	0.01	0.02	0.00	0.00	0.03	0.02	0.02	0.02	0.02	0.00	0.03	0.04	0.01	0.02	0.04	0.01	0.01	0.01	0.01	0.00	0.06					
Total	101.66	101.79	101.43	101.89	101.94	101.82	101.61	101.51	101.22	101.95	101.25	101.74	101.66	101.21	102.25	101.85	101.94	102.01	101.06	102.01	101.76	101.77	102.12	101.95	101.89					

Table C6. Chemistry of biotite in ultramafic rocks (distance is referred to as from physical boundary between granulite and zone D)

sample No.	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001		
analysis No.	3	4	9	16	19	20	28	1	2	21	26	42	33	4	65	66	68						
zone	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM
distance (cm)	60	60	60	60	60	60	60	58	58	58	58	58	58	58	56	56	56	56	56	56	56	56	56
SiO ₂	42.66	42.69	42.94	42.53	42.43	42.12	43.13	41.44	41.72	42.39	41.70	41.75	41.95	41.61	40.94	40.52	40.74						
TiO ₂	0.32	0.28	0.26	0.42	0.41	0.47	0.29	0.26	0.22	0.37	0.37	0.37	0.43	0.43	0.42	0.39	0.42						
Al ₂ O ₃	13.05	12.51	12.48	12.48	13.06	12.33	12.50	14.21	14.31	13.43	14.12	13.25	12.70	14.21	14.75	14.77	14.46						
FeO	0.59	0.40	0.44	0.55	0.33	0.42	0.43	0.34	0.41	0.41	0.42	0.46	0.45	0.41	0.46	0.47	0.48						
Cr ₂ O ₃	0.05	0.00	0.00	0.06	0.06	0.01	0.04	0.05	0.03	0.00	0.05	0.06	0.07	0.02	0.05	0.00	0.01						
MnO	0.04	0.00	0.04	0.00	0.03	0.04	0.00	0.00	0.00	0.00	0.02	0.03	0.04	0.00	0.02	0.00	0.02						
MgO	28.00	28.49	28.55	28.27	28.05	28.56	28.47	28.14	28.03	28.35	27.76	27.83	28.94	27.76	27.01	26.65	26.65						
CaO	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00						
Na ₂ O	0.20	0.17	0.19	0.21	0.18	0.12	0.18	0.18	0.19	0.18	0.17	0.23	0.12	0.23	0.45	0.51	0.54						
K ₂ O	9.68	9.43	9.33	9.31	10.02	9.09	9.60	10.11	10.14	9.94	10.07	9.61	9.14	10.12	9.91	9.64	9.65						
BaO	0.00	0.12	0.03	0.12	0.00	0.00	0.09	0.10	0.22	0.10	0.06	0.20	0.16	0.08	0.16	0.20	0.09						
F	1.39	1.70	1.50	1.44	1.52	1.41	1.36	1.43	1.63	1.83	1.42	1.54	1.21	1.33	1.96	1.90	2.05						
Cl	0.23	0.26	0.25	0.24	0.26	0.26	0.25	0.24	0.25	0.27	0.26	0.22	0.28	0.38	0.24	0.24	0.28						
Total	96.21	96.06	96.01	95.63	96.34	94.92	96.36	96.62	97.03	97.23	96.56	95.65	95.42	96.68	96.40	95.19	95.43						
formula on the basis of 22 oxygens																							
Si	5.867	5.875	5.903	5.881	5.836	5.861	5.917	5.703	5.711	5.780	5.739	5.788	5.813	5.724	5.649	5.651	5.671						
Ti	0.033	0.029	0.027	0.044	0.043	0.049	0.030	0.026	0.023	0.038	0.039	0.053	0.044	0.044	0.043	0.041	0.044						
Al	2.115	2.029	2.022	2.034	2.117	2.022	2.021	2.305	2.309	2.158	2.290	2.165	2.074	2.304	2.398	2.427	2.372						
Al ^{IV}	2.115	2.029	2.022	2.034	2.117	2.022	2.021	2.297	2.289	2.158	2.290	2.165	2.074	2.276	2.351	2.349	2.329						
Al ^{VI}	0	0	0	0	0	0	0	0.008	0.020	0	0	0	0	0.028	0.047	0.078	0.044						
Fe	0.068	0.046	0.051	0.064	0.037	0.049	0.049	0.039	0.047	0.047	0.048	0.053	0.052	0.047	0.053	0.055	0.056						
Cr	0.005	0.000	0.000	0.006	0.006	0.001	0.004	0.005	0.003	0.000	0.005	0.006	0.008	0.003	0.006	0.000	0.001						
Mn	0.005	0.000	0.004	0.000	0.003	0.004	0.000	0.000	0.000	0.000	0.003	0.003	0.005	0.000	0.003	0.000	0.002						
Mg	5.741	5.845	5.851	5.828	5.752	5.924	5.823	5.773	5.720	5.763	5.695	5.752	5.978	5.693	5.556	5.541	5.531						
Ca	0.000	0.001	0.000	0.000	0.000	0.000	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000						
Na	0.053	0.045	0.051	0.056	0.049	0.033	0.049	0.047	0.050	0.047	0.045	0.063	0.033	0.060	0.119	0.138	0.145						
K	1.698	1.655	1.636	1.642	1.758	1.613	1.680	1.775	1.771	1.729	1.768	1.699	1.616	1.776	1.744	1.715	1.714						
Ba	0.000	0.006	0.001	0.007	0.000	0.005	0.005	0.012	0.006	0.003	0.011	0.009	0.004	0.008	0.011	0.005	0.008						
F	0.603	0.740	0.652	0.630	0.661	0.618	0.592	0.622	0.706	0.789	0.618	0.675	0.530	0.579	0.855	0.838	0.902						
Cl	0.055	0.061	0.059	0.057	0.060	0.062	0.057	0.057	0.058	0.061	0.061	0.052	0.066	0.089	0.057	0.057	0.066						
OH	3.342	3.200	3.289	3.313	3.279	3.320	3.351	3.321	3.236	3.149	3.321	3.273	3.404	3.332	3.088	3.105	3.032						
X _{Ni}	0.988	0.992	0.991	0.989	0.994	0.992	0.992	0.993	0.992	0.992	0.992	0.991	0.991	0.992	0.991	0.990	0.990						
X _{Fe}	0.012	0.008	0.009	0.011	0.006	0.008	0.008	0.007	0.008	0.008	0.008	0.009	0.009	0.008	0.009	0.010	0.010						
X _{Cl}	0.014	0.015	0.015	0.014	0.015	0.016	0.014	0.014	0.015	0.015	0.015	0.013	0.016	0.022	0.014	0.014	0.017						
X _F	0.151	0.185	0.163	0.157	0.165	0.155	0.148	0.156	0.176	0.197	0.154	0.169	0.133	0.145	0.214	0.209	0.226						
X _{OH}	0.836	0.800	0.822	0.828	0.820	0.830	0.838	0.830	0.809	0.787	0.830	0.818	0.851	0.833	0.772	0.776	0.758						
all iron as Fe																							
OH calculated by stoichiometry																							

Table C6 contd.....

sample No.	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001	971001
analysis No.	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89
zone	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM	UM
distance (cm)	56	56	56	56	56	56	56	56	56	56	56	56	56	56	56	56	56	56
SiO ₂	40.55	41.20	41.61	41.03	41.01	41.44	40.00	41.85	41.08	40.86	41.16	40.84	40.68	40.76	40.99	40.48		
TiO ₂	0.39	0.41	0.38	0.40	0.42	0.35	0.38	0.42	0.37	0.38	0.41	0.35	0.34	0.41	0.39	0.44		
Al ₂ O ₃	14.71	14.84	14.03	14.43	14.80	14.85	14.27	14.09	14.85	14.22	14.43	14.59	14.66	14.46	14.54	14.47		
FeO	0.50	0.48	0.47	0.39	0.40	0.48	0.62	0.46	0.36	0.45	0.49	0.49	0.49	0.41	0.50	0.63		
Cr ₂ O ₃	0.04	0.04	0.00	0.04	0.04	0.02	0.06	0.00	0.05	0.00	0.00	0.01	0.07	0.00	0.00	0.01		
MnO	0.04	0.00	0.00	0.00	0.00	0.03	0.09	0.00	0.00	0.00	0.00	0.03	0.00	0.06	0.03	0.03		
MgO	27.39	27.20	27.37	27.27	26.95	27.07	28.34	27.61	27.14	26.75	27.12	26.95	27.27	26.69	26.98	26.88		
CaO	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.05	0.03	0.00	0.00	0.00		
Na ₂ O	0.51	0.53	0.49	0.55	0.73	0.45	0.46	0.48	0.47	0.49	0.49	0.58	0.47	0.53	0.46	0.46		
K ₂ O	9.83	9.66	9.86	9.70	9.77	9.68	8.76	9.60	9.50	9.55	9.84	9.57	9.27	9.86	9.86	9.61		
BaO	0.21	0.23	0.07	0.03	0.23	0.05	0.14	0.13	0.21	0.09	0.21	0.00	0.36	0.09	0.15	0.21		
F	1.91	2.04	1.98	1.97	1.82	1.95	1.75	1.92	1.87	1.94	1.92	2.24	1.92	1.66	2.10	1.93		
Cl	0.24	0.26	0.29	0.27	0.44	0.20	0.28	0.24	0.23	0.27	0.24	0.26	0.26	0.26	0.25	0.23		
Total	96.32	96.88	96.56	96.08	96.60	96.56	95.15	96.83	96.14	94.99	96.30	95.94	95.82	95.19	96.25	95.39		
formula on the basis of 22 oxygens																		
Si	5.607	5.649	5.723	5.667	5.652	5.686	5.576	5.729	5.665	5.705	5.683	5.648	5.638	5.691	5.662	5.645		
Ti	0.041	0.042	0.039	0.041	0.043	0.036	0.040	0.044	0.040	0.040	0.042	0.036	0.036	0.043	0.041	0.046		
Al	2.397	2.398	2.274	2.349	2.404	2.401	2.344	2.273	2.413	2.340	2.348	2.378	2.395	2.379	2.367	2.378		
Al ^{IV}	2.393	2.351	2.274	2.333	2.348	2.314	2.344	2.271	2.335	2.295	2.317	2.352	2.362	2.309	2.338	2.355		
Al ^{VI}	0.005	0.047	0	0.016	0.055	0.088	0	0.003	0.078	0.045	0.031	0.025	0.033	0.071	0.029	0.024		
Fe	0.057	0.055	0.054	0.045	0.046	0.055	0.073	0.052	0.042	0.052	0.056	0.057	0.057	0.048	0.058	0.074		
Cr	0.004	0.004	0.000	0.004	0.004	0.002	0.007	0.000	0.006	0.000	0.000	0.001	0.007	0.000	0.000	0.002		
Mn	0.005	0.000	0.000	0.000	0.000	0.003	0.010	0.000	0.000	0.000	0.000	0.003	0.000	0.008	0.003	0.004		
Mg	5.647	5.560	5.612	5.615	5.537	5.537	5.890	5.635	5.579	5.568	5.582	5.556	5.635	5.556	5.556	5.589		
Ca	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.007	0.004	0.000	0.000	0.000		
Na	0.137	0.141	0.132	0.148	0.195	0.120	0.125	0.127	0.126	0.132	0.132	0.155	0.127	0.144	0.123	0.123		
K	1.734	1.690	1.730	1.709	1.717	1.694	1.558	1.676	1.671	1.701	1.733	1.688	1.639	1.756	1.737	1.710		
Ba	0.011	0.012	0.004	0.002	0.012	0.003	0.008	0.007	0.011	0.005	0.011	0.000	0.020	0.005	0.008	0.012		
F	0.835	0.884	0.861	0.860	0.793	0.846	0.771	0.831	0.815	0.856	0.838	0.980	0.841	0.733	0.917	0.851		
Cl	0.057	0.060	0.068	0.063	0.102	0.047	0.065	0.057	0.053	0.064	0.055	0.060	0.061	0.062	0.058	0.053		
OH	3.108	3.056	3.071	3.077	3.105	3.107	3.163	3.112	3.131	3.080	3.107	2.961	3.098	3.205	3.025	3.096		
X _{Mg}	0.990	0.990	0.990	0.992	0.992	0.990	0.988	0.991	0.993	0.991	0.990	0.990	0.990	0.992	0.990	0.987		
X _{Fe}	0.010	0.010	0.010	0.008	0.008	0.010	0.012	0.009	0.007	0.009	0.010	0.010	0.010	0.008	0.010	0.013		
X _{Cl}	0.014	0.015	0.017	0.016	0.026	0.012	0.016	0.014	0.013	0.016	0.014	0.015	0.015	0.016	0.015	0.013		
X _F	0.209	0.221	0.215	0.215	0.198	0.212	0.193	0.208	0.204	0.214	0.210	0.245	0.210	0.183	0.229	0.213		
X _{OH}	0.777	0.764	0.768	0.769	0.776	0.777	0.791	0.778	0.783	0.770	0.777	0.740	0.774	0.801	0.756	0.774		
all iron as Fe																		
OH calculated by stoichiometry																		

Table C9. Chemistry of biotite in zone C (distance is referred to as from the physical boundary between granulite and zone C)

sample No.	9806	9806	9806	9806	9806
analysis No.	60	62	70	71	77
zone	C	C	C	C	C
distance (cm)	34	34	34	34	34
SiO ₂	37.33	36.53	37.50	38.27	37.26
TiO ₂	2.66	2.67	2.68	2.84	2.62
Al ₂ O ₃	17.99	17.89	18.11	17.95	17.85
FeO	2.77	2.78	2.44	2.18	3.26
Cr ₂ O ₃	0.00	0.05	0.05	0.01	0.00
MnO	0.01	0.00	0.01	0.02	0.05
MgO	22.50	21.74	23.08	23.48	21.98
CaO	0.01	0.00	0.00	0.00	0.01
Na ₂ O	0.13	0.10	0.12	0.09	0.10
K ₂ O	10.17	9.97	10.30	10.36	10.25
BaO	0.39	0.45	0.43	0.52	0.33
F	1.38	1.30	1.45	1.56	1.74
Cl	0.13	0.12	0.12	0.12	0.09
Total	95.47	93.60	96.28	97.40	95.54
formula on the basis of 22 oxygens					
Si	5.285	5.277	5.261	5.300	5.283
Ti	0.283	0.290	0.283	0.296	0.279
Al	3.001	3.046	2.994	2.929	2.983
Al ^{IV}	2.715	2.723	2.739	2.700	2.717
Al ^{VI}	0.286	0.323	0.256	0.229	0.266
Fe	0.328	0.336	0.286	0.252	0.387
Cr	0.000	0.005	0.005	0.002	0.000
Mn	0.001	0.000	0.001	0.002	0.006
Mg	4.749	4.682	4.828	4.848	4.646
Ca	0.002	0.000	0.000	0.000	0.002
Na	0.037	0.027	0.032	0.024	0.028
K	1.837	1.837	1.843	1.830	1.854
Ba	0.022	0.025	0.024	0.028	0.019
F	0.617	0.596	0.643	0.683	0.780
Cl	0.031	0.030	0.029	0.027	0.021
OH	3.352	3.374	3.328	3.290	3.199
X _{Al^{VI}}	0.935	0.933	0.944	0.951	0.923
X _{Fe}	0.065	0.067	0.056	0.049	0.077
X _{Cl}	0.008	0.007	0.007	0.007	0.005
X _F	0.154	0.149	0.161	0.171	0.195
X _{OH}	0.838	0.844	0.832	0.822	0.800
all iron as Fe					
OH calculated by stoichiometry					

Table C11. Chemistry of biotite in siliceous granulites (distance is referred to as from the physical contact of granulite)

sample No.	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708	9708				
analysis No.	28	30	31	35	37	39	43	45	47	85	87	89	92	97	99	101	103	107				
zone	granulite	granulite	granulite	granulite	granulite	granulite	granulite	granulite	granulite	granulite	granulite	granulite	granulite	granulite	granulite	granulite	granulite	granulite				
distance (cm)	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	-2	-2	-2	-2	-2				
SiO ₂	36.76	37.48	37.62	37.92	36.84	37.23	36.28	37.67	37.52	36.21	37.14	37.46	37.04	37.39	37.09	38.06	37.56	37.17				
TiO ₂	5.10	4.65	4.74	5.40	5.40	5.73	5.36	5.57	5.47	5.18	5.99	5.74	5.32	5.23	5.54	5.77	5.52	5.76				
Al ₂ O ₃	13.65	14.03	13.77	13.80	13.97	14.10	13.24	13.87	13.75	13.21	13.57	13.71	13.69	13.03	13.39	13.76	13.58	13.75				
FeO	13.93	14.54	14.42	14.81	14.69	14.89	15.82	14.98	15.08	14.11	14.76	14.64	14.63	14.62	14.40	15.03	15.00	15.26				
Cr ₂ O ₃	0.06	0.10	0.06	0.08	0.11	0.03	0.06	0.06	0.05	0.03	0.05	0.02	0.10	0.06	0.02	0.02	0.08	0.04				
MnO	0.19	0.13	0.21	0.12	0.16	0.13	0.18	0.12	0.18	0.18	0.23	0.15	0.20	0.18	0.17	0.14	0.19	0.19				
MgO	14.48	14.84	15.10	14.76	14.49	14.45	13.91	14.43	14.30	14.01	14.34	14.70	14.57	13.99	14.07	14.43	14.23	14.22				
CaO	0.04	0.09	0.00	0.00	0.00	0.03	0.06	0.00	0.00	0.07	0.01	0.00	0.05	0.18	0.00	0.00	0.02	0.00				
Na ₂ O	0.23	0.14	0.23	0.29	0.17	0.18	0.38	0.20	0.13	0.27	0.37	0.17	0.13	0.21	0.20	0.18	0.24	0.18				
K ₂ O	9.23	9.43	9.51	9.52	9.39	9.55	9.04	9.44	9.36	9.17	9.36	9.61	9.30	8.79	9.37	9.67	9.57	9.60				
BaO	0.25	0.38	0.45	0.39	0.30	0.43	0.30	0.37	0.30	0.21	0.15	0.36	0.32	0.18	0.28	0.31	0.14	0.31				
F	1.58	1.91	1.71	1.71	1.60	1.81	1.44	1.52	1.45	1.65	1.68	1.38	1.75	1.85	1.58	1.56	1.57	1.79				
Cl	0.36	0.37	0.38	0.44	0.35	0.37	0.42	0.35	0.34	0.36	0.31	0.34	0.31	0.39	0.32	0.33	0.35	0.35				
Total	95.85	98.10	98.20	99.24	97.47	98.92	96.49	98.58	97.93	94.65	97.95	98.27	97.41	96.10	96.42	99.25	98.04	98.61				
							formula on the basis of 22 oxygens															
Si	5.470	5.460	5.480	5.469	5.412	5.397	5.424	5.470	5.484	5.471	5.427	5.458	5.440	5.546	5.498	5.489	5.486	5.415				
Ti	0.571	0.510	0.519	0.586	0.597	0.625	0.603	0.608	0.601	0.589	0.658	0.629	0.588	0.583	0.618	0.626	0.606	0.631				
Al	2.394	2.409	2.364	2.346	2.419	2.409	2.333	2.374	2.369	2.352	2.337	2.354	2.370	2.278	2.339	2.339	2.338	2.361				
Al ^{IV}	2.394	2.409	2.364	2.346	2.419	2.409	2.333	2.374	2.369	2.352	2.337	2.354	2.370	2.278	2.339	2.339	2.338	2.361				
Al ^{VI}	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0				
Fe	1.733	1.771	1.757	1.786	1.805	1.805	1.978	1.819	1.843	1.783	1.803	1.784	1.797	1.813	1.785	1.812	1.832	1.859				
Cr	0.007	0.012	0.007	0.009	0.012	0.003	0.007	0.006	0.005	0.003	0.006	0.003	0.012	0.007	0.002	0.002	0.009	0.004				
Mn	0.024	0.017	0.026	0.015	0.020	0.016	0.023	0.015	0.023	0.023	0.028	0.018	0.025	0.023	0.021	0.016	0.023	0.023				
Mg	3.212	3.223	3.279	3.174	3.174	3.123	3.100	3.124	3.116	3.156	3.124	3.193	3.190	3.094	3.109	3.102	3.099	3.088				
Ca	0.006	0.014	0.000	0.000	0.000	0.004	0.009	0.000	0.000	0.011	0.002	0.000	0.008	0.028	0.000	0.000	0.003	0.000				
Na	0.065	0.040	0.064	0.082	0.049	0.050	0.109	0.056	0.037	0.078	0.105	0.047	0.036	0.060	0.056	0.051	0.067	0.050				
K	1.752	1.752	1.767	1.752	1.760	1.766	1.724	1.749	1.745	1.767	1.745	1.786	1.742	1.663	1.772	1.779	1.783	1.784				
Ba	0.014	0.022	0.026	0.022	0.017	0.024	0.018	0.021	0.017	0.012	0.008	0.021	0.018	0.010	0.016	0.018	0.008	0.018				
F	0.743	0.880	0.788	0.780	0.743	0.830	0.681	0.698	0.670	0.788	0.776	0.635	0.813	0.868	0.741	0.711	0.725	0.825				
Cl	0.092	0.092	0.095	0.106	0.088	0.090	0.107	0.087	0.083	0.092	0.077	0.083	0.077	0.099	0.080	0.080	0.087	0.086				
OH	3.165	3.028	3.118	3.114	3.169	3.080	3.212	3.215	3.246	3.119	3.147	3.282	3.110	3.034	3.180	3.208	3.188	3.089				
X _{Mg}	0.650	0.645	0.651	0.640	0.637	0.634	0.611	0.632	0.628	0.639	0.634	0.642	0.640	0.630	0.635	0.631	0.628	0.624				
X _{Fe}	0.350	0.355	0.349	0.360	0.363	0.366	0.389	0.368	0.372	0.361	0.366	0.358	0.360	0.370	0.365	0.369	0.372	0.376				
X _{Cl}	0.023	0.023	0.024	0.027	0.022	0.022	0.027	0.022	0.021	0.023	0.019	0.021	0.019	0.025	0.020	0.020	0.022	0.021				
X _F	0.186	0.220	0.197	0.195	0.186	0.207	0.170	0.174	0.168	0.197	0.194	0.159	0.203	0.217	0.185	0.178	0.181	0.206				
X _{OH}	0.791	0.757	0.779	0.778	0.792	0.770	0.803	0.804	0.812	0.780	0.787	0.820	0.777	0.758	0.795	0.802	0.797	0.772				
all iron as Fe																						
OH calculated by stoichiometry																						

Appendix D -Sample List

The following table contains a list of sample numbers and the rocks type referenced in this dissertation. The suffix RU, which is originally labelled in the samples, was not added to the sample numbers in this thesis.

Sample No.	Rock Type	Category
RU 9316	Carbonatized vein	Ultramafic rock
RU 9317	Carbonatized vein	Ultramafic rock
RU 9318	Carbonatized vein	Ultramafic rock
RU 9319	Pale green rock	Ultramafic rock
RU 9319A	Pale green rock	Ultramafic rock
RU 9320 S	Dark green rock	Ultramafic rock
RU 9320	Dark green rock	Ultramafic rock
RU 9327	Blackwall zone	Ultramafic rock
RU 9328	Blackwall zone	Ultramafic rock
RU 9703 A	Dark green rock	Ultramafic rock
RU 9703 B	Dark green rock	Ultramafic rock
RU 9710	Pale green rock	Ultramafic rock
RU 9710 A	Blackwall zone	Ultramafic rock
RU 9710 B	Blackwall zone	Ultramafic rock
RU 9712	Blackwall zone	Ultramafic rock
RU 9716	Dark green rock	Ultramafic rock
RU 9717	Dark green rock	Ultramafic rock
RU 9718	Dark green rock	Ultramafic rock
RU 9725	Blackwall zone	Ultramafic rock
RU 9725A	Dark green rock	Ultramafic Rock
RU 9725B	Dark green rock	Ultramafic Rock
RU 9725C	Dark green rock	Ultramafic Rock
RU 9728	Dark green rock	Ultramafic Rock
RU 9740 L	Pale green rock	Ultramafic rock
RU 9740 M	Pale green rock	Ultramafic rock
RU 9740 N	Pale green rock	Ultramafic rock
RU 9741	Pale green rock	Ultramafic rock
RU 9743	Pale green rock	Ultramafic rock
RU 9744 L	Pale green rock	Ultramafic rock
RU 9744 M	Pale green rock	Ultramafic rock
RU 9744 N	Pale green rock	Ultramafic rock
RU 9803	Dark green rock	Ultramafic rock
RU 9807	Blackwall zone	Ultramafic rock
RU 9821	Pale green rock	Ultramafic rock
RU 9822	Dark green rock	Ultramafic rock
RU 9824	Dark green rock	Ultramafic rock
RU 9829	Blackwall zone	Ultramafic rock
RU 9830	Blackwall zone	Ultramafic rock

Sample No.	Rock Type	Category
RU 9307 A	Zone A, B	Metasomatic reaction zones
RU 9307 B	Zone C	Metasomatic reaction zones
RU 9310	Zone C	Metasomatic reaction zones
RU 9310A	Zone C	Metasomatic reaction zones
RU 9311A	Zone A, B	Metasomatic reaction zones
RU 9311B	Zone C	Metasomatic reaction zones
RU 9312 A	Zone A, B	Metasomatic reaction zones
RU 9312 B	Zone C	Metasomatic reaction zones
RU 9713	Zone C	Metasomatic reaction zones
RU 9806	Zone A, B	Metasomatic reaction zones
RU 9806 SL	Zone A, B	Metasomatic reaction zones
RU 9806 SM	Zone A, B	Metasomatic reaction zones
RU 9806 SN	Zone A, B	Metasomatic reaction zones
RU 9806 CL	Zone C	Metasomatic reaction zones
RU 9806 CM	Zone C	Metasomatic reaction zones
RU 9806 CN	Zone C	Metasomatic reaction zones
RU 9809	Zone A, B, C	Metasomatic reaction zones
RU 9827	Zone A, B, C	Metasomatic reaction zones
RU 9828	Zone A, B, C	Metasomatic reaction zones
RU 9828A	Zone A, B, C	Metasomatic reaction zones
RU 9301	Zone D	Metasomatic reaction zones
RU 9302	Zone D	Metasomatic reaction zones
RU 9303	Zone D	Metasomatic reaction zones
RU 9322	Zone D	Metasomatic reaction zones
RU 9323	Zone D	Metasomatic reaction zones
RU 9324	Zone D	Metasomatic reaction zones
RU 9350	Zone D	Metasomatic reaction zones
RU 9706	Zone D	Metasomatic reaction zones
RU 9727	Zone D	Metasomatic reaction zones
RU 9701	Zone D	Metasomatic reaction zones
RU 9702	Zone D	Metasomatic reaction zones
RU 9801	Zone D	Metasomatic reaction zones
RU 9805 L	Zone D	Metasomatic reaction zones
RU 9805 M	Zone D	Metasomatic reaction zones
RU 9805 N	Zone D	Metasomatic reaction zones
RU 9805 AL	Zone D	Metasomatic reaction zones
RU 9805 AM	Zone D	Metasomatic reaction zones
RU 9805 AN	Zone D	Metasomatic reaction zones
RU 9810	Zone D	Metasomatic reaction zones
RU 9811	Zone D	Metasomatic reaction zones
RU 9813	Zone D	Metasomatic reaction zones
RU 9821	Zone D	Metasomatic reaction zones
RU 9825	Zone D	Metasomatic reaction zones
RU 9826	Zone D	Metasomatic reaction zones
RU 9827	Zone D	Metasomatic reaction zones

Sample No.	Rock Type	Category
RU 9703	Metabasite	Granulite
RU 9707 L	Metabasite	Granulite
RU 9707 M	Metabasite	Granulite
RU 9707 N	Metabasite	Granulite
RU 9708B	Charnockite	Granulite
RU 9708 C	Metabasite	Granulite
RU 9708 A	Garnet-biotite gneiss	Granulite
RU 9708 L	Garnet-biotite gneiss	Granulite
RU 9708 M	Garnet-biotite gneiss	Granulite
RU 9708 N	Garnet-biotite gneiss	Granulite
RU 9715	sillimanite-biotite gneiss	Granulite
RU 9721	Charnockite	Granulite
RU 9723	Charnockite	Granulite
RU 9722	Garnet-biotite gneiss	Granulite
RU 9801	Charnockite	Granulite
RU 9802	Charnockite	Granulite
RU 9804	Charnockite	Granulite
RU 9804 A	Charnockite	Granulite
RU 9814	Charnockite	Granulite
RU 9815	Migmatitized garnet-Bt gneiss	Migmatite
RU 9816	Charnockite	Granulite
RU 9817 A	Charnockite	Granulite
RU 9817 B	Charnockite	Granulite
RU 167	Calc Silicate Gneiss	Marble
RU 9314	Calc Silicate Gneiss	Marble
RU 9329	Calc Silicate Gneiss	Marble
RU 9701	Calc Silicate Gneiss	Marble
RU 9714	Calc Silicate Gneiss	Marble
RU 9724	Calc Silicate Gneiss	Marble
RU 9724A	Calc Silicate Gneiss	Marble
RU 9724B	Calc Silicate Gneiss	Marble
RU 9725A	Scapolite-plagioclase-scheelite	Retrograded overprints
RU 9726	Calc Silicate Gneiss	Marble
RU 9726 A	Scapolite-plagioclase-scheelite	Retrograded overprints
RU 9825 A	Scapolite-plagioclase-scheelite	Retrograded overprints
RU 9823	Quartz-feldspar gneiss	Pegmatite