

PYROXENE EQUILIBRIA IN ULTRAMAFIC ROCKS

by

TAKESHI MORI

Thesis submitted for the degree of
Doctor of Philosophy

Australian National University

October 1976.

Data and arguments presented in this thesis are my own unless
otherwise indicated.

Takeshi Mori
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Takeshi Mori

ACKNOWLEDGEMENTS

I am deeply indebted to my supervisor Dr D.H. Green for the continuous discussions, advice and encouragement without which this thesis would not have been finished.

Many staff and colleagues in the Research School of Earth Sciences and visitors participated in numerous discussions, which were invaluable to me. They are Dr G.M. Biggar (Univ. Edinburgh), Dr J.N. Boland, G. Brey, Dr R.S. Coe (Univ. California), D.J. Ellis, K.L. Harris, Dr B.J. Hensen (Univ. New South Wales), Dr I.A. Nicholls, Dr C.T. Prewitt (SUNY, Stony Brook), Dr A. Raheim, Prof. A.E. Ringwood, Dr J.R. Smyth (Lunar Sci. Inst.), and Prof. J.F.G. Wilkinson (Univ. New England).

During the course of study, I was given the opportunity to present a paper at the International Conference on Geothermometry and Geobarometry at Pennsylvania State University. During this occasion and a subsequent U.S. - Japan study trip, I met and enjoyed discussions with Dr F.R. Boyd and Dr I. Kushiro (Geophys. Lab.), Dr M.J. O'Hara (Univ. Edinburgh), M.Obata (M.I.T.), Dr S. Banno (Kanazawa Univ.), and Dr K. Aoki (Tohoku Univ.). The U.S. trip was subsidized by the N.S.F. grant of the United States through the courtesy of Dr A.L. Boettcher (Penn. State Univ.).

M. Obata and Dr S. Banno also continuously inspired me with many correspondences.

The ultramafic nodules in Lesotho kimberlites were donated by Prof. A.J.R. White (La Trobe Univ.).

Many individuals contributed to this project through their technical assistance and the patient instructions they gave me in the use of apparatus. I particularly thank W.O. Hibberson and A. Major (high pressure experiments), N.G. Ware (microprobe analysis), E.H. Pedersen (sample preparation), and P.H. Beasley and J.H. Pennington (X-ray techniques).

Dr R.A. Eggleton (Department of Geology) kindly allowed access to a Guinier camera. The typing of the manuscript was done by P.E. Foot.

It was my delight to have worked with these people, and their contributions are most gratefully acknowledged. This study was made possible by the generous support of an Australian National University scholarship.

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CHAPTER 1

INTRODUCTION

Thesis Scope and Objectives

Much geological activity observed on the Earth's surface has, however remote, an ultimate cause inside the Earth, particularly within the upper mantle where various kinds of ultramafic rocks are believed to be dominant. There is compelling evidence for ultramafic rocks as the dominant component of the upper mantle. Major petrological arguments among them are:

- 1) Ultramafic rocks with high pressure mineral assemblage occur as nodules in kimberlites and basalts
- 2) The majority of meteorites (random samples of extraterrestrial planet bodies) have similar bulk compositions to those of the nodules
- 3) Ultramafic compositions have the capability of producing the variety of basaltic magmas as shown in partial melting experiments of ultramafic rocks at high pressures.

Therefore it is not surprising that the ultramafic rocks have attracted many researchers. My thesis is a contribution to this research topic.

Ultramafic rocks observed at the Earth's surface dominantly occur as intrusives, most of which are often termed alpine type. Mineral constituents are rather simple: most of the rocks are primarily composed of some minerals among olivine, orthopyroxene, Ca-rich clinopyroxene, spinel, garnet, plagioclase and amphibole.

The other major occurrences are as nodules in magmas ranging from alkali olivine basalt to kimberlite. Nodules in basalts are dominantly spinel lherzolite and have world-wide occurrence. Kimberlites, almost entirely confined to shields of continents, occur as diatremes and dykes. Though they are much less significant in volume than basalts, they contain abundant nodules, mainly of garnet lherzolites and relatively minor eclogites.

Discrimination of plagioclase and amphibole as minor constituents of rather shallow origin leaves olivine, orthopyroxene, clinopyroxene, spinel and garnet as the minerals of major importance. This thesis deals with these minerals and consequently spinel lherzolite and garnet lherzolite as rocks of main interest.

In the recent history of ultramafic petrology, two main streams can be noticed: geological - petrological and experimental approaches. Both have long histories of their own. However, the fact that the two streams are easily recognizable indicates some gap between them. The research project was intended to fill this gap from both sides by covering both experimental study of phase equilibria among the five minerals and petrological study of natural lherzolites. The latter covered garnet lherzolite nodules in Lesotho kimberlites, spinel lherzolite nodules in Tasmanian basalts, Lizard peridotites (high temperature intrusive) and Mt. Higasi-Akai peridotites (low temperature intrusive). This thesis is, however, mainly devoted to the experimental study. Aspects of the petrological studies are only briefly referred to in chapters and appendices. The emphasis in my experimental studies has been put on phase equilibria of pyroxenes. This is because of the wide geological occurrences, diversity of chemical composition and variety of structural type of pyroxenes. Phase equilibria of pyroxenes and the other minerals will be clarified in the laboratory and will be compared to those in natural lherzolites. The natural lherzolites will be better understood in this way - and this is the aim of the thesis.

Thesis organization

Chapters and appendices 5 and 6 are written in paper form with references given at the end of each chapter or appendix. In fact, all those parts except chapters 1 (introduction) and 7 (conclusions) have been either published already or have been submitted for

publication.

The chapters are put in a logical order, that is, an order of compositional approach to natural lherzolites. This order is also the order in which the papers have been published. Study was, however, not carried out in this order: the experimental study on garnet lherzolites (Chapter 6) was completed at the earliest stage of the course, and it was the inability to reconcile this study with published data and inferences from simple systems which in part led to the restudy of the CaO-MgO-SiO_2 system and the approach from simple system to more complex systems.

Chapter 2 deals with experimental study of pyroxene equilibria in the simplest system of $\text{Mg}_2\text{Si}_2\text{O}_6\text{-CaMgSi}_2\text{O}_6$. This study was expanded into Chapter 3 taking SiO_2 as an independent component. The system with additional FeO is described in Chapter 4. Equilibria of olivine, orthopyroxene, clinopyroxene and spinel in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ are discussed in Chapter 5. This chapter also deals with a similar topic in a natural rock system. Chapter 6 is devoted to equilibria among olivine, orthopyroxene, clinopyroxene and garnet in synthetic multicomponent systems and in natural rock systems. Comparisons of phase equilibria between natural rocks and experimental counterparts are made in Chapters 5 and 6.

Three among Chapters 2-6 were written with Dr. D.H. Green as a coauthor. My contribution in these three papers were all the laboratory works unless indicated in the text, and initiative in discussions and writing. Two papers duplicated in Appendices 5 and 6 have been put there because they are not in total harmony with the main theme of the thesis, and more importantly, because I am the last author of those papers. Major contributions were from the coauthors: M.Obata, S. Banno and K. Yokoyama. My contributions in them were part of data collection and participation in discussions.

Appendices also cover numerous microprobe analyses of

coexisting minerals obtained in the laboratory. They are not listed in respective chapters because they are unnecessary for the general readers. However, they are indispensable for the specialists in total understanding of the chapters and in fair judgements of the respective conclusions.

CHAPTER 2

PYROXENES IN THE SYSTEM $\text{Mg}_2\text{Si}_2\text{O}_6 - \text{CaMgSi}_2\text{O}_6$ AT HIGH PRESSURE

TAKESHI MORI and DAVID H. GREEN

ABSTRACT

The enstatite-diopside solvus in the system $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ has been experimentally determined within the pressure range 5-40 kbars and the temperature range 900-1500°C. Experiments involving reversal of the phase boundaries by unmixing from glass starting material and by reaction of pure clinoenstatite and diopside showed difficulty in achieving equilibration due to persistence of metastable, subcalcic clinopyroxene and to the sluggishness of reaction rate. The experimental data showed that the temperature dependence of the diopside limb is less than previously accepted. At 1500°C and 30 kbars subcalcic diopside found by Davis and Boyd (1966) is shown to be metastable with respect to enstatite and more calcic diopside of composition $\text{En}_{42.3}\text{Di}_{57.7}$. The solvus widens with increasing pressure between 5 and 40 kbars at 1200°C, but at 900°C the pressure effect on the solvus is very small. The stability relationships of the four pyroxenes, protoenstatite, enstatite, iron-free pigeonite and diopside are summarized, based on data from the literature and the present study.

INTRODUCTION

Previous studies [1-7] have shown that the solvus between enstatite and diopside in the system $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ narrows with increasing temperature and suggest that the pressure effect on the solvus is small and may be opposite to that of temperature. However, because of the possible uncertainty of measurement and some scattering of the experimental data, the pressure effect on the solvus remains uncertain. A further problem at high pressure and temperature is the strong curvature of the diopside limb above 1400°C at 30 kbars [4] with diopside becoming subcalcic ($\text{En}_{70}\text{Di}_{30}$ in mole %, at 1500°C and 30 kbars). Kushiro [3] suggested that these subcalcic clinopyroxenes might be pigeonitic.

In the present investigation we have concentrated our experiments

on accurate determination of the pressure effect on the solvus from 5 to 40 kbars at 1200°C and on delineation of the temperature dependence of the solvus at 30 kbars. The practicability of the project was also dependent on the high accuracy and reproducibility of analysis on small grains, combined with excellent optics and contemporaneous analysis for all elements attainable with TPD electron probe and energy dispersive analytical system [8].

PREPARATION OF STARTING MATERIALS

Several kinds of starting materials were prepared.

En₅₀Di₅₀ glass

Three separate glasses of the same composition, En₅₀Di₅₀ (mole %), were prepared from A.R. grade chemicals of SiO₂, MgO, and CaCO₃. Weighed mixtures of the reagents were melted on an iridium-strip heater and were stirred by a platinum rod to homogenize, then quenched by cutting off the power and simultaneously cooling by compressed air. The glasses were ground to average 25-μm grain size. One piece of glass from each batch was polished and examined by microscope, microprobe and, in some cases, X-ray powder photography. Two batches among the three contained a trace amount (<1%) of quench clinopyroxene and olivine. Compositions of quenched clinopyroxene were similar to those of the host glasses. The third glass was free from any crystals. Composition of the three glasses varied from En_{48.4}Di_{51.6} to En_{49.6}Di_{50.4} with an inhomogeneity of ±0.2 to ±0.5 mole % end member.

En₈₀Di₂₀ glass

A glass with the composition of En₈₀Di₂₀ was made in the same way as above. A trace amount of crystals (≪1%) was found in the glass, but they were not identified because of their scarcity and tiny sizes. Analyzed composition of the glass was En_{81.6}Di_{18.4}.

Synthetic pyroxenes

In some homogenization runs, synthetic diopside (CaMgSi₂O₆) and clinoenstatite (Mg₂Si₂O₆) of Tem-Pres Research Co. were used. Microprobe

analysis showed the presence of trace amount of CaO (<0.05 wt.%) in the clinoenstatite.

SYNTHESIS AND CHEMICAL ANALYSIS OF PYROXENES

The high-pressure apparatus used was a Boyd and England [9] design piston-cylinder device and a pressure correction of -10% of nominal load pressure, using piston-in technique, was applied. This method of correction is based on calibrations on quartz-coesite at 1100°C [10] and albite=jadeite + quartz at 600°C (G. Brey and D.H. Green, unpublished data). Temperature measurement was by Pt/Pt₉₀Rh₁₀ thermocouple with no correction applied for pressure effect on thermocouple emf. Samples were encased in sealed Pt capsules or in Pt capsules with a crimped end in those cases where the catalytic effect of low water-vapour pressures was desired.

Chemical analyses were by means of the TPD-electron probe, with an analysis area of about 3 µm diameter as judged by fluorescence on periclase. The visible fluorescence of the pyroxenes made positioning for analysis easier and more reliable. All relevant elements were measured simultaneously and at least ten analyses were made on each pyroxene phase in every run. Some analyses with structural formulae deviating from stoichiometry were discarded. These were less than 10% of all the analyses.

In some of the homogenization experiments the capsule was loaded with a layer of clinoenstatite in contact with a layer of diopside. A polished thin section across this contact was prepared after the run and the contact between the two pyroxene types was examined optically and with the electron probe.

EXPERIMENTAL RESULTS

The run procedures, products and pyroxene compositions are summarized (Table 1 and brief comments in the Appendix). Pyroxene analyses* are shown (Fig. 1) except for the runs 2,3 and 7 which are of shorter

* A list of pyroxene analyses is obtainable by writing to the authors.

TABLE 1

Details of experiments and chemical ranges of pyroxenes (number of analyses are shown in parentheses)

Run. No.	P (kbars)	T (°C)	Time (hours)	Starting composition	H ₂ O	Products	Chemical range (CaMgSi ₂ O ₆ mole %)	
							orthopyroxene	clinopyroxene
1	40	1200	4	En ₅₀ Di ₅₀	*	EnDi	2.6–5.6 (14)	88.0–89.4 (10)
2	30	1200	0.1	En ₅₀ Di ₅₀	anhy- drous	EnDi		
3	30	1200	0.75	En ₅₀ Di ₅₀	anhy- drous	EnDi	6.0–11.6 (4)	71.2–77.0 (5)
4	30	1200	4	En ₅₀ Di ₅₀	*	EnDi glass	4.8–6.4 (10)	85.8–88.4 (13)
5	30	1200 ²	170	synthetic EnDi	*	EnDi glass	2.2–6.2 (15)	84.2–100.0 (15)
6	10	1200	4	En ₅₀ Di ₅₀	*	EnDi glass (tr)	7.4–10.0 (10)	78.6–82.4 (10)
7	5	1200	4	En ₅₀ Di ₅₀	*	EnDi glass Ol?	9.4–12.2 (10)	71.4–77.6 (10)
8	5	1200	11	En ₅₀ Di ₅₀	*	EnDi glass(tr)	9.6–12.6 (10)	74.8–80.0 (10)
9	30	1500	2.5	En ₅₀ Di ₅₀	*	clinopyrox- ene	45.6–55.0 (12)	
10	30	1200/1500	2.5/2.0	En ₅₀ Di ₅₀	*	EnDi glass (tr)	6.4–10.2 (11)	55.4–67.6 (16)
11	30	1500 ²	3.2	En ₈₀ Di ₂₀	anhy- drous	EnDi Qz?	10.4–11.6 (10)	49.6–57.6 (10)
12	30	1200/1500 ²	2.1/4.2	En ₈₀ Di ₂₀	anhy- drous	EnDi	9.0–10.0 (6)	57.8–68.2 (8)
13	30	900	23	En ₅₀ Di ₅₀	a few %	EnDi Amph	1.6–2.6 (12)	91.0–92.8 (7)
14	30	900	214	synthetic EnDi	3% ¹	EnDi Amph (tr) magnesite (tr)	0.2–1.6 (5)	93.4–99.8 (25)
15	10	900	72	En ₅₀ Di ₅₀	a few %	Qz(tr)	4.2–6.4 (6)	76.4–87.8 (15)
16	10	900	212	synthetic EnDi	4% ¹	EnDi Qz(tr)	1.4–2.8 (9)	93.2–98.8 (11)

* Starting materials were slightly moistened by breathing.

¹ 22% silver oxalate was also added.² In the middle of the experiment indicated temperature decreased possibly due to chemical contamination of the thermocouple, and temperature was then controlled by maintaining power equal to the earlier condition. In run 5, an accidental "correction" of +70°C occurred for less than 1 hour after 100 hours of the experiment.

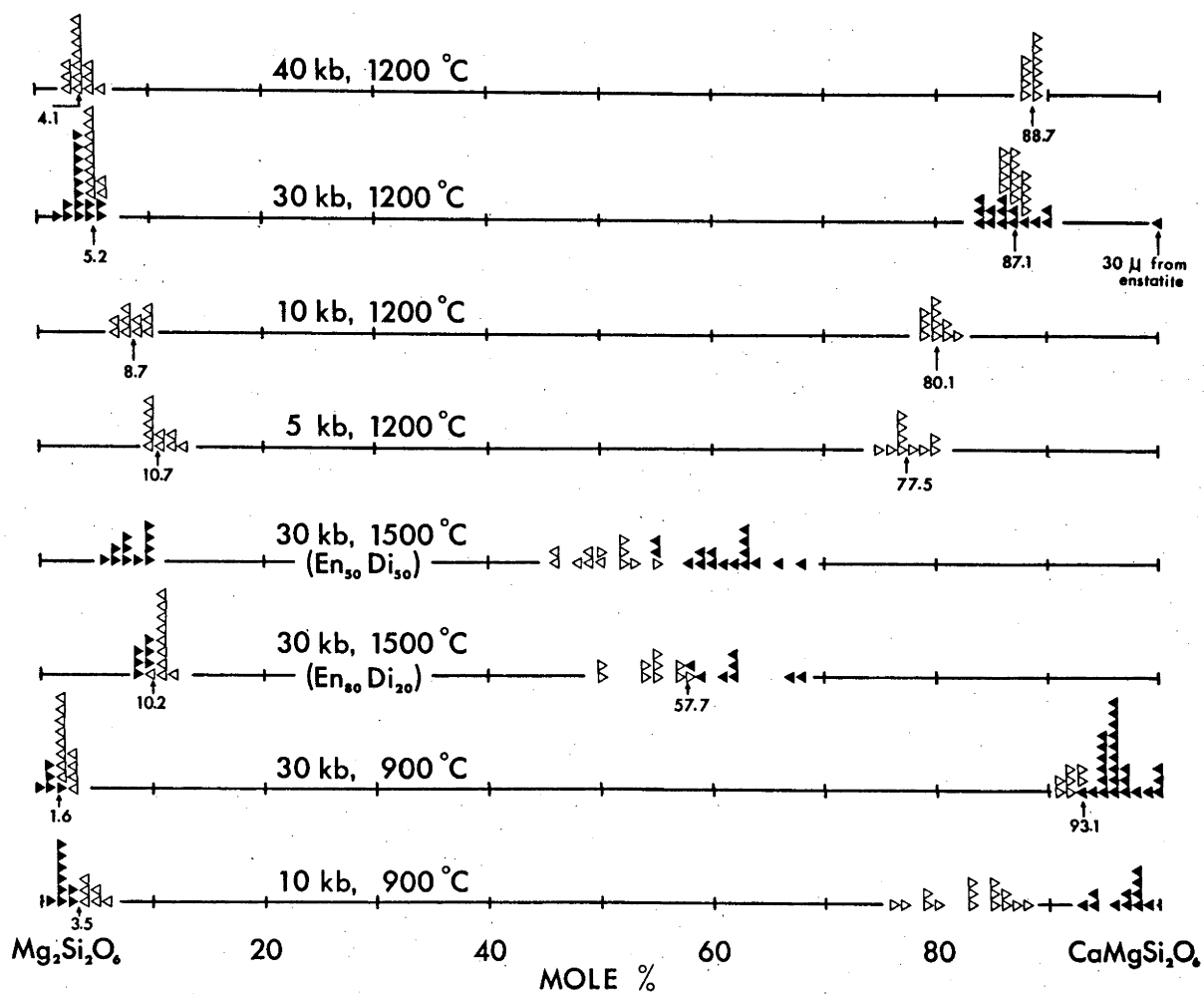


Fig. 1. Microprobe analyses of pyroxenes. Filled and open symbols are of homogenization and unmixing experiments, respectively. Decimal fractions in the raw data have been rounded to the nearest integer. Selected compositions are shown with arrows (see text).

reaction time.

The spread of data in some of the unmixing and homogenization experiments is related to mechanisms and sluggishness of chemical reactions. As shown in run 2, the $\text{En}_{50}\text{Di}_{50}$ glass crystallized both orthopyroxene and clinopyroxene within only 6 minutes at 30 kbars and 1200°C . The glasses found in other experiments with longer run duration are, therefore, not unreacted starting glasses but melts generated by presence of water and equilibrated with pyroxenes. The water-saturated melting point of $\text{En}_{50}\text{Di}_{50}$ is about 1050°C at 30 kbars [7], and water added to or allowed to enter the capsules naturally causes melting at higher temperature. The run duration of 45 minutes at 30 kbars and 1200°C (run 3, Table 1) crystallized orthopyroxene and clinopyroxene of compositions lying between the original bulk composition and the equilibrium compositions. The 4-hour experiment (run 4) gave pyroxenes with a wider composition gap and appears to have reached the equilibrium compositions (see later discussion). Comparison of runs 7 and 8 shows a similar time dependent relationship for pyroxenes crystallizing from glass starting material. Although from these experiments we have no information on the initial steps of crystallization from glass, since even after 6 minutes we have two pyroxenes present, we have obtained further information in Fe-bearing experiments with varying run duration. The crystallization sequence in these runs was firstly to single-phase clinopyroxene with composition similar to that of the starting glass, then nucleation of orthopyroxene and change of clinopyroxene towards the equilibrium composition, as in runs 2-4 and 7,8 in Table 1. It is apparent that a glass with a composition within the pyroxene solvus crystallizes rapidly to form clinopyroxene of compositions similar to the glass composition, then or at the same time orthopyroxene nucleates, and the composition gap between the two pyroxenes widens until the solvus limit is reached.

In contrast to glasses, starting material of synthetic diopside

($\text{CaMgSi}_2\text{O}_6$) and enstatite or clinoenstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$) react inwards until the solvus limits are reached. This is well demonstrated by the experiments in which layers of diopside and clinoenstatite were allowed to react across their boundary surface. In runs 5, 14 and 16, the $\text{CaMgSi}_2\text{O}_6$ content of diopside 30 μm from the boundary was 100%, and rapidly decreased to the boundary zone (10 μm) in which orthopyroxene occurred. The $\text{CaMgSi}_2\text{O}_6$ content of enstatite decreased away from the boundary zone and approached $\text{Mg}_2\text{Si}_2\text{O}_6$ at the other end. Additional examples of the inward reaction of natural pyroxenes towards the solvus are found in Hensen [11].

Thus, a pair of unmixing and homogenization experiments establishes or limits the position of a solvus even if chemical hysteresis remains and the data in either of the experiments are themselves scattered between starting composition and equilibrium composition.

Both unmixing and homogenization experiments were done at 30 kbars and 1200°C, 30 kbars and 900°C, 10 kbars and 900°C, and 30 kbars and 1500°C (Fig. 1), the last of which is separately discussed in the next section. The pair of experiments at 30 kbars and 1200°C yielded an overlap of the data by two experiments (Fig. 1). At 30 and 10 kbars at 900°C, the data could limit positions of solvus within analytical error except for the clinopyroxene limb at 10 kbars and 900°C where either the unmixing or homogenization experiments (or both) did not reach solvus and its position was only bracketted between $\text{En}_{12.2}\text{Di}_{87.8}$ and $\text{En}_{6.8}\text{Di}_{93.2}$.

At 40, 10 and 5 kbars at 1200°C, only unmixing experiments were made. Inferred solvus positions at these conditions are averages of the data.

STABILITY OF SUBCALCIC CLINOPYROXENE AT 30 KBARS AND 1500°C

There are four runs which are relevant to the problem of stability of subcalcic clinopyroxene found by Davis and Boyd [4]: runs 9 and 10 are on $\text{En}_{50}\text{Di}_{50}$, and runs 11 and 12 are on $\text{En}_{80}\text{Di}_{20}$. In runs 10 and 12, the charges were first kept at 1200°C and 30 kbars for a time considered sufficient (runs

2-4) to bring all the pyroxene compositions outside the solvus of 1500°C and 30 kbars, then temperature was increased to 1500°C. Thus, runs 9 and 10, and runs 11 and 12 can be regarded as pairs of unmixing and homogenization experiments. The results of runs 11 and 12 define the solvus very well. Run 9, however, resulted in a single-phase clinopyroxene and is inconsistent with run 10 where two pyroxenes remained and did not homogenize to a single phase. Two analyses of clinopyroxene in run 10 are slightly inconsistent with the solvus defined by runs 11 and 12, but only 15°C difference between them would explain the inconsistency. This choice of the solvus is in agreement with the data of Nehru and Wyllie [7] who carried out synthesis experiments using sintered gel of $\text{En}_{50}\text{Di}_{50}$ as starting material (Fig. 2).

Generally, in unmixing runs yielding two pyroxenes, measured chemical ranges may be attributed to incomplete unmixing reactions, but if the single-phase pyroxene in run 9 were stable, there would be no reason for it to show such a wide chemical range as shown in Fig. 1. In run 11, two pyroxenes appeared within 3.2 hours, a slightly longer run duration than run 9, but the difference in run time appears unlikely to explain the absence of orthopyroxene. It is highly probable that $\text{En}_{50}\text{Di}_{50}$ is within the metastable composition range where Ca-Mg internal diffusion fails to occur at this P - T condition [12].

Further support for the revised position of solvus at 1500°C and 30 kbars is found in a partial melting experiment on natural garnet lherzolite [13]. In this run, clinopyroxene coexists with orthopyroxene as well as olivine, spinel and glass. The composition of the clinopyroxene ($\text{Ca}_{29.3}\text{Mg}_{66.2}\text{Fe}_{4.5}, \text{Al}_2\text{O}_3=5.3\%$) is near to the revised solvus. Since Al_2O_3 solid solution stabilizes a wider solvus [5], correction for the Al_2O_3 effect in their result will move the composition of the clinopyroxene even closer to the solvus defined above. Thus the experiment in the multicomponent system supports the stability and wide solvus between two pyroxenes at 30 kbars and 1500°C in the simple system.

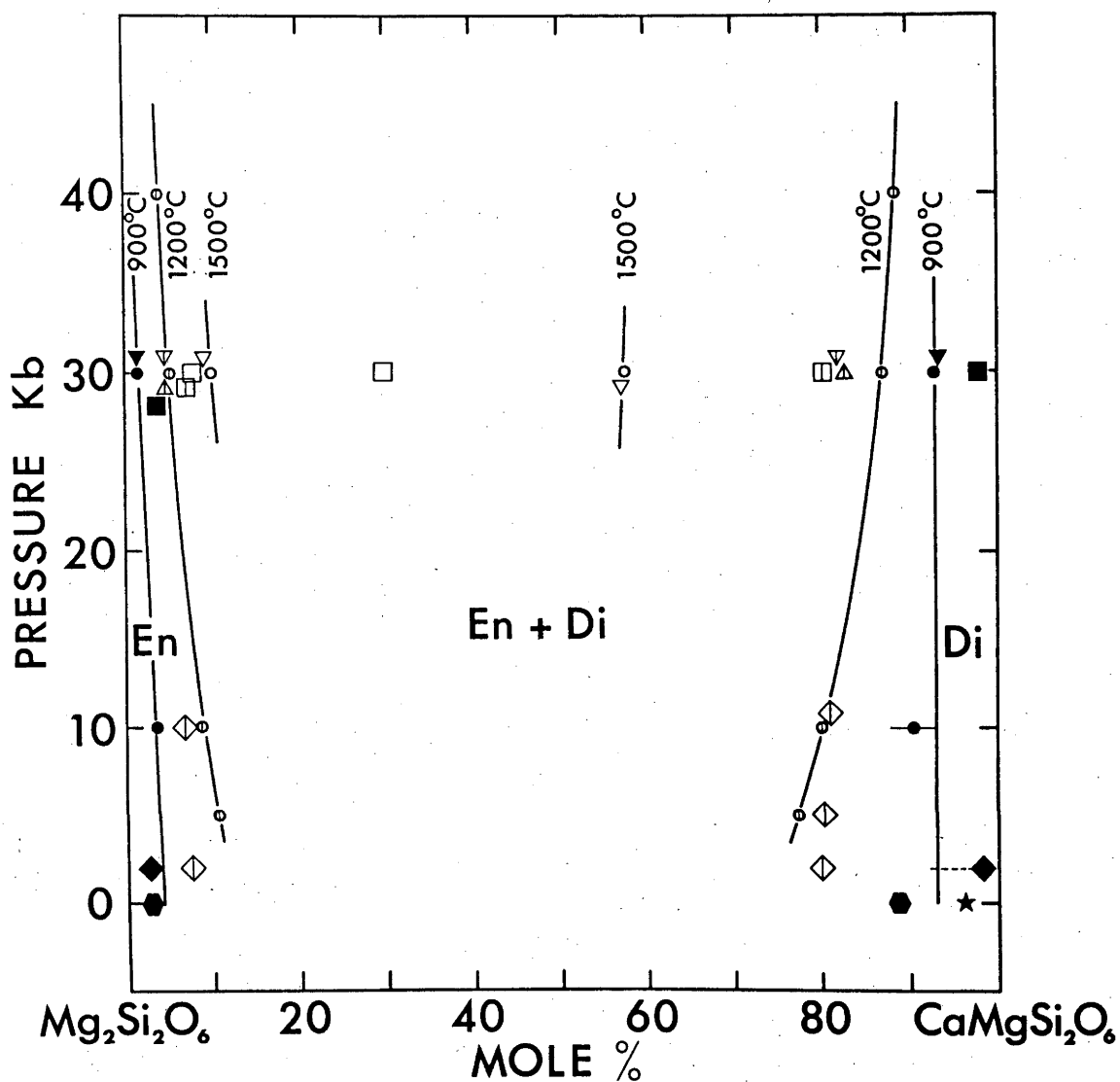


Fig. 2. Pressure-composition diagram of the enstatite-diopside solvus. Data are from Fig. 1 (circle, microprobe), Davis and Boyd [4] (square, optical), Boyd [5] (triangle, microprobe), Boyd and Schairer [1] (star, optical and X-ray), Atlas [14] (hexagon, X-ray), Warner and Luth [6] (diamond, X-ray), and Nehru and Wyllie [7] (inverted triangle, microprobe). Open symbols are at 1500°C, those with vertical line are at 1200°C, and the solid symbols are at 900°C. Some data at 10 and 30 kbars are plotted above or below the actual pressure to avoid confusion. En = enstatite, Di = diopside.

TEMPERATURE AND PRESSURE EFFECTS ON THE ENSTATITE-DIOPSIDE SOLVUS

The positions of the solvus determined in preceding sections and shown in Fig. 1 are plotted on the pressure - composition diagram (Fig. 2) and temperature - composition diagram (Fig. 3). Available data from the literature are also shown. These data were obtained by three methods: optical identification of minerals in experimental charges, X-ray calibration of pyroxene composition, and microprobe analysis of pyroxenes. It should be noted that all the data plotted in both the figures are the respective authors' ultimate selections after statistical treatment or simple curve fittings, and are not their raw data which often deviate from the selections.

Accuracy of the first method depends on the quality of identification of minerals and the spacing of the composition grid employed, and that of X-ray method is ± 1 to ± 3 mole % end member [6,14]. The inconsistency seen among the data including ours should be viewed in relation to the accuracy of the method employed and the type of reaction, i.e. homogenization or unmixing. Particularly, it should be noted that determination of pyroxene composition from homogenization experiments using the X-ray calibration is very uncertain. This is because, in those experiments, chemical hysteresis can hardly be avoided, and the X-ray method will bias towards compositions outside the solvus.

The differences between the various data plotted in Fig. 2 are not entirely within analytical or method-derived error. We will examine particularly the data for the clinopyroxene limb at 1200°C and 30 kbars and at 900°C, 30 kbars to 1 atmosphere. Our reversal experiments at 30 kbars and 1200°C yielded overlapping compositional ranges with the unmixing experiment (run 4) giving strongly clustered data. We consider that the spread of the homogenization (run 5) data to lower diopside contents is due to greater temperature uncertainty in this run (see Table 1). In Fig. 2 we have drawn the solvus at 1200° as a function of pressure as defined by our own data.

At 900°C and 30 kbars our closely bracketted reversal gives a

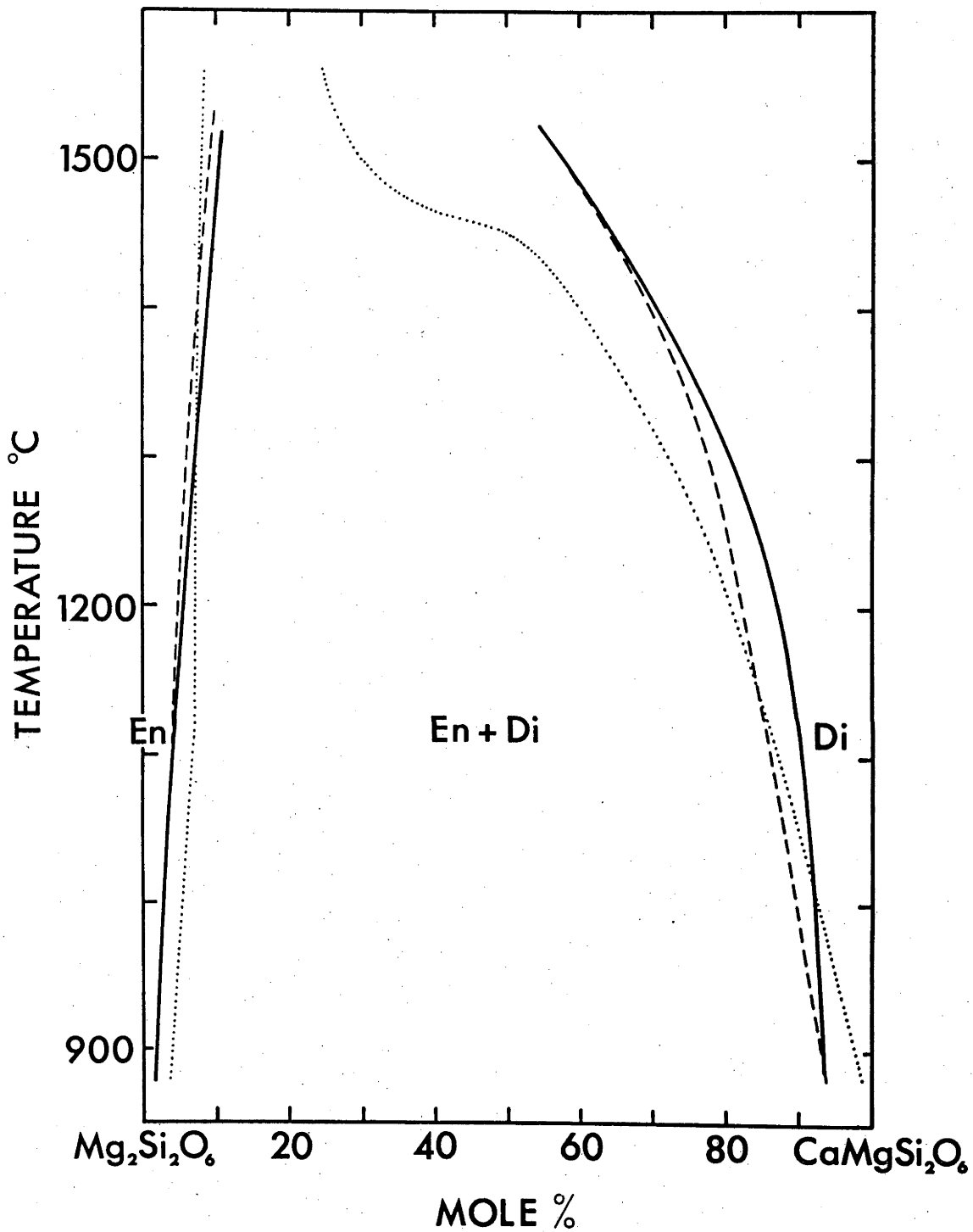


Fig. 3. The enstatite—diopside solvus at 30 kbars. Solid line: our data, dotted line: Davis and Boyd [4], and dashed line: Nehru and Wyllie [7].

clinopyroxene composition coincident with that predicted by extrapolation of Nehru and Wyllie's [7] data (1500-1000°C) and this composition is less calcic than that previously accepted [4]. At 900°C and 10 kbars our data bracket the clinopyroxene limb of the solvus within 5 mole % end member. At 900°C and 2 kbars, earlier data [6] led to selection of a more calcic composition but it should be noted that in their unmixing experiments, Warner and Luth [6] did not obtain clinopyroxene more calcic than $\text{En}_8\text{Di}_{92}$ (Fig. 2). The clinopyroxene limb at 900°C has been drawn through the reversal brackets at 30, 10 and 2 kbars but its extrapolation is then inconsistent with 1-atmosphere data [1,14]. Boyd and Schairer's [1] determination was based on optical identification of phases and some of the crucial phase identifications at and below 900°C were reported as doubtful (queried) [1, table 5]. Their data thus permit the interpretation that the clinopyroxene limb at one atmosphere lies between $\text{En}_{5.3}\text{Di}_{94.7}$ and $\text{En}_{10.7}\text{Di}_{89.3}$. We conclude, in the light of this and earlier studies, that there is little or no pressure effect on the diopside limb of the pyroxene solvus at 900°C from 0 to 30 kbars.

To summarize (Fig. 2), at higher temperature ($\geq 1200^\circ\text{C}$) the pyroxene solvus widens considerably as pressure increases, and at low temperature ($\leq 900^\circ\text{C}$) there is no perceptible pressure effect on the clinopyroxene limb and a slight pressure effect on the orthopyroxene limb. The pressure dependence of the orthopyroxene limb is of the same character as inferred in the Fe-bearing system [11]. Although pressure effects on emf of the thermocouple have not been corrected for and remain uncertain, the correction would raise indicated temperature to higher real values and would thus enhance the widening of the solvus with increasing pressure.

The temperature dependence of the solvus is shown in Figs. 2 and 3 which reaffirm the well-established increase of mutual solubility with increasing temperature. At 30 kbars, however, the shape of the re-determined solvus is very different from that of Davis and Boyd [4] and similar to that of Nehru and Wyllie [7]. Our new data show that the clinopyroxene limb

is less sensitively dependent on temperature between 900 and 1200°C. This means that the pyroxene geothermometer is less effective between 900 and 1200°C at high pressure than previously accepted.

SOME PROBLEMS IN PETROLOGIC APPLICATIONS TO NATURAL PYROXENES

Applying Figs. 2 and 3, one may in theory estimate both pressure and temperature simultaneously from chemistry of coexisting enstatite and diopside. However, this is impractical as the isochemical contour lines for the two pyroxenes are nearly parallel throughout the P - T field except at temperatures above 1200°C where the two lines cross with a rather high angle between them. Even at high temperature, however, the application of this method to natural pyroxenes requires a full understanding of chemical effects in the multicomponent system. Consequently, the enstatite - diopside solvus can be used as a geothermometer only if the pressure of formation is estimated by another method, except in those cases where temperature is so low that the clinopyroxene limb is independent of pressure.

Application of the present results will necessitate revision of many temperature estimates found in the literature, particularly for assemblages of low-temperature peridotites and granulites and for high-pressure, high-temperature assemblages such as peridotite nodules in kimberlites. For example, estimates of temperature in the range 1200 - 1400°C at 30 kbars based on Davis and Boyd [4] would be revised upwards by about 100°C based on Fig. 3. An estimate of 1000°C at 30 kbars would be little changed but estimates of 900°C at 30 kbars would be revised downwards by more than 100°C. We emphasize, however, that data on the multi-component pyroxene system are required before unambiguous P - T determinations can be obtained for natural two-pyroxene assemblages.

PHASE RELATIONS OF PYROXENES IN THE SYSTEM $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$

Not only are enstatite and diopside stable in the system $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$, but at least two more stable phases exist, protoenstatite and pigeonite*. Protoenstatite is restricted to a low-pressure, high-temperature region [2, 16]. Recent work by Smyth [17] reported protoenstatite of the composition $\text{Mg}_2\text{Si}_2\text{O}_6$ is stable up to melting point at 1 atm. Pigeonite appears over a wide P - T range from 1 atm to at least 20 kbars [2, 18, 19].

Three univariant assemblages known to occur are protoenstatite - enstatite - diopside at 1 atm and about 1100°C [1], enstatite - pigeonite - diopside at 17.5 kbars and 1450°C [18], and protoenstatite - pigeonite - diopside at 1 atm and about 1230°C [2]. For conditions for the last assemblage, the temperature, 1276°C [20], was preferred. This choice, in spite of the presence of Al_2O_3 in the system studied by Yang [20] was made because the coexistence of protoenstatite, pigeonite and diopside was confirmed at that temperature, and the Al_2O_3 content of less than 0.5 wt.% in the pyroxenes should have little effect on the temperature of the equilibrium. An invariant assemblage of all the four pyroxenes almost certainly occurs and Warner and Luth [6] estimate this to be at about 2 kbars and 1320°C.

A geometrical arrangement of four univariant lines around the invariant point is obtained following Schreinemakers' method [21]. An assumption here is that the $\text{CaMgSi}_2\text{O}_6$ content of pyroxenes at the invariant point increases in the order protoenstatite, enstatite, pigeonite, diopside. The shaded area in Fig. 4 limits the conditions for the invariant point. This area is partly defined by: (1) demands by the arrangement of the univariant lines, (2) three fixed points noted above, (3) a bracket for the univariant line (Pr) at 5 kbars [18], and (4) stability of enstatite and

* This mineral is called iron-free pigeonite in the literature but the term "pigeonite" is used in this paper for convenience.

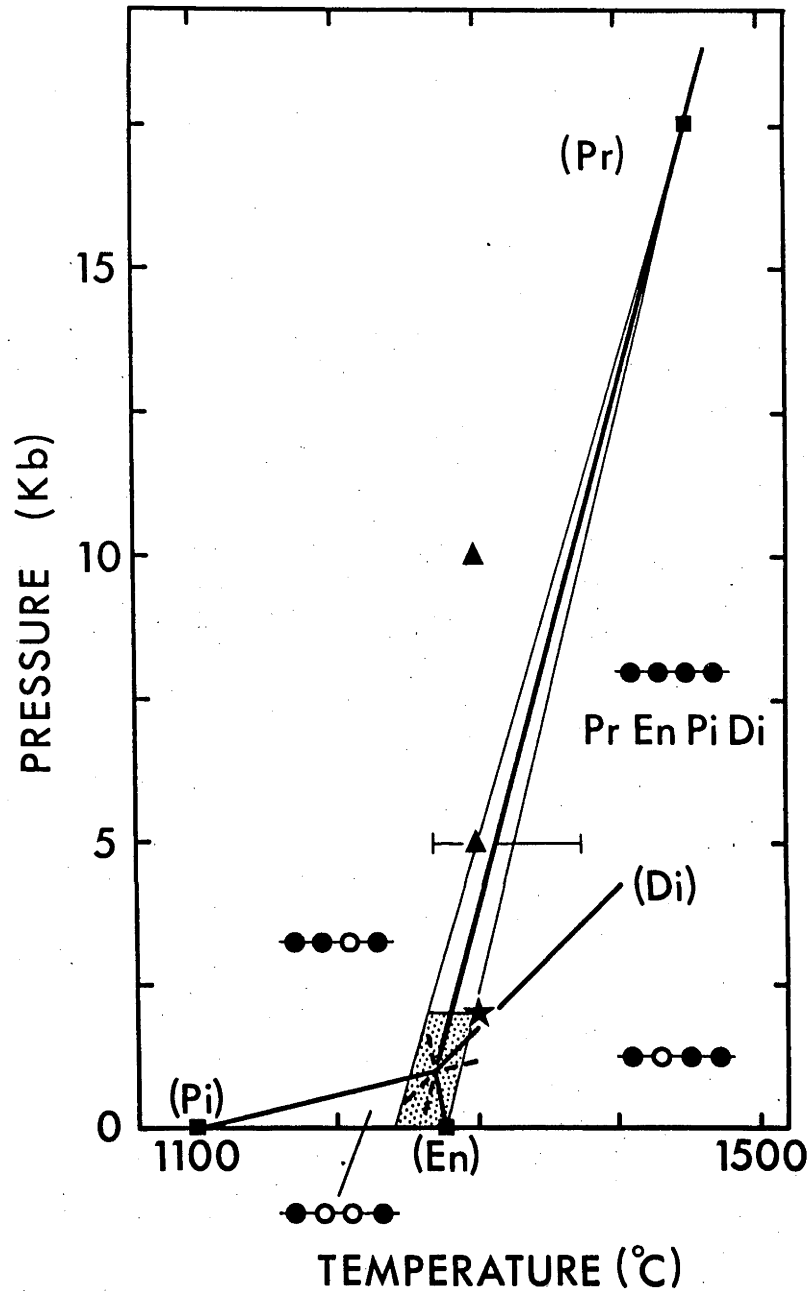


Fig. 4. An arrangement of the univariant lines around the invariant point where protoenstatite, enstatite, pigeonite and diopside coexist. Each line is identified by the missing phase from the invariant assemblage. Composition-assemblage diagrams are shown in each divariant field with, from left to right: Pr = protoenstatite, En = enstatite, Pi = pigeonite, Di = diopside. Open circle: unstable phase, filled circle: stable phase.

Data: squares [1,18,20], a bracket at 5 kbars [18], triangles: enstatite and diopside assemblage is stable [6], star: either enstatite-diopside, or pigeonite-bearing assemblage is stable [6,18]. See text for discussions.

diopside at 10 and 5 kbars and 1300°C [6].

The nature of the stable assemblage at 2 kbars and 1300°C is confusing: it is enstatite and diopside (homogenization experiment) or pigeonite-bearing assemblage (unmixing experiment) [6, 18]. This confusion might imply that a reaction, pigeonite=enstatite+diopside, characteristic of the univariant line (Pr), occurs near 2 kbars and 1300°C. If so, the invariant point will be further restricted to less than 2 kbars.

The deviation of the area thus restricted from Warner and Luth's estimate [6] is small but critical: their value implies that (En) is at a higher temperature than 1320°C at 1 atm [6, Fig. 5]. In fact it is not [2, 20]. The conditions of the invariant point are hereafter referred to as P_0 and T_0 .

It is now easy to draw the geometry of phase diagram at any T - P conditions. Fig. 5A, B shows examples at constant pressure and temperature around P_0 and T_0 . They are only schematic, and partly exaggerated. Fig. 5B is drawn on an assumption that the slope of (En) is negative. A positive slope removes the protoenstatite - diopside solvus from the figure. The detail of the phase relations around P_0 , T_0 must be determined by experiments, which should be concentrated in the shaded area (Fig. 4). However, such experiments will be extremely difficult because of the difficulties in fine P - T control, sluggish reaction rate and appearance of metastable phases.

The univariant line (Pr) will be extrapolated to about 1590°C at 30 kbars (Fig. 4), which means that pigeonite becomes stable at this condition. Thus, as Kushiro [3] suggested, some of the subcalcic clinopyroxenes coexisting with orthopyroxene at high temperatures in the phase diagram by Davis and Boyd [4] are possibly pigeonite and the diopside - pigeonite solvus should appear at temperatures higher than about 1590°C. This interpretation is similar to that for pyroxenes in the system $\text{Fe}_2\text{Si}_2\text{O}_6$ - $\text{CaFeSi}_2\text{O}_6$ at 20 kbars [22].

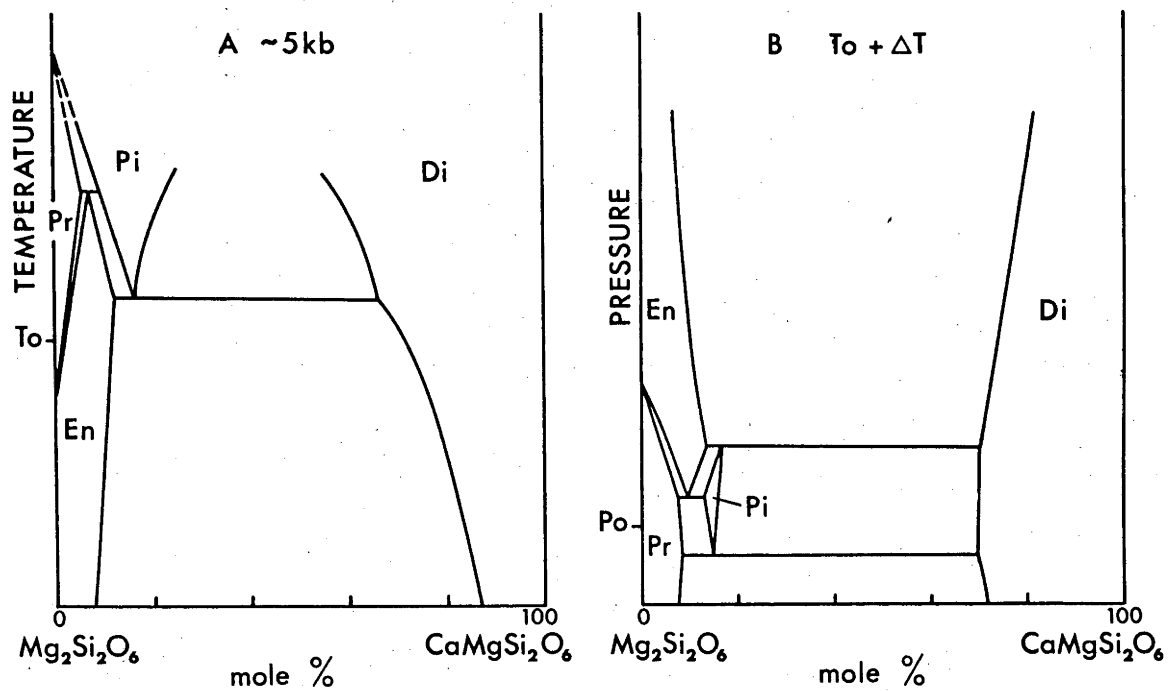


Fig. 5. A. A schematic phase diagram at about 5 kbars. B. A schematic phase diagram at just above T_0 , based on the assumption that the slope of the univariant line (En) is negative as shown in Fig. 4.

APPENDIX. RUN DETAILS

Run 1 (40 kbars, 1200°C unmixing from glass). Enstatite and diopside were commonly euhedral, up to 70 μm in grain size and in some cases in parallel growth or as inclusions one within the other.

Run 2 (30 kbars, 1200°C, unmixing). Within 6 minutes, all the starting glass crystallized into pyroxenes. They were identified optically and by X-ray as minor enstatite and common diopside, but were too small for microprobe analysis.

Run 3 (30 kbars, 1200°C, unmixing). Enstatite and diopside grew up to 20 μm .

Run 4 (30 kbars, 1200°C, unmixing). Enstatite (up to 50 μm) and diopside (up to 20 μm) were subhedral to euhedral. About 20% of glass was present.

Run 5 (30 kbars, 1200°C, homogenization). At the interface between diopside and enstatite layers in the capsule, pyroxenes with two different textures were found, i.e. orthoenstatite and diopside crystals as large as the original synthetic pyroxenes (30 μm), and small pyroxenes ($\leq 8\mu\text{m}$) interpreted as products of new nucleation of pyroxene. Both types of pyroxene were analyzed.

No clinoenstatite remained after the experiment. However, at one corner of the capsule originally occupied by diopside, partial melting occurred and euhedral enstatite (80 μm) were formed. The glass contained 11% Al_2O_3 , 0.3% Na_2O and 0.5% K_2O . This contamination may be due to fracturing of the capsule during the run, with exposure to the ceramic enclosing the capsule. Contamination by Al_2O_3 , Na_2O or K_2O , however, was not detected in the diopside even where directly contacting the glass.

Run 6 (10 kbars, 1200°C, unmixing). Enstatite and diopside were $\leq 30\mu\text{m}$ in grain size and there was a small amount of glass.

Run 7 (5 kbars, 1200°C, 4 hours, unmixing). Enstatite, diopside, glass, and probably minor olivine occurred in anhedral texture.

Run 8 (5 kbars, 1200°C, 11 hours, unmixing). Enstatite ($\leq 30\mu\text{m}$) and diopside ($\leq 15\mu\text{m}$) occurred as subhedral crystals, probably with trace amounts

of glass. Some diopside crystals are simply twinned. The diopside is more calcic than that in run 5 (Table 1) and this run is preferred to run 7.

Run 9 (30 kbars, 1500°C, unmixing). Only clinopyroxene was observed optically, as subhedral grains up to 30 μm in grain size.

Run 10 (30 kbars, 1500°C, homogenization). A glass ($\text{En}_{50}\text{Di}_{50}$) was subjected to 30 kbars and 1200°C for 2.5 hours and then the temperature was raised to 1500°C for 2 hours. From runs 2-4 we infer that the charge crystallized to two pyroxenes with a wide composition gap at 1200°C and that these pyroxenes then approached re-equilibration at 1500°C. Euhedral diopside and enstatite (up to 20 μm) and a trace amount of glass were produced.

Run 11 (30 kbars, 1500°C, unmixing). A glass of $\text{En}_{80}\text{Di}_{20}$ yielded euhedral enstatite (up to 50 μm) with small anhedral or subhedral diopside.

Run 12 (30 kbars, 1500°C, homogenization). The same techniques as for run 10 were used for a glass of $\text{En}_{80}\text{Di}_{20}$ composition. Some enstatite crystals were up to 30 μm long and had parallel growth of diopside. Diopside was generally much smaller and anhedral.

Run 13 (30 kbars, 900°C, unmixing). Enstatite was frequently acicular (up to 70 μm long) while diopside was equant and $\leq 15 \mu\text{m}$. An amphibole ($\text{Ca}_{3.2}\text{Mg}_{3.8}\text{Si}_{8.0}\text{O}_{23}$) occurred and is probably metastable (judged by its unusual composition).

Run 14 (30 kbars, 900°C, homogenization). Originally, in order to try both homogenization and unmixing experiments at one time, layers of synthetic diopside, clinoenstatite and glass ($\text{En}_{50}\text{Di}_{50}$) were loaded successively into the capsule. However, the unmixing experiment in the glass layer proved ambiguous and unusable because of mechanical contamination of the synthetic pyroxenes into this layer during loading, and eventually only the homogenization experiment was usable. To minimise the likelihood of amphibole stability in the presence of approximately 3% H_2O , about 22% silver oxalate was mixed into each layer. However, amphibole of similar composition to that in run 13 was formed locally at the boundary between

synthetic pyroxene layers, and within the glass layer. Trace amounts of silica mineral and magnesite were formed as well. Very small pyroxenes appeared to have nucleated at the enstatite/diopside boundary but were difficult to distinguish from relict grains.

Run 15 (10 kbars, 900°C, unmixing). Enstatite ($\leq 10 \mu\text{m}$) and diopside ($\leq 5 \mu\text{m}$) were so fine grained that it is not clear whether the wide compositional range of diopside (Table 1) is real, and due to incomplete equilibration, or results from enstatite contamination in the diopside analyses.

Run 16 (10 kbars, 900°C homogenization). The same preparation of the starting material, together with water and silver oxalate, was used as in run 14 and the unmixing experiment was unsuccessful for the same reason. At the boundary between the two synthetic pyroxene layers, the same texture was present as in run 14. Two pyroxenes and a trace of silica mineral were present.

REFERENCES

1. F.R. Boyd and J.F. Schairer, The system $\text{MgSiO}_3\text{-CaMgSi}_2\text{O}_6$, J. Petrol. 5 (1964) 275.
2. I. Kushiro, Determination of liquidus relations in synthetic silicate systems with electron probe analysis: the system forsterite - diopside - silica at 1 atmosphere, Am. Mineral. 57 (1972) 1260.
3. I. Kushiro, The system forsterite - diopside - silica with and without water at high pressures, Am. J. Sci. Schairer Vol. 267-A (1969) 269.
4. B.T.C. Davis and F.R. Boyd, The join $\text{Mg}_2\text{Si}_2\text{O}_6\text{-CaMgSi}_2\text{O}_6$ at 30 kilobars pressure and its application to pyroxenes from kimberlites, J. Geophys. Res. 71 (1966) 3567.
5. F.R. Boyd, Garnet peridotites and the system $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$, Mineral. Soc. Am. Spec. Pap. 3 (1970) 63.
6. R.D. Warner and W.C. Luth, The diopside - orthoenstatite two-phase region in the system $\text{CaMgSi}_2\text{O}_6\text{-Mg}_2\text{Si}_2\text{O}_6$, Am. Mineral, 59 (1974) 98.
7. C.E. Nehru and P.J. Wyllie, Electron microprobe measurement of pyroxenes coexisting with H_2O - under saturated liquid in the join $\text{CaMgSi}_2\text{O}_6\text{-Mg}_2\text{Si}_2\text{O}_6\text{-H}_2\text{O}$ at 30 kilobars, with applications to geothermometry, Contrib. Mineral. Petrol. 48 (1974) 221.
8. S.J.B. Reed, and N.G. Ware, Quantitative electron microprobe analysis using a Lithium drifted silicon detector. X-ray Spectrom. 2 (1973) 69.
9. F.R. Boyd and J.L. England, Apparatus for phase equilibrium measurements at pressures up to 50 kb and temperatures up to 1750°C , J. Geophys. Res. 65 (1960) 741.
10. T.H. Green, A.E. Ringwood and A. Major, Friction effects and pressure calibration in a piston cylinder apparatus at high pressure and temperature, J. Geophys. Res. 71 (1966) 3589.
11. B.J. Hensen, Pyroxenes and garnets as geothermometers and barometers, Carnegie Inst. Wash. Year Book 72 (1973) 527.
12. J.B. Thompson Jr., Thermodynamic properties of simple solutions, in:

- Researches in Geochemistry, 2, P.H. Abelson, ed. (New York, 1967) 340.
13. I. Kushiro, N. Shimizu, Y. Nakamura and S. Akimoto, Compositions of coexisting liquid and solid phases formed upon melting of natural garnet and spinel lherzolites at high pressures: a preliminary report, *Earth Plan. Sci. Lett.* 14 (1972) 19.
 14. L. Atlas, The polymorphism of MgSiO_3 and solid-state equilibria in the system $\text{MgSiO}_3\text{-CaMgSi}_2\text{O}_6$, *J. Geol.* 60 (1952) 125.
 15. I.C. Gettings and G.C. Kennedy, Effect of pressure on the emf of chromel-alumel and platinum-platinum 10% rhodium thermocouples, *J. Appl. Phys.* 41 (1970) 4552.
 16. P. Anastasiou and F. Seifert, Solid solubility of Al_2O_3 in enstatite at high temperatures and 1 - 5 kb water pressure, *Contrib. Mineral. Petrol.* 34 (1972) 272.
 17. J.R. Smyth, Experimental study on the polymorphism of enstatite, *Am. Mineral.* 59 (1974) 345.
 18. I. Kushiro and H.S. Yoder, Jr., Stability field of iron-free pigeonite in the system $\text{MgSiO}_3\text{-CaMgSi}_2\text{O}_6$, *Carnegie Inst. Wash. Year Book* 68 (1970) 226.
 19. H.Y. Yang and W.R. Foster, Stability of iron-free pigeonite at atmospheric pressure, *Am. Mineral.* 57 (1972) 1232.
 20. H.Y. Yang, Crystallization of iron-free pigeonite in the system anorthite - diopside - enstatite - silica at atmospheric pressure, *Am. J. Sci.* 273 (1973) 488.
 21. E.-An. Zen, Construction of pressure-temperature diagrams for multicomponent systems after the method of Schreinemakers - a geometric approach, *Bull. U.S. Geol. Surv.* 1225 (1966).
 22. D.H. Lindsley and J.L. Munoz, Subsolvus relations along the join hedenbergite - ferrosilite, *Am. J. Sci.* Schairer Vol. 267-A (1969) 295.

CHAPTER 3

SUBSOLIDUS EQUILIBRIA BETWEEN PYROXENES IN THE CaO-MgO-SiO_2 SYSTEM
AT HIGH PRESSURES AND TEMPERATURES

TAKESHI MORI and DAVID H. GREEN

ABSTRACT

The extent of pyroxene solid solutions has been experimentally determined in the CaO-MgO-SiO_2 system at 30 kbar and 1500°C . The results show the enstatite and diopside mutual solid solutions and also define the limited solid solutions towards olivine and quartz. Although the enstatite-diopside solvus is wider when olivine rather than quartz is a coexisting phase, the difference does not seriously affect the pyroxene solvus as a geothermometer. Thus, this geothermometer can be used without taking the coexisting phases other than pyroxenes into account.

The study of the enstatite-diopside solvus in the $\text{Mg}_2\text{Si}_2\text{O}_6\text{-CaMgSi}_2\text{O}_6$ system has been extended above 1500°C at 20 and 30 kbar. These pyroxenes show almost complete solid solution at solidus temperatures. The iron-free pigeonite-diopside solvus which was previously found at 20 kbar and inferred to be stable at 30 kbar did not appear at these pressures. The phase equilibrium data in this paper are combined with those in the literature to make a compilation of the enstatite-diopside solvus over a wide temperature-pressure range.

Some difficulties in use of the pyroxene solvus geothermometer are discussed, taking the garnet lherzolite nodules from Lesotho kimberlites as examples.

INTRODUCTION

The past few years have seen much interest in the phase equilibrium studies of pyroxenes (Lindsley et al., 1974a; Warner and Luth, 1974; MacGregor, 1974; Smyth, 1974; Nehru and Wyllie, 1974; Howells and O'Hara, 1975; Mori and Green, 1975; and Chen and Presnall, 1975). We note particularly Howells and O'Hara's (1975) treatment of pyroxenes as solid solutions towards forsterite and quartz. The present study, although a continuation of our earlier work, was in part undertaken to evaluate their suggestions.

The enstatite-diopside solvus has long been used as a geothermometer

and applied to temperature estimates of natural rocks. An implicit assumption in using the geothermometer is that pyroxenes had no solid solutions towards forsterite and/or quartz. Thus temperatures have been estimated without taking coexisting phases into account. However, Howells and O'Hara (1975) suggested that pyroxenes have solid solutions towards forsterite and quartz and that these solid solutions greatly affect the degree of mutual solid solution. Since all minerals are solid solutions in a strict sense, it is important whether or not the magnitudes of solid solution towards forsterite and quartz are enough to alter the practical application of the solvus as a geothermometer. In this paper we describe experiments made to define these solution limits.

The second problem treated in this paper is a reexamination of the stability of iron-free pigeonite* at high pressures. Kushiro (1969) presented a phase diagram in the system $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ at 20 kbar. Pigeonite was thought to be stable above 1450°C , producing two solvi between enstatite and pigeonite, and pigeonite and diopside. Howells and O'Hara (1975) reexamined this system at the same pressure, and contrary to Kushiro's experiments found homogeneous clinopyroxenes well within the pigeonite-diopside solvus as determined by Kushiro. We have reexamined this system at 20 kbar and obtained results supporting Howells and O'Hara's conclusions.

*Hereafter, this mineral is called pigeonite for convenience. We use this term for low-calcium clinopyroxene which is distinguished from diopsode (high-calcium clinopyroxene) by a solvus between them. This definition is also applicable to iron-bearing pigeonite. Note that if the two minerals have the same crystal structure of C2/c , it is not necessary to call them by different names.

The third experimental problem discussed in this paper is the enstatite-diopside solvus at temperatures above 1500°C at 20 and 30 kbar. The data are supplementary to those previously obtained at lower temperatures by us (Mori and Green, 1975).

Throughout this paper we use mole percent rather than weight percent in describing pyroxene compositions in terms of their end members. Data referred to from the literature have also been converted to mole percent.

EXPERIMENTAL METHOD AND RESULTS

All the starting materials used in the experiments were mechanical mixtures of two or three synthetic minerals among diopside ($\text{CaMgSi}_2\text{O}_6$), clinoenstatite ($\text{Mg}_2\text{Si}_2\text{O}_6$), forsterite (Mg_2SiO_4), and quartz (SiO_2). The mixtures were dried and loaded into Pt capsules. We used a piston-cylinder pressure apparatus (Boyd and England, 1960a), and the furnace assemblage included alumina sleeve and alumina thermocouple-insulator to minimize thermocouple contamination and pyrex glass instead of boron nitride outside the graphite heater. A pressure correction of -10 percent of nominal load pressure, using piston-in technique, was applied. No pressure correction was made to thermometry by $\text{W}_{97}\text{Re}_3/\text{W}_{75}\text{Re}_{25}$ thermocouples.

All the run products were analyzed by means of the TPD-electron microprobe. Phases were almost free from inclusions and were large enough to avoid chemical contamination from surrounding minerals: the sizes of crystals were up to 60, 40, 20, and 20 microns for enstatite, diopside, forsterite, and quartz, respectively, except for quartz in trace amount (grain size around 4 microns).

The details of experiments are listed in Table 1. Chemical analyses of the run products are shown in Tables 2 and 3.

Table 1: Results of Experiments in the Systems $\text{Di}(\text{CaMgSi}_2\text{O}_6)$ - $\text{Fo}(2\text{Mg}_2\text{SiO}_4)$ - $\text{Qz}(2\text{SiO}_2)$ and $\text{En}(\text{Mg}_2\text{Si}_2\text{O}_6)$ - $\text{Di}(\text{CaMgSi}_2\text{O}_6)$.

Run No.	Starting materials	Bulk compositions (mole %)	P (kb)	T (°C)	hrs	Products
2B1	Fo, C-En	$\text{Fo}_{63.3} \text{Qz}_{36.7}$	30	1500	4	Fo, En
2B2	C-En, Qz	$\text{Fo}_{27.1} \text{Qz}_{72.9}$	30	1500	4	En, Qz
2B3	Di, Qz	$\text{Di}_{52.8} \text{Qz}_{47.2}$	30	1500	4	Di, Qz
2B4	Fo, Di	$\text{Di}_{73.0} \text{Fo}_{27.0}$	30	1500	4	Fo, Di
2F	Fo, C-En, Di	$\text{Di}_{29.5} \text{Fo}_{40.9} \text{Qz}_{29.6}$	30	1500	20	Fo, En, Di
2G	Qz, C-En, Di	$\text{Di}_{30.0} \text{Fo}_{29.3} \text{Qz}_{40.7}$	30	1500	24	Qz, En, Di
Y1	C-En, Di	$\text{En}_{66.8} \text{Di}_{33.2}$	20	1600	6	Di, Qz (tr)
2A3	C-En, Di	$\text{En}_{87.0} \text{Di}_{13.0}$	20	1600	8	En, Di
Y2*	C-En, Di	$\text{En}_{83.1} \text{Di}_{16.9}$	30	1700	2	En, Di
Y3*	C-En, Di	$\text{En}_{83.1} \text{Di}_{16.9}$	30	1600	4	En, Di
2A4	C-En, Di	$\text{En}_{71.5} \text{Di}_{28.5}$	30	1600	10	En, Di, Qz (tr)

C-En: clinoenstatite, En: enstatite, Di: diopside, Fo: forsterite, Qz: quartz. The minerals in the starting materials are of synthetic end member components and those in the run products are solid solutions.
*: disequilibrium.

Table 2: Electron Probe Analyses of Olivine, Pyroxenes and Quartz in the System Di-Fo-Qz at 30 kb and 1500°C.

Run No.	2B1		2B2		2B3		2B4	
Phase	En	Fo	En	Qz	Di	Qz	Di	Fo
SiO ₂	59.55(63)	42.70(20)	60.05(50)	100.37(17)	55.23(63)	98.7(1.8)	54.95(51)	42.32(30)
MgO	39.98(34)	56.49(15)	39.33(33)	0.41(5)	18.18(31)	0.05(4)	19.35(43)	56.10(17)
CaO	-	-	-	-	25.98(32)	0.28(4)	24.82(57)	0.79(9)
Total	99.53(96)	99.19(12)	99.39(70)	100.78(22)	99.4(1.1)	99.1(1.9)	99.12(71)	99.20(46)
Number of ions (olivine: 0=4, pyroxene: 0=6, quartz: 0=4)								
Si	2.000(3)	1.007(4)	2.016(6)	1.994(1)	2.003(2)	1.996(1)	1.994(5)	1.001(3)
Mg	2.001(5)	1.986(7)	1.968(12)	0.012(1)	0.983(10)	0.002(1)	1.047(23)	1.978(5)
Ca	-	-	-	-	1.010(9)	0.006(1)	0.965(22)	0.020(3)
Molecular percent (Di: CaMgSi ₂ O ₆ , Fo: 2Mg ₂ SiO ₄ , Qz: 2SiO ₂)								
Di	-	-	-	-	100.8(9)	0.6(1)	96.8(2.3)	4.0(5)
Fo	50.0(2)	98.6(7)	48.8(5)	0.3(1)	-0.7(5)	-0.1(1)	2.1(1.1)	97.8(5)
Qz	50.0(2)	1.4(7)	51.2(5)	99.7(1)	-0.1(5)	99.5(1)	1.2(1.3)	-1.8(5)

Run No.	2F			2G			11*	
Phase	En	Di	Fo	En	Di	Qz	En	Di
SiO ₂	59.10	56.57	42.79(40)	59.04	57.38	100.26(18)	60.27	57.60
MgO	37.96	26.46	56.78(43)	37.56	26.66	0.21(6)	37.31	26.94
CaO	2.68	16.13	0.35(2)	2.84	15.51	0.15(5)	2.86	15.15
Total	99.74	99.15	99.92(81)	99.44	99.54	100.61(25)	100.44	99.69
Number of ions								
Si	1.996	1.998	1.003(2)	2.000	2.012	1.995(1)	2.018	2.014
Mg	1.911	1.393	1.985(5)	1.897	1.394	0.006(2)	1.862	1.404
Ca	0.097	0.610	0.009(1)	0.103	0.583	0.003(1)	0.103	0.568
Molecular percent								
Di	9.7	61.1	1.7(1)	10.3	57.9	0.3(1)	10.2	56.4
Fo	45.4	19.6	98.5(5)	44.8	20.2	0.1(1)	43.6	20.8
Qz	44.9	19.3	-0.2(4)	44.8	21.9	99.6(1)	46.2	22.9

The numbers in parentheses represent estimated standard errors (1 sigma) and refer to the last decimal place(s). See text for explanations of the data without standard error. *: referred from the supplemental analytical list to Mori and Green (1975). About 10 analyses were obtained for pyroxenes, and 4 for olivine and quartz in each charge.

THE EXTENTS OF PYROXENE SOLID SOLUTIONS IN THE CaO-MgO-SiO_2 SYSTEM

Figure 1 is an isothermal, isobaric diagram of the $\text{Di}(\text{CaMgSi}_2\text{O}_6)\text{-Fo}(\text{2Mg}_2\text{SiO}_4)\text{-Qz}(\text{2SiO}_2)$ system which is itself a portion of the CaO-MgO-SiO_2 system. Though solid solution fields are much exaggerated and are schematic only, two aspects suggested by Howells and O'Hara (1975) are illustrated: first, the diopside limb of the enstatite-diopside solvus is less calcic when pyroxenes are coexisting with forsterite rather than with quartz, and secondly, enstatite-diopside tie lines cross the stoichiometric En-Di join from upper left to lower right.

Among the six runs (2B1-2G in Table 1) made at 30 kbar and 1500°C , two had bulk compositions within the three-phase fields, namely, one in the forsterite-enstatite-diopside field and the other in the quartz-enstatite-diopside field, and the remaining four runs were on the edges of the Di-Fo-Qz triangle.

For the analyses in Table 2, synthetic forsterite, clinoenstatite, diopside, and quartz were used as substandards additional to the standards used in routine analysis in our laboratory (Reed and Ware, 1973). Thus, we could locate phase boundaries more precisely and could also lower the background uncertainties in trace element analyses which were caused by X-ray pulse pile-up problems (MgO in quartz, *cf.* Reed and Ware, 1973) and improve accuracy for low concentrations (e.g. CaO in olivine and quartz).

The mean compositions and their standard deviations are listed in Table 2. The compositions of pyroxenes in runs (2F and 2G) within the three-phase fields were not well-clustered: enstatite compositions scattered within 3 mole percent Di, and diopside within 6 mole percent. Because our starting materials were the pure phases, we have chosen the most-reacted compositions, i.e. diopside with the lowest Di content and enstatite with the highest Di content. The validity of this procedure was discussed by Mori and Green (1975). Table 2 also lists the most-reacted

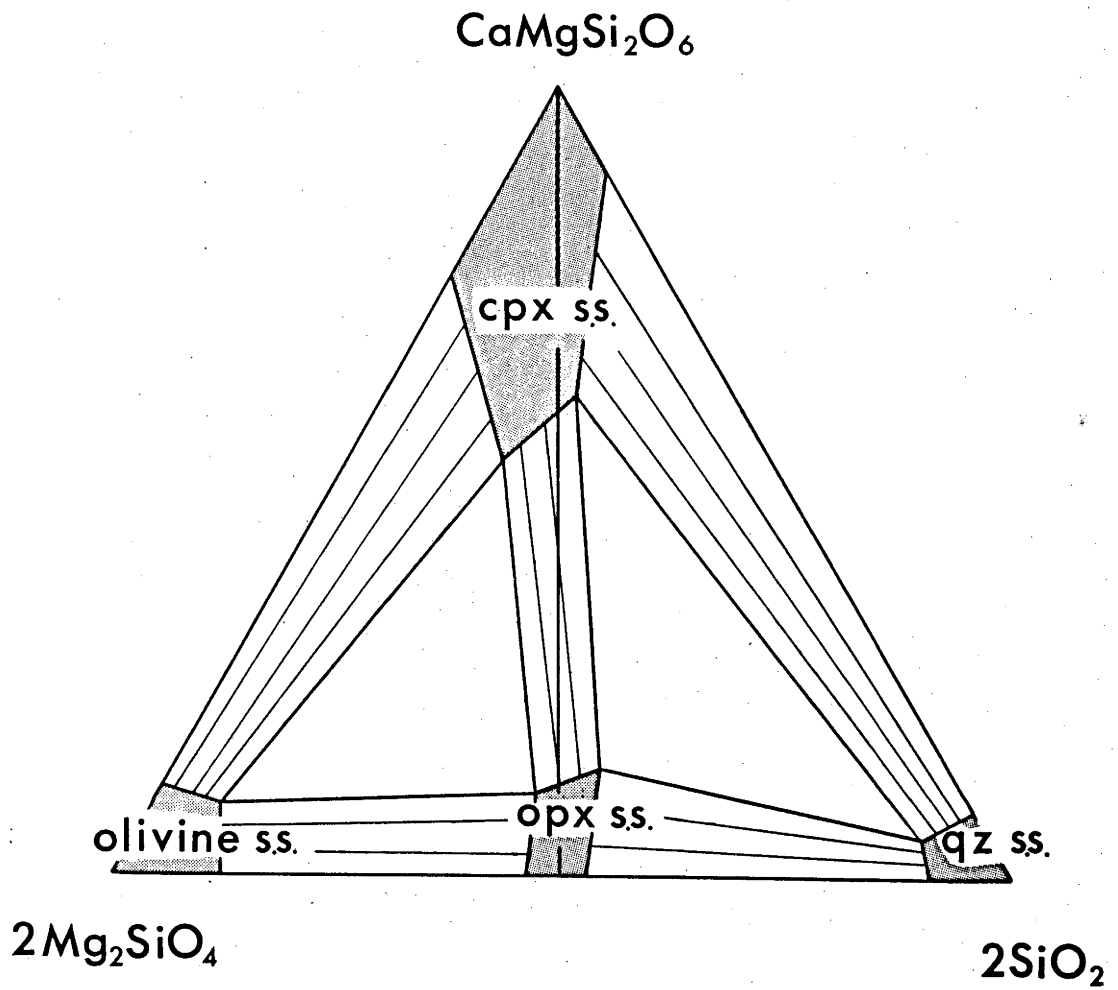


Fig. 1 Isothermal, isobaric phase relations of pyroxenes, olivine and quartz.
Schematic only. See text for explanations.

compositions of pyroxenes in an unmixing run (Run 11 of Mori and Green, 1975, the data are from the supplement prepared for the paper). The run charge is saturated or nearly saturated with quartz, and these data plot within 1.5 mole percent from the run 2G of Table 2.

Figure 2 shows the phase relations in a real scale. Note that molar units of Fo and Qz presented in Figure 2 are twice the conventional formulae, so that En has a formula of $\text{Mg}_2\text{Si}_2\text{O}_6$. As shown in the figure, both enstatite and diopside are solid solutions not only between En and Di, but also form limited solid solutions towards Fo and Qz. Non-stoichiometry of pyroxenes has been experimentally shown or suggested by Kushiro (1972) for diopside, by Onuma and Arima (1975) for protoenstatite, and by Boyd and England (1960b) for enstatite. It is also described from natural rocks (*cf.* Sobolev *et al.*, 1968).

The solvus is wider when pyroxenes are saturated with forsterite rather than with quartz. This feature is opposite to that inferred by Howells and O'Hara (1975). The difference of the diopside limb in terms of the Di component is about 3 mole percent. This suggests that when the pyroxene solvus is used as a geothermometer at approximately 1500°C and 30 kbar without taking the coexisting phases into account, errors in the temperature estimates of the order of 20°C may result (*cf.* Nehru and Wyllie, 1974; and Mori and Green, 1975). Thus, silica activity does not seriously affect the pyroxene solvus as a geothermometer.

It should also be noted that the enstatite-diopside tie-lines are almost parallel to the En-Di join. The diopside-forsterite tie-line for a charge with a bulk composition on the Di-Fo join clearly crosses the join, in agreement with observations of coexisting natural forsterite and diopside.

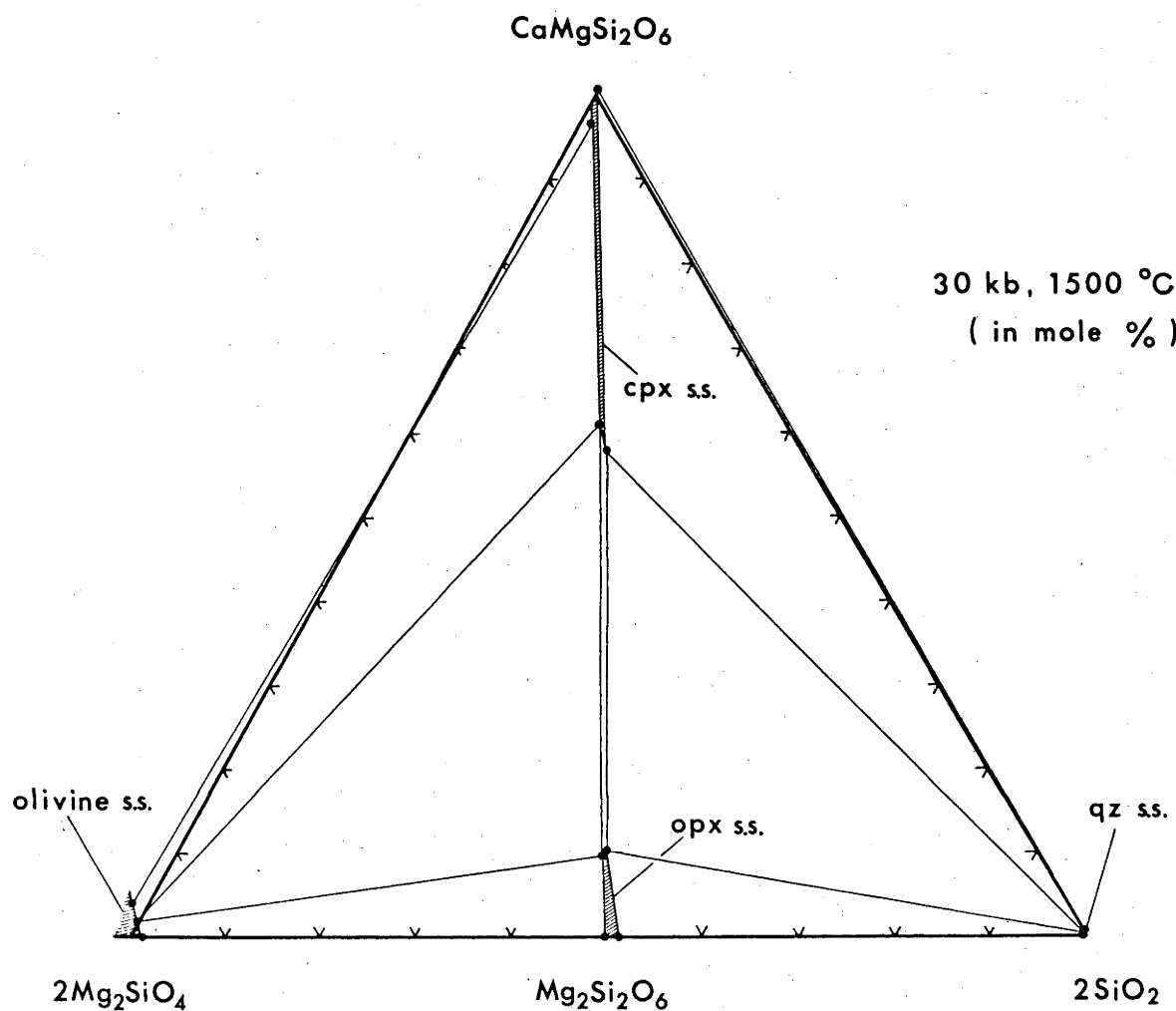


Fig. 2 Experimentally-deduced phase equilibria of olivine, pyroxenes and quartz at 30 kb and 1500°C. The hatched areas represent solid solutions. The data (dots) are from Table 2. Note that molar units of forsterite and quartz presented here are twice the conventional formulae.

STABILITY OF PIGEONITE-DIOPSIDE SOLVUS AT HIGH PRESSURES IN THE $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ SYSTEM

Two runs (Y1 and 2A3) at 20 kbar and 1600°C yielded results supporting Howells and O'Hara's (1975) conclusion that there is no stability field of coexisting pigeonite and diopside at this pressure, in contradiction to Kushiro's (1969) phase diagram. The measured compositions of enstatite and diopside grains are shown in Figure 3 and are summarized in Table 3. The synthetic diopside and clinoenstatite loaded into the run Y1 with a bulk composition well within Kushiro's (1969) pigeonite-diopside solvus ($\text{En}_{82}\text{Di}_{18}$ - $\text{En}_{50}\text{Di}_{50}$) and within Howells and O'Hara's (1975) diopside field homogenized to clinopyroxene although there is some compositional hysteresis. Enstatite was not found in the charge.

The run 2A3 at the same T - P conditions had a less calcic bulk composition. Compositions of enstatite and diopside were well clustered with a definition of the diopside limb which coincides with that of Howells and O'Hara (1975) within estimated errors.

Kushiro's (1969) main reason for deducing the presence of a pigeonite-diopside solvus at 20 kbar was the systematic change in intensities of paired 311 X-ray reflections with bulk composition of starting materials. Thus the solvus was located by observing the presence or absence of the paired reflections. For example, the diopside limb of the solvus at 1600°C and 20 kbar was estimated to be at $\text{En}_{50}\text{Di}_{50}$.

Alternatively, the 2θ angle of the 311 peak can be more directly used in determining the pyroxene compositions (McCallister, 1974). 2θ values read from Kushiro's Figure 4, combined with McCallister's 2θ -composition equation, which we found very satisfactory, allowed us to estimate the diopside limb of the solvus to be on $\text{En}_{28}\text{Di}_{72}$, $\text{En}_{36}\text{Di}_{64}$, or $\text{En}_{31}\text{Di}_{69}$ at 1600°C and 20 kbar, and on $\text{En}_{32}\text{Di}_{68}$ at 1650°C and 20 kbar. All the data locate more calcic pyroxenes than the diopside limb as determined by Kushiro at corresponding temperatures. The difference is about 20 mole percent $\text{CaMgSi}_2\text{O}_6$. In addition, according to Kushiro's Figure 3, liquid, instead

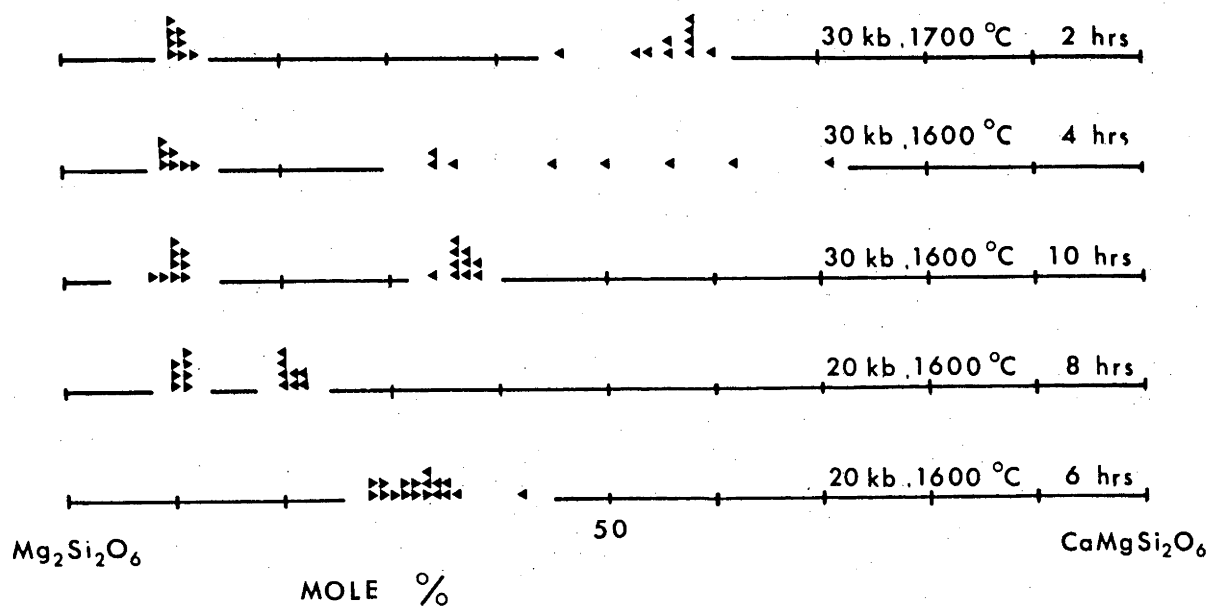


Fig. 3 Microprobe analyses of pyroxenes. All are of homogenization experiments. Direction of triangles shows direction of chemical reaction. Decimal fractions in the raw data have been rounded to the nearest integer.

of clinopyroxene, is stable for the last composition at 1650°C and 20 kbar. These facts show difficulties in the use of paired X-ray reflection to infer the presence or absence of the pigeonite-diopside solvus.

We also cast doubt on the pigeonite-diopside solvus at 17.5 kbar as inferred by Kushiro and Yoder (1970, Fig. 19), which we believe, was constructed by an analogy to the solvus at 20 kbar by Kushiro (1969).

Thus, our experiments refute the existence of the pigeonite-diopside solvus at 1600°C and 20 kbar, and the X-ray data of Kushiro (1969), reinterpreted by McCallister's (1974) calibration, can be shown to be inconsistent with the interpretations placed on them by Kushiro (1969). However, there still remains a possibility that a very narrow pigeonite-diopside solvus could exist at 20 kbar and a temperature lower than 1600°C. This possibility is discussed in the next section.

The present state of knowledge is that the pigeonite-diopside solvus is definitely stable only at 1 atmosphere (Yang, 1973; Yang and Foster 1972, and Kushiro 1972), and the maximum pressure for the stability of the solvus remains unknown.

Iron-bearing pigeonite has been observed at 15 kbar and 980°C (Lindsley et al. 1974b), coexisting with more calcium-rich pyroxene and hypersthene. If pigeonite is unstable in the iron-free system at this pressure, then the pigeonite_{ss}-diopside_{ss}-hypersthene_{ss} three-phase triangle must converge to a diopside_{ss}-hypersthene_{ss} tie-line with decreasing FeSiO₃ content (associated with increasing temperature) within the magnesian part of the pyroxene quadrilateral.

THE ENSTATITE-DIOPSIDE SOLVUS IN THE $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ SYSTEM

Four runs (Y2, Y3, 2A3 and 2A4 in Table 1) at temperatures above 1500°C are relevant to determination of the enstatite-diopside solvus. These are complementary to our previous results at and below 1500°C (Mori and Green, 1975). Again in this study, we experienced sluggishness of

chemical reaction, even at temperatures as high as 1700°C. In the runs Y2 (30 kbar and 1700°C) and Y3 (30 kbar and 1600°C), although compositions of enstatite were rather well clustered those of diopside showed extensive hysteresis in the change in chemistry from the pure diopside ($\text{CaMgSi}_2\text{O}_6$) of the starting mixes. The run at 30 kbar and 1600°C was repeated with prolonged run duration (10 hours). More closely clustered compositions of diopside resulted. The chemical compositions of pyroxenes in those runs including enstatite of Y2 (30 kbar and 1700°C) are listed in Table 3, and are compared with the data by Howells and O'Hara (1975) in Figure 4. Our data are in good agreement with theirs and further confirm the large pressure effect on the enstatite-diopside solvus at high temperatures.

At the solidus between 20-30 kbar, the enstatite and diopside show almost complete solid solution, but melting occurs just below the temperatures at which the enstatite and diopside (with their different crystal structures) limbs would intersect.

A peculiar feature observed in Figure 4 is that the diopside limbs at both 20 and 30 kbar show a slight inflection between 1500 and 1600°C. Although we prefer to regard the figure as an equilibrium phase diagram, there still remains a possibility, as suggested by the presence of the inflection, that the pigeonite-diopside solvus exists around the inflection point at 20 and 30 kbar. In this regard, it is interesting to note that Eggler (1974) suggested a coexistence of two clinopyroxenes at 20 kbar and around 1540°C based on synthesis data in the system $\text{CaO-MgO-SiO}_2\text{-CO}_2$. However, the pigeonite-diopside solvus, should it exist at temperatures lower than 1600°C at 20 kbar, must be much narrower than indicated by Kushiro (1969).

The data in Figure 4 were used together with those of Mori and Green (1975) in construction of the pressure-composition section (Fig. 5) which shows enstatite and diopside limbs as a function of temperature and pressure.

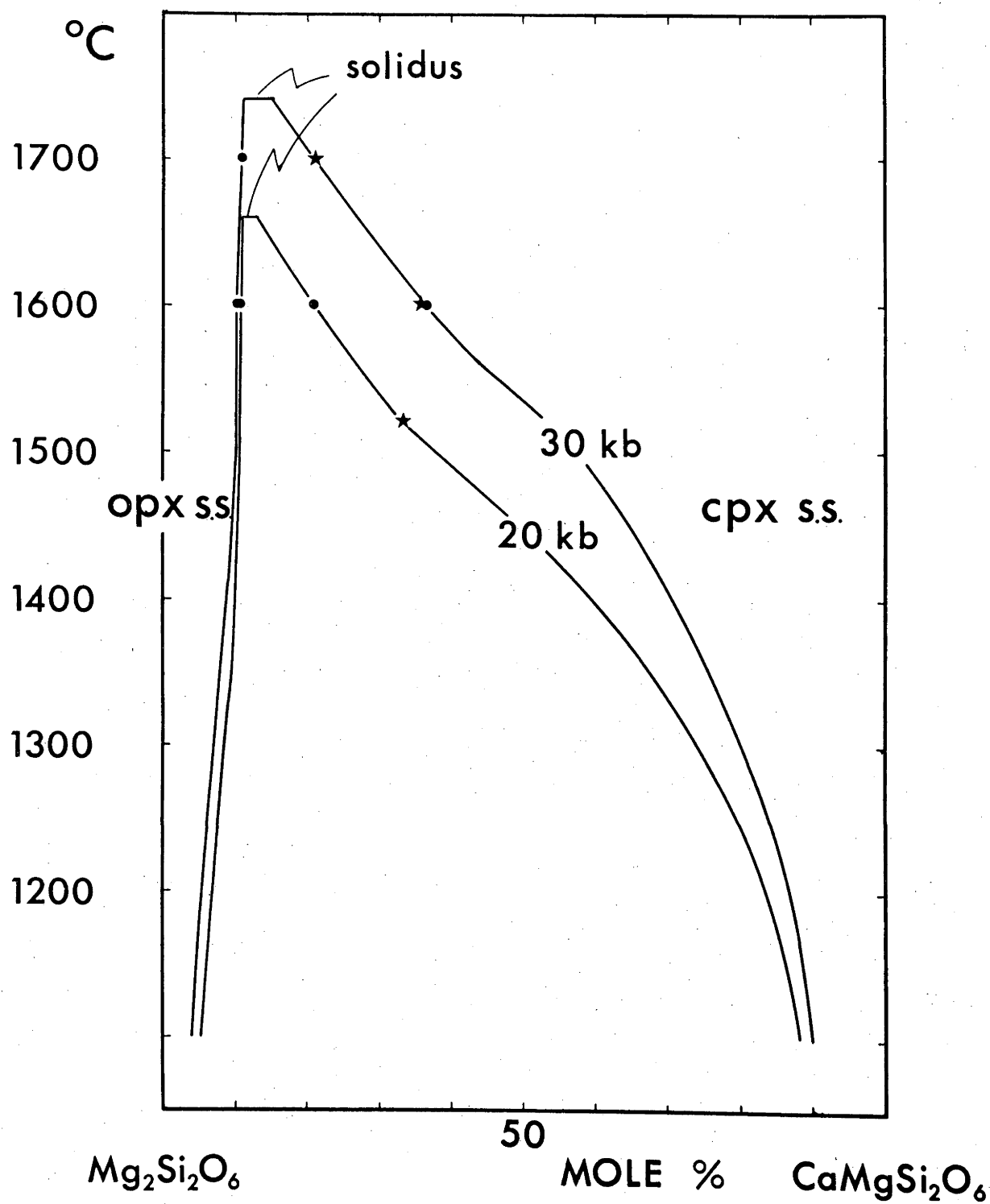


Fig. 4 Comparison of enstatite-diopside solvi at 20 and 30 kb. Dots are from Table 3. Stars and solidus at 30 kb are from Howells and O'Hara (1975). The solvi below 1500 °C are after Mori and Green (1975). Solidi are only partly drawn. Solidus at 20 kb is from Kushiro (1969).

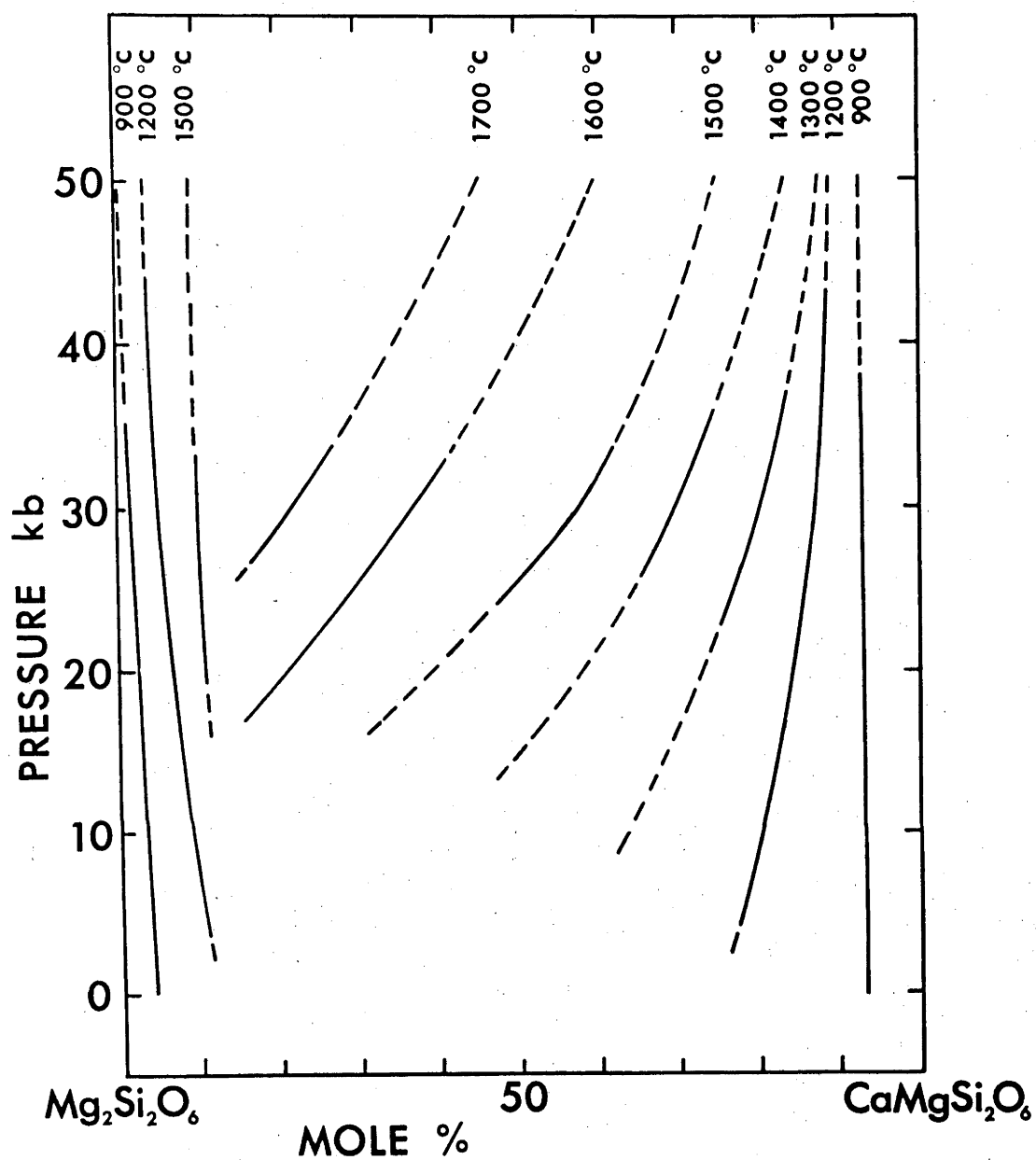


Fig. 5 Compilation of enstatite limbs (the left-side batch of lines) and diopsidite limbs (the right-side batch of lines) based on the data from Fig. 4 and Mori and Green (1975).

APPLICATION TO TEMPERATURE AND PRESSURE ESTIMATES OF GARNET LHERZOLITE NODULES FROM LESOTHO KIMBERLITES, AND CONSTRAINTS ON THE PYROXENE-SOLVUS GEOTHERMOMETRY

Garnet lherzolite nodules from Lesotho kimberlites have been extensively studied (e.g. Boyd, 1973). Physical conditions of equilibration for these nodules can be estimated by solving two independent geothermo-barometers. For this purpose, the MacGregor (1974) and Davis and Boyd's (1966) grids or modifications of them have been commonly used (Boyd, 1973 and Mercier and Carter, 1975).

In this section, we will also try to estimate pressures and temperatures of these nodules using Boyd's extensive chemical data for the minerals of the garnet lherzolite nodules (Boyd, in Nixon, 1973). Although the principle of the method is the same, we will employ the enstatite-diopside solvus presented in the previous section rather than that of Davis and Boyd (1966). $\text{Ca}/(\text{Mg} + \text{Ca})$ ratio of diopside from the nodules gives one temperature-pressure equation. Al_2O_3 contents of enstatite coexisting with diopside and garnet and with or without olivine were compiled from the experimental data by Akella and Boyd (1972, 1973, and 1974), Hensen (1973), Mysen and Boettcher (1975), Green (1973), and Mori and Green (unpublished data in the pyrolite system). All the chemical systems include at least SiO_2 , TiO_2 , Al_2O_3 , FeO , MgO , and CaO . Their temperatures and pressures vary from 900 to 1410°C and from 15 to 45 kbar. Consistency among the data is, however, not fully satisfactory. In addition, both geothermo-barometers have to be greatly extrapolated towards higher pressures and temperatures in order to be applied to the garnet lherzolite nodules. These two features greatly limit reliability of this method of temperature-pressure estimates.

Figure 6 shows a graphic method of solving the two equations. Diopside-component isopleths cross the Al_2O_3 (enstatite) isopleths giving unique solutions of temperature and pressure. Boyd's analytical data (Boyd, in Nixon 1973) show that Al_2O_3 content in enstatite is rather constant through the nodules ($\text{Al}_2\text{O}_3 = 1.1 \pm 0.3 \text{ wt.}\%$), while the $\text{Ca}/(\text{Mg} + \text{Ca})$ ratio varies

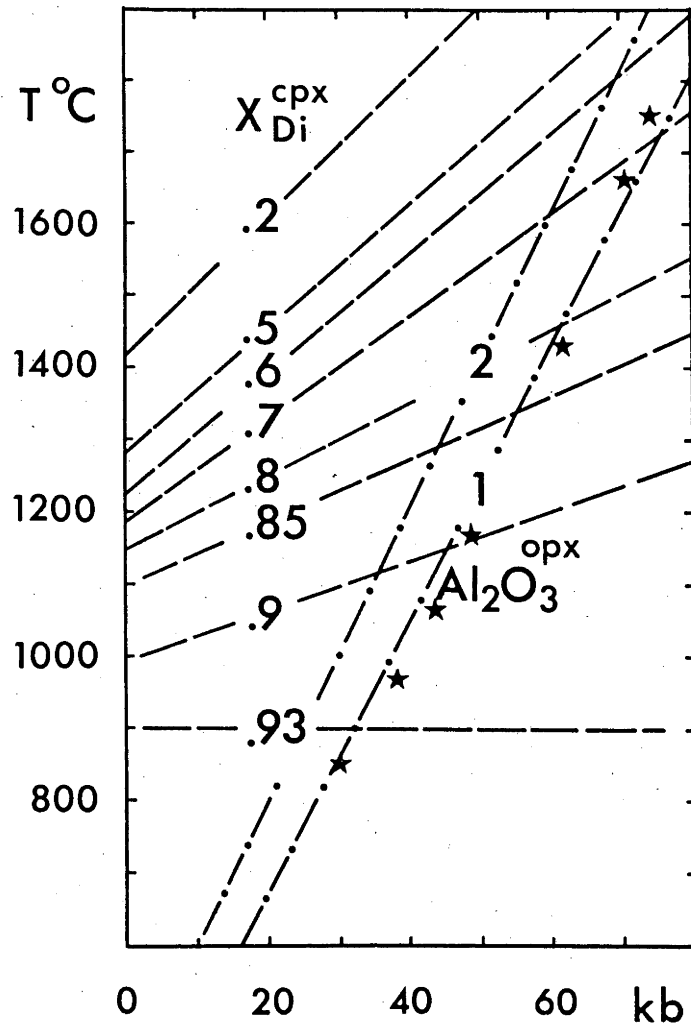


Fig. 6 Method of temperature and pressure estimates. Compositions of diopside limbs (broken lines, in $\text{CaMgSi}_2\text{O}_3$ mole fraction) are from Mori and Green (1975) and this paper. Al_2O_3 contents in enstatite (lines with dots, in wt %) are from Akella and Boyd (1972, 1973 and 1974), Hensen (1973), Green (1973), Mysen and Boettcher (1975) and our unpublished data. The stars represent temperature-pressure estimates for garnet lherzolite nodules (1572, 2302A, 1559B, 1859N, 2273, E3, and 1924) from Lesotho kimberlites (Nixon, 1973). In plotting the natural diopsides, we have used the ratio $2\text{Ca}/(\text{Ca}+\text{Mg})$. Construction of this figure involved large extrapolation of the data and neglect of some inconsistencies among Al_2O_3 data. The deduced P,T conditions may be far from the true values (see text).

extensively from 0.481 to 0.287. This means that the temperature-pressure trend is dependent on the Al_2O_3 isopleths and is linear within ± 3 kbar, which roughly corresponds to the variation of ± 0.3 percent Al_2O_3 . If the nodules are classified into granular and sheared types (Boyd, 1973), we can find that the sheared type is more aluminous than the granular type by 0.3 weight percent. The diopside-component isopleths only limit the extent of the temperature-pressure trend determined by the Al_2O_3 isopleths.

A few data points from Boyd (in Nixon, 1973) are plotted in Figure 6. The highest temperature-pressure rock (1597, not plotted in Fig. 6) is estimated at about 85 kbar and 1950°C , and other sheared nodules approach these conditions (Fig. 6). The granular nodules yield temperatures up to 1170°C . Many granular type nodules plot at lower temperatures than 900°C , but the diopside-component isopleths become temperature-insensitive. Thus, the lowest temperature-pressure values cannot be reasonably estimated.

Our estimates are very different from those by Boyd (1973) and Mercier and Carter (1975). The rather narrow range of pressure (up to 70 kbar) and temperature (up to 1430°C) by Boyd (1973) is mainly due to his use of the enstatite-diopside solvus of Davis and Boyd (1966) at 30 kbar, which shows a more calcic diopside limb below 1000°C and less calcic limb above it compared to our solvus. Mercier and Carter's (1975) revision shows temperature and pressure values up to 80 kbar and 1600°C . Again, the difference from the trend in Figure 6 is mainly due to their scheme for the enstatite-diopside solvus, which has less pressure effect on the solvus than ours.

It might be considered that the temperature-pressure trend in Figure 6 is too steep to represent a palaeogetherm. From present knowledge, we do not know whether the nodule trend is an artifact due to lack of data for phase equilibria at very high pressures and temperatures. In addition, we do not know that the temperature-pressure thus estimated represents a palaeogetherm.

The principal difficulty in temperature estimates on the basis of the pyroxene solvus is, as shown in the example above, the fact that we have to know pressure values by an independent method. In addition, the solvus is almost useless at temperatures below 900°C. We emphasize that the pressure-temperature estimates of Figure 6 are an *illustration* of the effect that the new solvus data have on the method of pressure-temperature estimation used by Boyd (1973). We consider that the estimates of pressure-temperature in Figure 6 have very large uncertainties indeed.

APPENDIX. ACCURACY OF TPD-MICROPROBE ANALYSIS

Standard rocks (JG-1 and JB-1) of Geological Survey of Japan were melted on an iridium strip heater following the melting procedure of Nicholls (1974). The glasses were analyzed by TPD-microprobe using the energy-dispersive analytical system with the routine analytical procedure in our laboratory (Reed and Ware, 1973) but with defocussed beam (about 100 microns). The raw data and the recommended values for the standard rocks (Ando et al. 1974) were recalculated to total of 100. This was necessary in order to compare the two sets of data since H_2O^+ and H_2O^- etc. evaporate during the melting process.

The results are listed in Table 4. The probe data are satisfactory except for MnO. Concentrations of MnO in these rocks are nearly the same or just above the detection limit of MnO by TPD-probe (about 0.08 wt.%). For those elements with very low concentrations, the conventional wavelength-dispersive microprobe system must be used instead of the energy-dispersive TPD-microprobe. It should be noted that the standard deviations in Table 4 are due almost entirely to heterogeneities of the glasses.

Table 4: Accuracy of TPD-probe Analysis.

	JG-1		JB-1	
	recommended value	TPD-probe	recommended value	TPD-probe
SiO ₂	72.95	73.06(41)	53.53	53.64(21)
TiO ₂	.26	.26(4)	1.38	1.33(4)
Al ₂ O ₃	14.36	14.42(30)	14.87	14.83(13)
FeO _{total}	1.99	1.89(4)	8.31	8.53(8)
MnO	.06	n.d.	.15	.03(7)
MgO	.75	.99(4)	7.91	7.93(12)
CaO	2.22	2.21(5)	9.50	9.47(7)
Na ₂ O	3.41	3.25(9)	2.87	2.75(14)
K ₂ O	4.00	3.93(5)	1.47	1.47(5)

The recommended values for the standard rocks are from Ando et al. (1974). Both sets of data are recalculated to total of 100. The numbers in parentheses represent estimated standard errors (1 sigma) of the probe analysis, and refer to the last decimal place(s).

REFERENCES

- AKELLA, J. AND F.R. BOYD (1972) Partitioning of Ti and Al between pyroxenes, garnets, and oxides. *Carnegie Inst. Wash. Year Book* 71, 378-384.
- AND ——— (1973) Effect of pressure on the composition of co-existing pyroxenes and garnet in the system. CaSiO_3 - MgSiO_3 - FeSiO_3 - $\text{CaAlTi}_2\text{O}_6$. *Carnegie Inst. Wash. Year Book*, 72, 523-526.
- AND ——— (1974) Petrogenetic grid for garnet peridotites. *Carnegie Inst. Wash. Year Book*, 73, 269-273.
- ANDO, A., H. KURASAWA, T. OHMORI AND E. TAKEDA (1974) 1974 compilation of data on the G.S.J. geochemical reference samples JG-1 granodiorite and JB-1 basalt. *Geochem. J.* 8, 175-192.
- BOYD, F.R. (1973) A pyroxene geotherm. *Geochim. Cosmochim. Acta*, 37, 2533-2546.
- AND J.L. ENGLAND (1960a) Apparatus for phase equilibrium measurements at pressures up to 50 kb and temperatures up to 1750°C. *J. Geophys. Res.* 65, 741-748.
- AND ——— (1960b) Minerals of the mantle. *Carnegie Inst. Wash. Year Book*. 59, 47-52.
- CHEN, C-H. AND D.C. PRESNALL (1975) The system Mg_2SiO_4 - SiO_2 at pressures up to 25 kilobars. *Am. Mineral.* 60, 398-406.
- DAVIS, B.T.C. AND F.R. BOYD (1966). The join $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ at 30 kilobars pressure and its application to pyroxenes from kimberlites. *J. Geophys. Res.* 71, 3567-3576.
- EGGLER, D.H. (1974) Effect of CO_2 on the melting of peridotite.. *Carnegie Inst. Wash. Year Book*, 73, 215-224.
- GREEN, D.H. (1973) Conditions of melting of basanite magma from garnet peridotite. *Earth Planet. Sci. Lett.* 17, 456-465.
- HENSEN, B.J. (1973) Pyroxenes and garnets as geothermometers and barometers. *Carnegie Inst. Wash. Year Book*, 72, 527-534.

HOWELLS, S. AND M.J. O'HARA (1975) Palaeogeotherms and the diopside-enstatite solvus. *Nature*, 254, 406-408.

KUSHIRO, I (1969) The system forsterite-diopside-silica with and without water at high pressures. *Am.J.Sci.Schairer Vol.* 267-A, 269-294.

———(1972) Determination of liquidus relations in synthetic silicate systems with electron probe analysis: the system forsterite-diopside-silica at 1 atmosphere. *Am. Mineral.* 57, 1260-1271.

———AND H.S. YODER, JR. (1970) Stability field of iron-free pigeonite in the system $\text{MgSiO}_3\text{-CaMgSi}_2\text{O}_6$. *Carnegie Inst. Wash. Year Book*, 68, 226-229.

LINDSLEY, D.H., H.E. KING JR. AND A.C. TURNOCK (1974a). Compositions of synthetic augite and hypersthene coexisting at 810°C ; application to pyroxenes from lunar highlands rocks. *Geophys. Res. Lett.* 1, 134-136.

———, ———, ——— AND J.E. GROVER (1974b) Phase relations in the pyroxene quadrilateral at 980°C and 15 kbar. *Geol. Soc. Am. Abstracts with Programs*, 1974 Annu. Meet. 846.

MACGREGOR, I.D. (1974) The system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$: solubility of Al_2O_3 in enstatite for spinel and garnet peridotite compositions. *Am. Mineral.* 59, 110-119.

MCCALLISTER, R.H. (1974) The exsolution kinetics of a diopside solid solution having the composition 54.1 mole % $\text{CaMgSi}_2\text{O}_6$, 45.9 mole % $\text{Mg}_2\text{Si}_2\text{O}_6$. *Carnegie Inst. Wash. Year Book*, 73, 392-396.

MERCIER, J-C. AND N.L. CARTER (1975) Pyroxene geotherms. *J. Geophys. Res.* 80, 3349-3362.

MORI, T. AND D.H. GREEN (1975) Pyroxenes in the system $\text{Mg}_2\text{Si}_2\text{O}_6\text{-CaMgSi}_2\text{O}_6$ at high pressure. *Earth Planet. Sci. Lett.* 26, 277-286.

MYSEN, B.O. AND A.L. BOETTCHER (1975) Melting of a hydrous mantle: II. Geochemistry of crystals and liquids formed by anatexis of mantle peridotite at high pressures and high temperatures as a function of controlled activities of water, hydrogen, and carbon dioxide. *J. Petrol.* 549-593.

- NEHRU, C.E. AND P.J. WYLLIE (1974) Electron microprobe measurement of pyroxenes co-existing with H₂O-undersaturated liquid in the join CaMgSi₂O₆-Mg₂Si₂O₆-H₂O at 30 kilobars, with applications to geothermometry. *Contrib. Mineral. Petrol.* 48, 221-228.
- NICHOLLS, I.A. (1974) A direct fusion method of preparing silicate rock glasses for energy-dispersive electron microprobe analysis. *Chem. Geol.* 14, 151-157.
- NIXON, P.H. (Ed.) (1973) *Lesotho Kimberlites*. Lesotho National Development Corporation, Maseru, Lesotho. 350 p.
- ONUMA, K. AND M. ARIMA (1975) The join MgSiO₃-MgAl₂SiO₆ and the solubility of Al₂O₃ in enstatite at atmospheric pressure. *J. Japan. Assoc. Mineral. Petrol. Econ. Geol.* 70, 53-60.
- REED, S.J.B. AND N.G. WARE (1973) Quantitative electron microprobe analysis using a lithium drifted silicon detector. *X-Ray Spectrometry*, 2, 69-74.
- SMYTH, J.R. (1974) Experimental study on the polymorphism of enstatite. *Am. Mineral.* 59, 345-352.
- SOBOLEV, N.V. Jr. I.K. KUZNETSOVA AND N.I. ZYUZIN (1968). The petrology of grosspyroxite xenoliths from the Zagadochnaya kimberlite pipe in Yakutia. *J. Petrol.* 9, 253-280.
- WARNER, R.D. AND W.C. LUTH (1974) The diopside-orthoenstatite two-phase region in the system CaMgSi₂O₆-Mg₂Si₂O₆. *Am. Mineral.* 59, 98-109.
- YANG, H-Y (1973) Crystallization of iron-free pigeonite in the system anorthite-diopside-enstatite-silica at atmospheric pressure. *Am. J. Sci.* 273, 488-497.
- _____ AND W.R. FOSTER (1972) Stability of iron-free pigeonite at atmospheric pressure. *Am. Mineral.* 57, 1232-1241.

CHAPTER 4

EXPERIMENTAL STUDY ON PYROXENE EQUILIBRIA
IN THE SYSTEM CaO-MgO-FeO-SiO_2

TAKESHI MORI

ABSTRACT

Subsolidus phase equilibria of pyroxenes in the CaO-MgO-FeO-SiO_2 system have been experimentally determined at 30 and 15 kbar, and mainly at 1200°C . While phase relations at 30 kbar and 1200°C are characterized only by orthopyroxene and clinopyroxene, at 15 kbar and 1200°C phase relations are complicated by the appearance of the two-clinopyroxene solvus. The stability of Ca-free clinopyroxene was demonstrated at 15 kbar and 1200°C and higher temperatures, and at 30 kbar and 1450°C .

The new experimental data were combined with the data from the literature to yield a generalized phase equilibrium scheme of pyroxenes in temperature-pressure-composition space. Though the majority of naturally occurring pyroxenes can be understood in the light of the scheme, there are a few samples not fully consistent with it. These are briefly mentioned.

INTRODUCTION

Diversity of pyroxenes in crystal structure and chemistry is closely related to their wide chemical and physical circumstances of formation. Pyroxenes widely occur in ultrabasic to intermediate rocks, extrusive and intrusive rocks, igneous and metamorphic rocks, and terrestrial and extraterrestrial rocks. In particular, they are supposed to be common minerals in the earth's upper mantle. Therefore, it is reasonable that extensive investigations have been carried out on pyroxenes both petrographically and experimentally. Although we owe a large amount of knowledge to the previous investigators, phase relations of pyroxenes are not fully understood. A most serious problem is the difficulty in distinguishing stable and metastable pyroxenes appearing in nature and laboratory studies. Consequently, our knowledge at present is clouded by contradictions and confusion.

One of the topics of current interest is the occurrence at high pressure of a three-pyroxene field where orthopyroxene and two kinds of

clinopyroxene coexist in the CaO-MgO-FeO-SiO_2 system. Smith's (1972) experiments along the join of $\text{Fe}/(\text{Mg} + \text{Fe}) = 0.85$ in the pyroxene quadrilateral $\text{Di}(\text{CaMgSi}_2\text{O}_6) - \text{En}(\text{Mg}_2\text{Si}_2\text{O}_6) - \text{Fs}(\text{Fe}_2\text{Si}_2\text{O}_6) - \text{Hd}(\text{CaFeSi}_2\text{O}_6)$, at ~ 15 kbar show two types of two-pyroxene field above 880°C , i.e. orthopyroxene/Ca-poor clinopyroxene, and Ca-poor clinopyroxene/Ca-rich clinopyroxene, and an orthopyroxene/Ca-rich clinopyroxene field below 880°C . Smith inferred the three-phase field for this composition at 15 kbar to lie at about 880°C . Similarly, Grover et al., (1972) observed similar topology for phase diagrams along the joins of $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.6$ and 0.75 at 15 kbar. In the former system but at 20 kbar, no three-phase field was observed by Turnock (1970). More recently Lindsley et al. (1974a,b) determined phase relations at 15 kbar and 810°C with the result that orthopyroxene/Ca-rich clinopyroxene two-phase field prevails over the pyroxene quadrilateral, and at 980°C with the result that a two-clinopyroxenes and orthopyroxene three-phase field locates near the join of $\text{Fe}/(\text{Mg} + \text{Fe}) = 0.6$. From the three-pyroxene field, stem three two-phase fields, i.e. orthopyroxene/Ca-rich clinopyroxene, orthopyroxene/Ca-poor clinopyroxene and Ca-rich/Ca-poor clinopyroxenes. Simmons et al. (1974) also found coexisting three-pyroxenes at 2 kbar and 800°C along the join of $\text{Fe}/(\text{Mg} + \text{Fe}) = 0.75$.

In natural rock systems, Hensen (1973) reported homogenization experiments of pyroxenes in wide range of pressure, temperature and chemistry. Owing to the sluggish reaction rate in the homogenization reaction, the data are not conclusive, but he interpreted the data assuming the presence of the three-pyroxene field.

The importance of knowledge on the three-pyroxene field is in the fact that once its location is established, topological features of phase boundaries in the pyroxene quadrilateral can be easily understood in conjunction with the knowledge of phase relations along the edges and at the apexes of the quadrilateral.

The present study is a logical expansion of our earlier works on

pyroxenes in the CaO-MgO-SiO₂ system (Mori and Green, 1975, 1976) into the FeO-bearing system. Our aim is to understand the pyroxene phase relations at high pressures. No direct application to petrology is intended in this paper, though some unusual natural pyroxenes are mentioned.

EXPERIMENTAL METHODS

Starting Materials

Four types of starting material used in the high pressure experiments are 1) glass, 2) single phase clinopyroxene or orthopyroxene, 3) a mechanical mixture of orthopyroxene and clinopyroxene, 4) a mechanical mixture of two clinopyroxenes with different compositions. The glasses were prepared from A.R. grade chemicals of SiO₂, MgO, CaCO₃, Fe₂O₃ and Fe, or stoichiometric wustite synthesized at high pressure by A. Major as an alternative to Fe₂O₃ and Fe. Since glasses with exact pyroxene stoichiometry are difficult to make with confidence, weighing of the chemicals was made such that deviation from stoichiometry, if any, was to SiO₂ excess side. These mixtures of chemicals were then melted by either an induction heater and sample within a platinum crucible or on an iridium strip heater. Both methods were carried out in argon gas flow. Microprobe analyses of the glasses thus made, showed deviations of compositions from those intended by 1.5 mole percent pyroxene end member (Wo, En or Fs) at worst. No chemical contamination was detected. Pyroxene starting materials used as either single phase or mixture with another pyroxene were synthesized from the glasses at 30 kbar and 1200°C for 1 hour using Ag₅₀Pd₅₀ capsules. Again maximum deviation of pyroxene compositions was up to 1.5 mole percent end member. It should be noted that this short run duration on glass starting material readily produces metastable clinopyroxenes with compositions well within the orthopyroxene-clinopyroxene solvus, thus syntheses of these pyroxenes may not have anything to do with pyroxene equilibria at 30 kbar and 1200°C. Tem-Pres clinoenstatite was used for Mg₂Si₂O₆-clinopyroxene

starting material.

High Pressure Experiments

Experiments were carried out in a piston-cylinder apparatus with combination of piston-in technique and a -10% pressure correction. Sample assemblies contained a boron nitride or pyrex sleeve, and a mullite or alumina thermocouple insulator. Various kinds of capsule material were used: iron, platinum, silver-palladium alloy and graphite.

Thermometry was by Pt/Pt₉₀Rh₁₀ thermocouples for short runs. To avoid thermocouple shift, W₉₇Re₃/W₇₅Re₂₅ thermocouples were successfully used for long runs. Run details are listed in Table 1.

Identification and Analyses of Run Products

Powders of run products either mounted in Canadian balsam or dispersed in immersion liquids were examined by microscope. The universal stage was needed for identification in critical cases.

Powders of most of the run products were also examined by X-ray diffractometer or Guinier Camera. The calculated X-ray powder patterns of pyroxenes by Borg and Smith (1969) and the unit cell parameters of Ca-Mg-Fe pyroxenes (Turnock et al, 1973) were used in identification of the run products.

TPD-microprobe analyses were tried on all the minerals of the run product. The size of pyroxenes in subsolidus runs varied from 8 to 100 microns depending on starting material, temperature, and run duration. Each quantitative probe analysis was started only after it was established that slight movement of beam around the analysis point did not cause observable change in count rates of diagnostic elements. Thus, the possible contamination from surrounding minerals was kept down to a minimum. Bulk analyses of the run products by a defocussed beam showed chemical deviation from those of starting materials by no more than 1.5 mole percent pyroxene end member except at the narrow rims to the capsules where FeO content showed more deviation, either increased or decreased depending on the capsule material.

Table 1
Run details

Run No.		Reactants		Pressure kbar	Temperature °C	Time hours	Capsule	Products
		compositions (Ca-Mg-Fe)	ratio(in wt.%)					
2H2	cpx	0-100-0		30	1200	0.07	Pt	opx
Z3	2 cpx	0-100-0,45-45-10	(51:49)	30	1200**	50	C	opx,cpx
P1*	glass	15-65-20		30	1200	4	Fe	opx,cpx
2C1	2 cpx	45-45-10,0-76-24	(49:51)	30	1200**	92	Ag ₅₀ Pd ₅₀	opx,cpx
T4	glass	15-55-30		30	1200	0.08	Fe	cpx
T5	glass	15-55-30		30	1200	0.75	Fe	opx,cpx
O1	glass	15-55-30		30	1200	4	Fe	opx,cpx
P7*	glass	5-60-35		30	1200	4	Fe	opx,cpx(tr)
2A5*	opx+cpx	0-61-39,35-39-26	(49:51)	30	1200**	45	Ag ₅₀ Pd ₅₀	opx,cpx,Qz(tr)
P5	glass	15-50-35		30	1200	4.5	Fe	opx,cpx
2B6	opx+cpx	0-61-39,17-46-37	(21:79)	30	1200**	93	C	opx,cpx,Qz(tr)
Q1	glass	22-44-34		30	1200	4	Fe	cpx
2D2	glass	22-44-34		30	1200**	50.5	Ag ₅₀ Pd ₅₀	opx(tr),cpx,Qz(tr)
Q2	glass	10-50-40		30	1200	4	Fe	opx,cpx
2B5	2 cpx	35-39-26,17-46-37	(25:75)	30	1200**	69	Ag ₅₀ Pd ₅₀	opx,cpx,Qz(tr)
P9	glass	5-50-45		30	1200	4	Fe	opx,cpx
P11	glass	0-50-50		30	1200	4.5	Fe	opx
Q3	glass	5-25-70		30	1200	4	Fe	opx,cpx
Z4	opx+cpx	0-26-74,15-22-63	(61:39)	30	1200**	83	Ag ₅₀ Pd ₅₀	opx,cpx
R1	glass	10-50-40		30	1000	24	Fe	opx,cpx
2D1	2 cpx	35-39-26,17-46-37	(17:83)	30	1220**	85	Ag ₅₀ Pd ₅₀	opx(tr),cpx,Qz(tr)
R2	glass	0-50-50		30	1400	2.3	Fe	opx
2O1	opx	0-26-74		30	1450	0.75	Fe	cpx(Mg _{0.39} Fe _{0.61} SiO ₃),glass,Qz(tr)
P2	glass	15-65-20		15	1200	4.8	Fe	opx,cpx
Q4	glass	10-60-30		15	1200	4	Fe	cpx
2N2	glass	10-60-30		15	1200**	12	Ag ₅₀ Pd ₅₀	cpx,Qz(tr),(opx+cpx)***
O2	glass	15-55-30		15	1200	3	Fe	cpx
P8	glass	5-60-35		15	1200	6	Fe	opx,cpx
Q7	glass	22-48-30		15	1200	4	Fe	2 cpx
P6	glass	15-50-35		15	1200	5.2	Fe	cpx
2E2	glass	15-50-35		15	1200**	70	Ag ₅₀ Pd ₅₀	cpx,Qz(tr)
Q5	glass	10-50-40		15	1200	4	Fe	opx(?),cpx
P10	glass	5-50-45		15	1200	5.5	Fe	opx,cpx
P12	glass	0-50-50		15	1200	5.6	Fe	opx
Q6	glass	5-25-70		15	1200	4	Fe	cpx
2O4	opx	0-26-74		15	1200	2	Ag ₅₀ Pd ₅₀	cpx,Qz(tr)
R3	glass	10-50-40		15	1000	24	Fe	opx,cpx
2O2	opx	0-26-74		15	1350	2	Fe	cpx(Mg _{0.35} Fe _{0.65} SiO ₃),Qz(tr),glass

*: The runs for which microchemical analyses of FeO and Fe₂O₃ was done on the bulk run products. In every case, Fe₂O₃ was less than 0.01 wt% (Analyst: E. Kiss).

** : The runs for which W₉₇Re₃/W₇₅Re₂₅ thermocouples were used for thermometry. Pt/Pt₉₀Rh₁₀ thermocouples were used for other runs.

***: Mineral assemblage found at the margins of the charge (see text).

Spectrophotometric microanalysis of FeO and Fe₂O₃ (Kiss, 1974) was done by E. Kiss on portions of three run products (Table 1). Fe₂O₃ contents of <0.01 wt. % were found leading us to believe that iron in all the run products is in the ferrous state.

Phases appeared in the run products were pyroxenes with or without trace amount of quartz. In two runs (201, 202), glass was found as well. Though these runs were at comparatively high temperatures, it was probably access of water which caused melting.

EXPERIMENTAL RESULTS

Runs were made mainly at 1200°C and either 30 kbar or 15 kbar. Table 2 lists compositions of coexisting pyroxenes in some typical runs. A listing of the 599 microprobe analyses of pyroxenes on which this paper is based are available from the author on request. Some runs were planned to understand the processes of chemical reactions which defined the pyroxene solvus.

Chemical processes in the reactions

In these and in some of our earlier experiments (Mori and Green, 1975 and 1976) clinoenstatite was used as a mixture with Ca-rich clinopyroxene instead of a combination of orthoenstatite and Ca-rich clinopyroxene which would be better starting material for reversal experiments to define the solvus. However, as the run 2H2 shows, 4 minutes are sufficient for total inversion of clinoenstatite to orthoenstatite at 30 kbar and 1200°C. The run duration needed for the pyroxenes to react and define the solvus is so long that the use of the clinoenstatite would not have caused any problem of metastability in the run products.

Some information on the process of devitrification of pyroxene-composition starting glass is worth noting. A glass composition well within the pyroxene solvus was chosen to study its devitrification and crystallization of pyroxenes from it. As is shown in Figure 1-A, the glass totally

Table 2

Some representative microprobe analyses of synthesized pyroxenes

Run No.	SiO ₂	FeO	MgO	CaO	Total	Si	Fe	Mg	Ca	Total	Wo-En-Fs	
P1	opx	56.07	15.85	27.64	1.75	101.31	1.997	0.472	1.467	0.067	4.003	3.3-73.1-23.5
P1	cpx	54.47	9.08	17.66	18.60	99.81	2.008	0.280	0.970	0.735	3.993	37.0-48.9-14.1
2C1	opx	56.20	14.79	27.16	2.18	100.33	2.012	0.443	1.450	0.084	3.988	4.2-73.4-22.4
2C1	cpx	54.40	9.10	17.86	18.46	99.82	2.005	0.280	0.981	0.729	3.995	36.6-49.3-14.1
2A5	opx	52.83	24.16	20.51	2.39	99.89	1.994	0.762	1.154	0.097	4.007	4.8-57.3-37.9
2A5	cpx	52.11	18.29	15.28	13.57	99.25	1.994	0.585	0.871	0.556	4.006	27.6-43.3-29.1
P5	opx	52.44	25.73	20.08	2.19	100.44	1.983	0.814	1.132	0.089	4.018	4.4-55.6-40.0
P5	cpx	52.17	19.11	15.17	13.16	99.61	1.993	0.611	0.864	0.539	4.007	26.8-42.9-30.3
Q3	opx	47.27	42.28	8.44	1.43	99.42	1.969	1.473	0.524	0.064	4.030	3.1-25.4-71.5
Q3	cpx	47.50	40.14	7.89	3.95	99.48	1.971	1.393	0.488	0.176	4.028	8.5-23.7-67.7
Z4	opx	47.85	42.80	8.33	2.00	100.98	1.966	1.470	0.510	0.088	4.034	4.3-24.7-71.1
Z4	cpx	47.16	41.18	7.71	3.26	99.31	1.968	1.437	0.480	0.146	4.031	7.1-23.3-69.7
P2	opx	55.57	14.94	27.68	2.33	100.52	1.992	0.448	1.479	0.089	4.008	4.4-73.4-22.2
P2	cpx	54.41	10.07	19.01	16.45	99.94	2.000	0.310	1.042	0.648	4.000	32.4-52.1-15.5
P8	opx	52.91	23.16	22.08	2.06	100.21	1.980	0.725	1.232	0.083	4.020	4.1-60.4-35.5
P8	cpx	52.89	21.04	17.98	8.86	100.77	1.987	0.661	1.007	0.357	4.012	17.6-49.7-32.6
Q7	cpx	51.95	21.15	17.79	8.52	99.41	1.982	0.675	1.012	0.348	4.017	17.1-49.7-33.2
Q7	cpx	52.50	17.62	16.21	13.90	100.23	1.984	0.557	0.913	0.563	4.017	27.7-44.9-27.4
P10	opx	51.77	28.50	18.42	1.67	100.36	1.983	0.913	1.052	0.069	4.017	3.4-51.7-44.9
P10	cpx	51.14	28.12	16.55	4.38	100.19	1.978	0.909	0.954	0.181	4.022	8.9-46.7-44.5

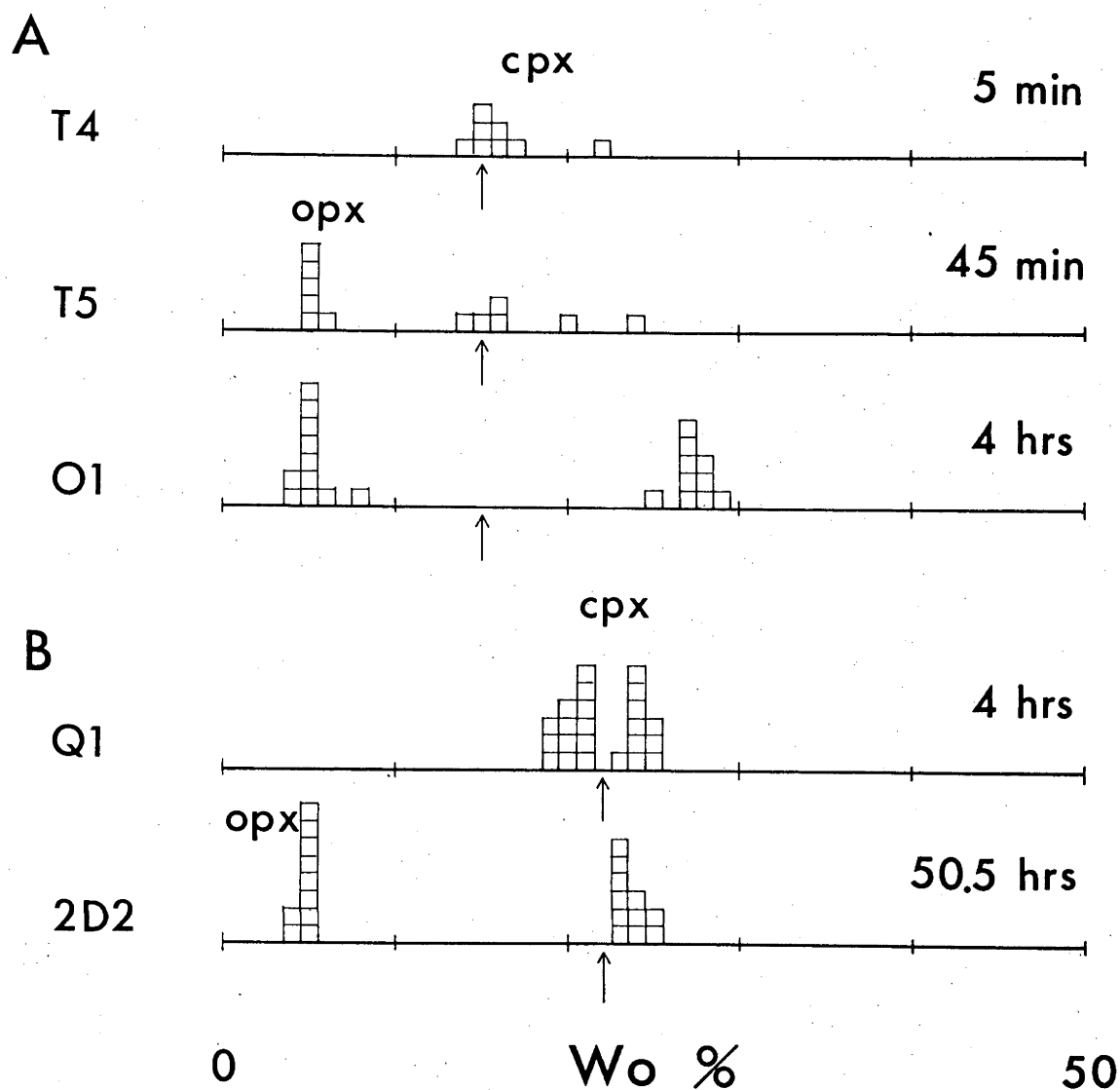


Fig. 1 Frequency of measured pyroxene compositions plotted against Wo mole percent. The compositions of starting glasses are indicated by arrows.

A) $\text{Ca}_{0.15}\text{Mg}_{0.55}\text{Fe}_{0.30}\text{SiO}_3$, B) $\text{Ca}_{0.22}\text{Mg}_{0.44}\text{Fe}_{0.34}\text{SiO}_3$.

Both sets of experiments are at 30 kbar and 1200°C .

Abbreviations: opx - orthopyroxene, cpx - clinopyroxene.

crystallized within 5 minutes into clinopyroxene with compositional spread around that of the glass. With time, orthopyroxene appeared and clinopyroxene composition became more calcic and less scattered. In this particular case, orthopyroxene appeared within a rather short time, but in another case, (Figure 2-B) where the bulk composition was near the clinopyroxene limb, orthopyroxene was not found within 4 hours but found in the run 2D2 with prolonged duration. More seriously, two glasses with compositions supposed to be well within the solvus did not crystallize orthopyroxene (Q4, 2N2, O2), which will be discussed later.

Mineral mixes of orthopyroxene and clinopyroxene with compositions outside the solvus yielded new compositions approaching the equilibrium solvus as if reaction happened by diffusion process (cf. Mori and Green, 1975).

Measured pyroxene compositions are shown in Figure 2 (30 kbar and 1200°C) and Figure 3 (15 kbar and 1200°C). Note that the frequency is simply of probe analyses, and does not represent modal ratio of orthopyroxene and clinopyroxene. The figures show that even the runs with long durations show chemical hysteresis and that the spread of the data is not a simple function of the run duration.

Phase relations at 30 kbar

As is shown in Figure 2, compositions of orthopyroxenes are more closely clustered than those of clinopyroxenes. The worst example of chemical hysteresis in clinopyroxene is seen in the run, P5: some compositions are still almost the same as the bulk composition of starting glass. In spite of that, the best reacted compositions in this unmixing experiment are matched well with the best reacted compositions of clinopyroxene in the corresponding homogenization experiment, the run 2A5. However, it should be noted that the experiments of this pair are not of mutually reversal nature in the most strict sense, since the two orthopyroxene-clinopyroxene tie lines are not exactly coincidental and were not particularly intended to be so. This is also true of the other pairs in

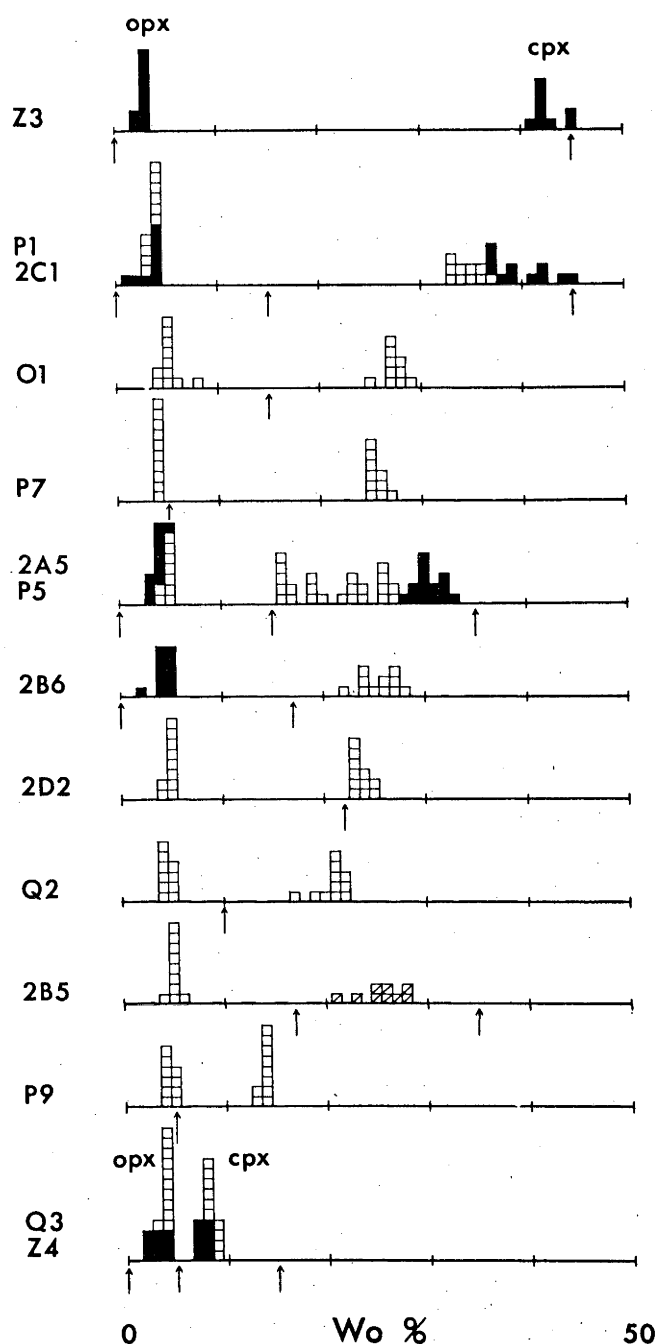


Fig. 2 Measured compositions of synthesized pyroxenes at 30 kbar and 1200°C. The open squares represent pyroxene compositions approached the equilibrium solvus from inside, and the filled ones from outside. The data for which the reaction direction is not known are shown by squares with an oblique line. The compositions of starting glasses and pyroxenes are indicated by arrows.

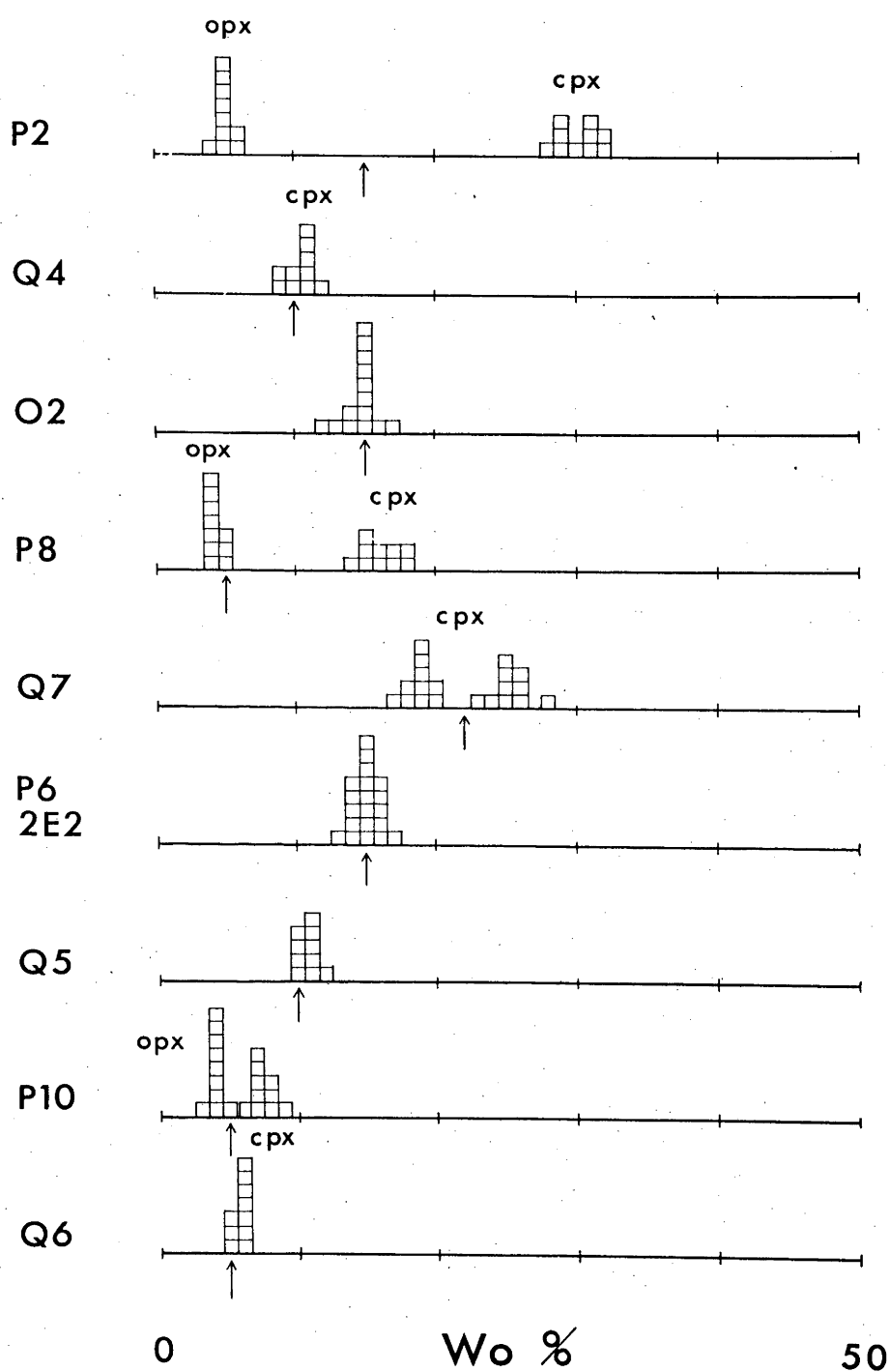


Fig. 3 Measured compositions of pyroxenes synthesized at 15 kbar and 1200°C. All the experiments are from homogeneous glasses with the compositions indicated by arrows.

Figure 2.

Figure 4 depicts the pyroxene solvus at 30 kbar and 1200°C. The phase relations are simple: the solvus starts from the En-Di join as determined by Mori and Green (1975), goes through the data presented in this paper and rapidly narrows until it reaches the join of $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.75$. The solvus seems to extend further to the Hd-Fs join. This inference is in harmony with the stable FeSiO_3 orthopyroxene (Akimoto et al., 1965; Lindsley, 1965; Smith, 1971) and the probably stable $\text{Ca}_{0.15}\text{Fe}_{0.85}\text{SiO}_3$ clinopyroxene (Lindsley and Burnham, 1970) at 30 kbar and 1200°C. The narrow solvus along the Fs-Hd join is much the same as that found on the same join at 20 kbar and around 1000°C (Lindsley and Munoz, 1969). Apart from the pyroxene solvus, the quadrilateral is occupied by only orthopyroxene and clinopyroxene fields. No protoenstatite, fayalite, quartz, pyroxenoid or liquid appears at 30 kbar and 1200°C.

We have only one set of data of coexisting orthopyroxene and clinopyroxene at 1000°C (run R1). The data set can be linked to that of the En-Di system (Mori and Green, 1975) to partially define the solvus at 1000°C. In comparison with the solvus at 1200°C, these data depict the well known temperature effect.

By contrast to the stability of orthopyroxene all over the join along En-Fs at 1200°C, $\text{Mg}_{0.39}\text{Fe}_{0.61}\text{SiO}_3$ clinopyroxene seems stable at 1450°C and coexists with glass and quartz (run 201). Orthopyroxene is, however, still stable for the composition of $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{SiO}_3$ at 1400°C (run R2)

Phase realtions at 15 kbar

The pyroxene compositions are shown in Figure 3, and the solvi at 1200°C and 1000°C are in Figure 5. Phase relations at 15 kbar and 1200°C is more complicated than at 30 kbar and 1200°C by the presence of Ca-rich clinopyroxene/Ca-poor clinopyroxene solvus which was shown by the bimodal distribution of pyroxene composition in the run Q7 (Figure 3), though X-ray peaks were not sharp enough to show double peaks.

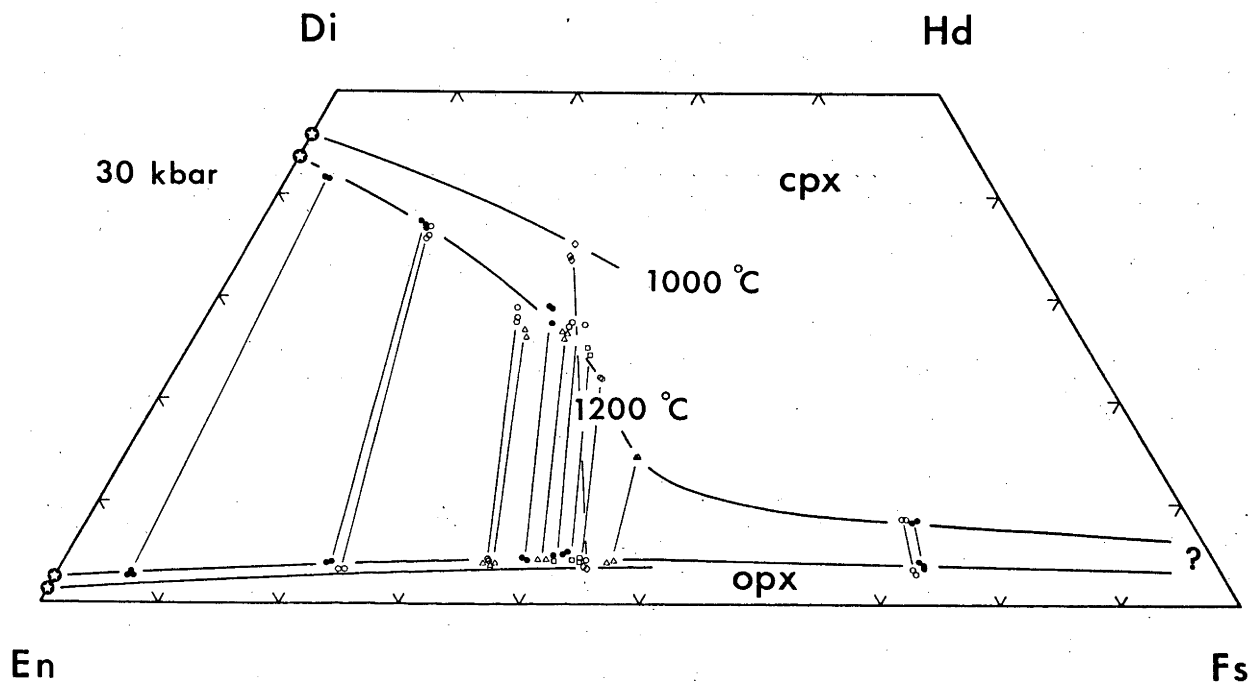


Fig. 4 Isothermal, isobaric sections of pyroxene quadrilateral (in mole percent) at 30 kbar and 1200°C, and 1000°C. Only the three best-reacted compositions are plotted though one may be omitted when it is almost the same to other. The filled symbols are for compositions approached the solvus from outside, and the open ones from inside. Different symbols are to distinguish runs. The data on the En-Di join are referred from Mori & Green (1975).

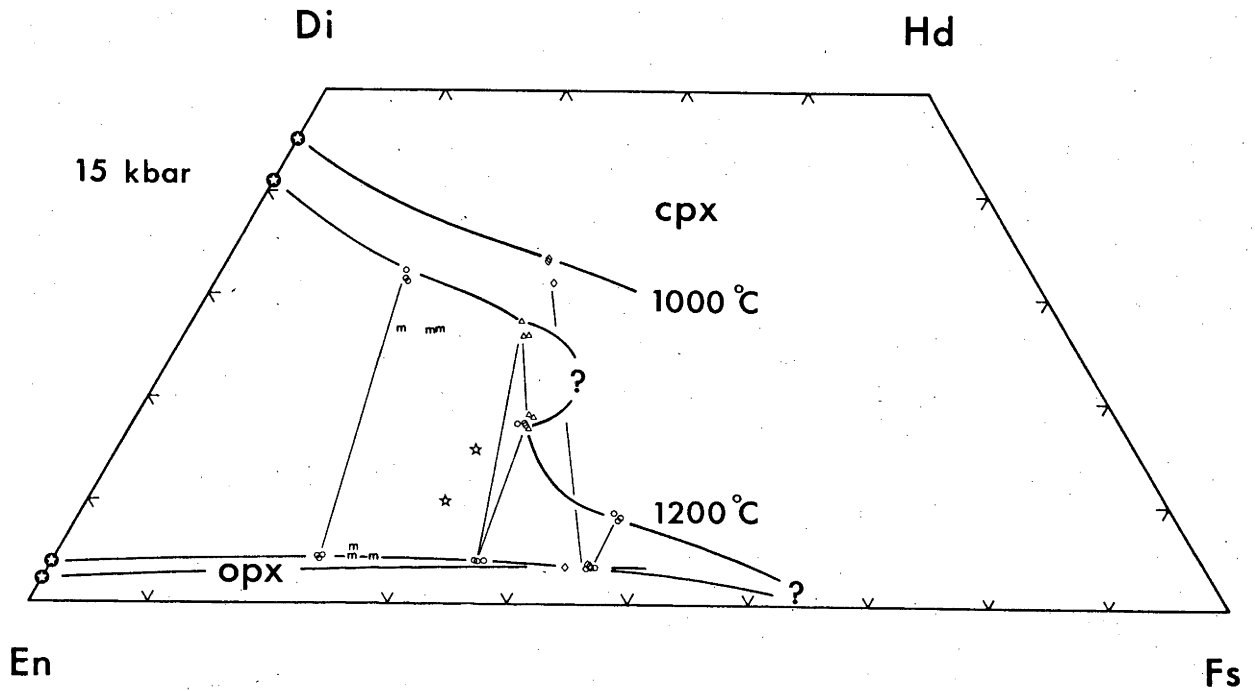


Fig. 5 Isothermal, isobaric sections of the pyroxene quadrilateral at 15 kbar and 1200°C, and 1000°C. The meanings of the symbols are the same to those in Figure 4, except the open stars (metastable clinopyroxenes in runs Q4, 2N2 and O2) and m (pyroxenes found at the margins of the charge in run 2N2). Only the three best-reacted compositions are plotted though one may be omitted when it is almost the same to other.

Since the Ca-poor clinopyroxene is chemically very similar to the clinopyroxene coexisting with orthopyroxene in the run P8, the position of three-pyroxene field was inferred to be near the two tie lines defined by the runs Q7 and P8.

Another difference from the phase relation at 30 kbar and 1200°C is the appearance of stable clinopyroxene at a Fe-rich side of the En-Fs join: $\text{Mg}_{0.26}\text{Fe}_{0.74}\text{SiO}_3$ orthopyroxene converted to clinopyroxene (run 204). Clinopyroxene is also stable for $\text{Ca}_{0.05}\text{Mg}_{0.25}\text{Fe}_{0.70}\text{SiO}_3$ composition (run Q6), thus the extension of orthopyroxene-clinopyroxene solvus must reach to the En-Fs join somewhere between $\text{Mg}_{0.26}\text{Fe}_{0.74}\text{SiO}_3$ and $\text{Mg}_{0.50}\text{Fe}_{0.50}\text{SiO}_3$ (run P12) instead of reaching to the Fs-Hd join.

The phase diagram at 15 kbar and 1200°C is further complicated by appearances of phases other than pyroxenes at the portion near Fs corner (not shown in Figure 5). Fayalite plus quartz, instead of ferrosilite is stable for FeSiO_3 composition (Akimoto et al., 1965; Lindsley, 1965; Smith, 1971), and pyroxenoid would be stable for $\text{Ca}_{0.15}\text{Fe}_{0.85}\text{SiO}_3$ composition (Lindsley and Burnham, 1970). Thus, the stable phases would be in the following order from Fs corner to outwards: fayalite - quartz, fayalite - quartz - pyroxenoid, pyroxenoid, pyroxenoid - clinopyroxene, clinopyroxene. No liquid, wollastonite or protopyroxene appears at this *P-T* condition (Lindsley, 1967; Chen and Presnall, 1975).

A serious internal inconsistency was found in this series of experiments, i.e., two runs (Q4 and O2) at $\text{Ca}_{0.10}\text{Mg}_{0.60}\text{Fe}_{0.30}\text{SiO}_3$ and $\text{Ca}_{0.15}\text{Mg}_{0.55}\text{Fe}_{0.30}\text{SiO}_3$ compositions resulted in single phase clinopyroxene, which is out of harmony with the inferred solvus boundaries defined by other runs with bulk compositions with both higher and lower $\text{Fe}/(\text{Fe} + \text{Mg})$. The former composition was again tried with a prolonged run duration to facilitate nucleation of orthopyroxene (run 2N2). The result was again single phase clinopyroxene except at the 100 micron-wide margins of the charge to the $\text{Ag}_{50}\text{Pd}_{50}$ capsule where orthopyroxene and clinopyroxene were found (Figure 5). The region where orthopyroxene and clinopyroxene occurred was also the region where Fe loss was detectable. Compositions of the

clinopyroxenes in the inner parts are almost the same as those found in the run Q4 with shorter duration. By contrast, those of the orthopyroxenes and clinopyroxenes in the margins are not in serious contradiction with the results from neighbouring runs, although the pyroxene analyses show much spread partly due to differential iron loss. We believe that Ca-rich clinopyroxene and orthopyroxene, instead of single phase Ca-poor clinopyroxene, are stable around these two starting compositions. The nucleation of orthopyroxene in the margins of the run 2N2 is not well understood, but it is probable that the energy barrier for orthopyroxene nucleation was overcome either by catalytic role of capsule walls or by the change of the bulk chemistry due to the iron loss to the capsule.

At a higher temperature of 1350°C (run 202), $\text{Mg}_{0.35}\text{Fe}_{0.65}\text{SiO}_3$ clinopyroxene was found to be coexisting with glass and a trace amount of quartz, which further demonstrates the stability of Ca-free clinopyroxene at high temperatures.

TOPOLOGY OF PYROXENE EQUILIBRIA IN THE SYSTEM CaO-MgO-FeO-SiO₂

Before going to the detailed discussion on the pyroxene equilibria in the temperature-pressure-composition space, we will present two generalized pictures of pyroxene phase relations. Figure 6 is a temperature-composition diagram at a certain pressure. Figure 7 depicts the phase relations in the pressure-composition space at a constant temperature. Though both the figures are schematic and directly applicable to only certain ranges of pressure and temperature, they reveal essential topology of single-, two- and three-pyroxene fields, and serve as aids in understanding the phase relations. In the pyroxene quadrilateral, at least four stable pyroxenes are known, i.e., orthopyroxene (Pbca), protopyroxene (Pbcn), Ca-rich clinopyroxene (C2/c) and Ca-poor clinopyroxene or pigeonite (P2₁/c) at room temperature but probably C2/c at high temperatures (cf. Brown et al., 1972). Iron-free

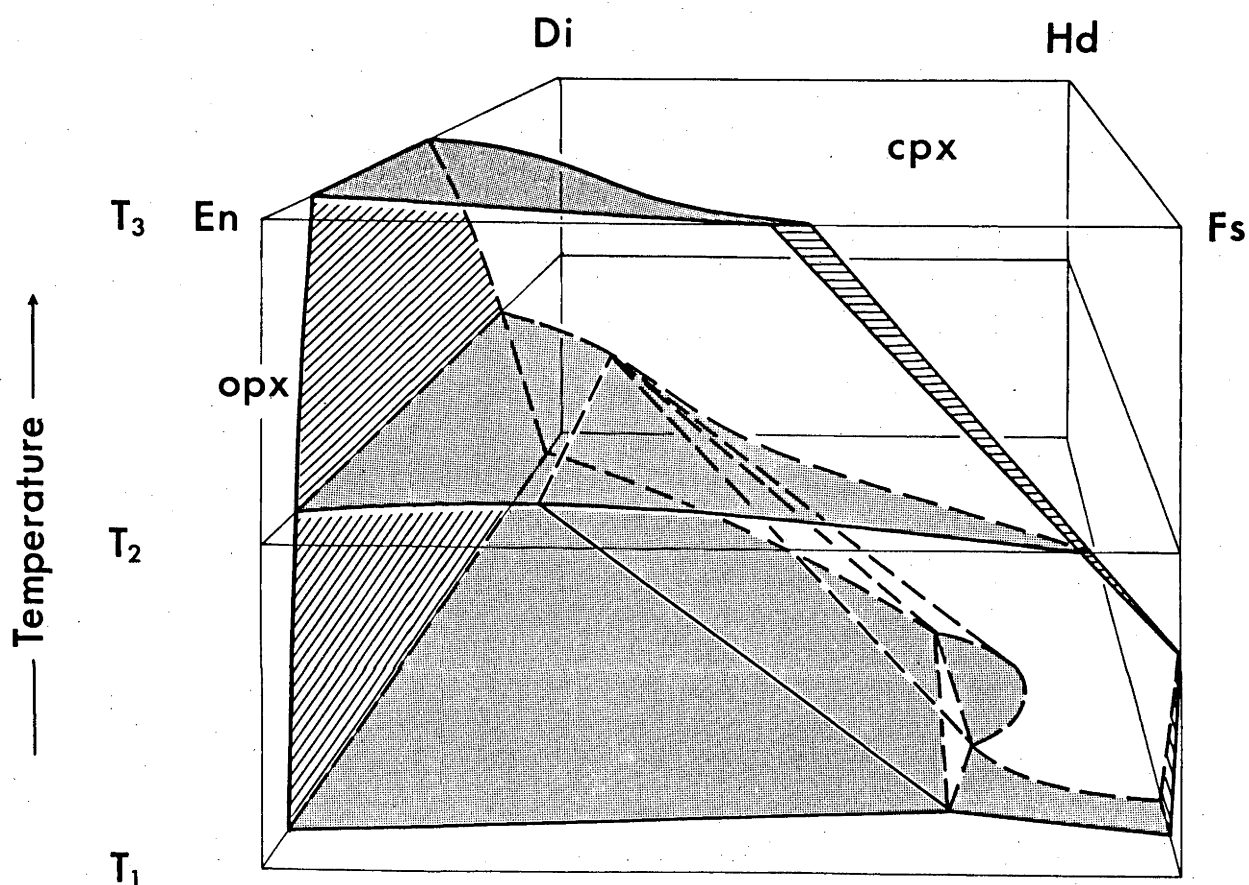


Fig. 6 Schematic phase diagram of pyroxenes in the temperature-composition space. Only orthopyroxene (opx) and Ca-rich and Ca-poor clinopyroxenes (cpx) are depicted. See text for explanation.

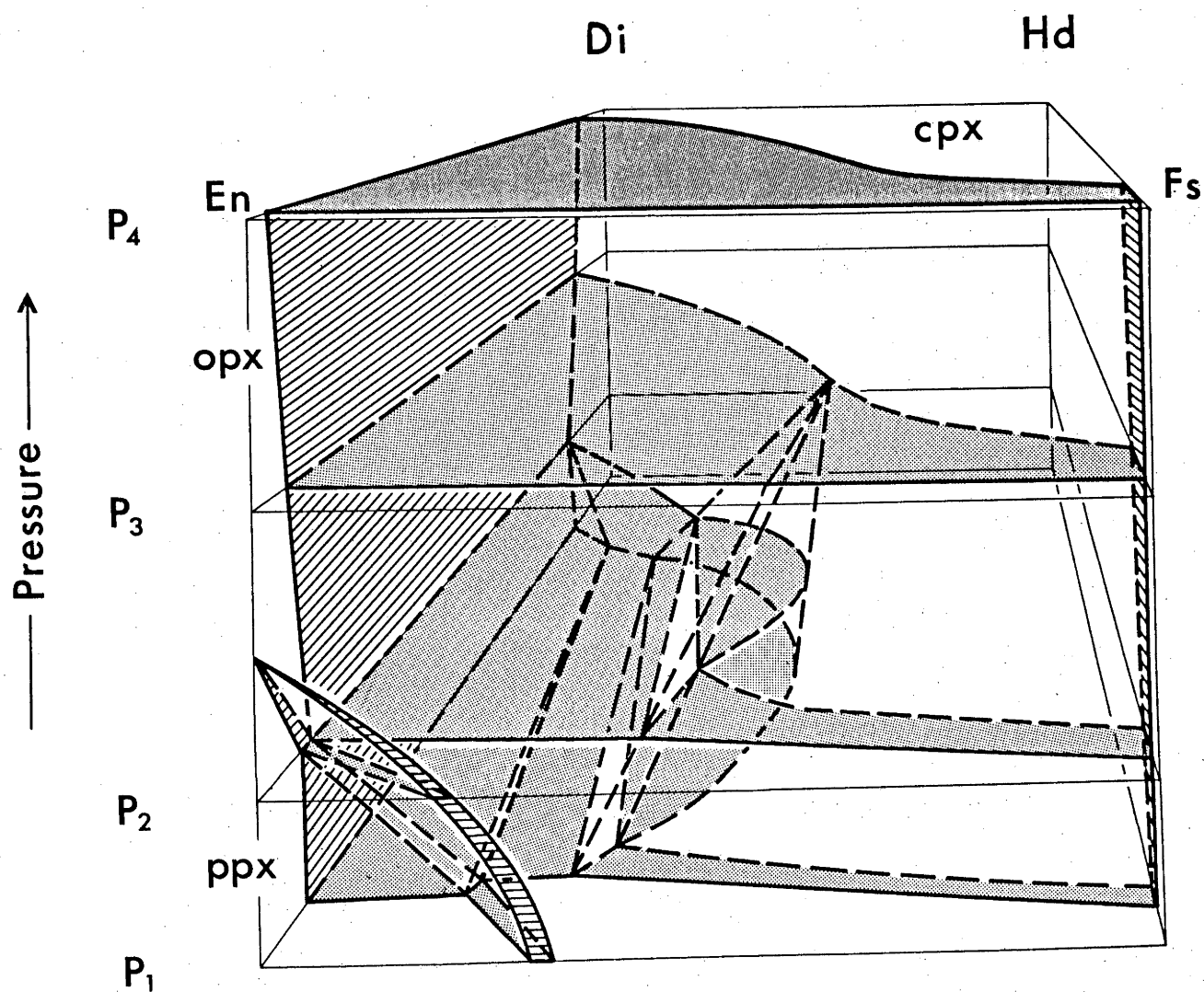


Fig. 7

Schematic phase diagram of pyroxenes in the pressure-composition space. Abbreviations are: *opx* - orthopyroxene, *cpx* - clinopyroxene, *ppx* - protopyroxene. See text for explanation.

pigeonite (Yang and Foster, 1972 ; Kushiro, 1972; Yang, 1973) would be merely an iron-free variant of the last category. The fifth and sixth phases, P_{21}/c low clinopyroxene (Lindsley, 1965; Grover, 1972) and P_{21}/c low orthopyroxene (Smyth, 1974) are still problematical in view of their stability, and are not included in the discussion. Should they be stable, however, the low pyroxenes occur at lower temperatures than P_{bca} orthopyroxene, thus only the low temperature regions of orthopyroxene field would be modified.

Among the four pyroxenes, three are depicted in Figure 6: Ca-rich and Ca-poor clinopyroxenes and orthopyroxene. There is a field where these three pyroxenes coexist at the temperature of T_1 . As temperature increases Ca-rich clinopyroxene/orthopyroxene solvus narrows and the three phase field moves toward the En-Di join. After the appearance of Ca-free clinopyroxene, the topology of phase boundaries holds unchanged until T_2 is reached where the two-clinopyroxene solvus vanishes and the triangle converges into an orthopyroxene-clinopyroxene join. With further increase of temperature, the orthopyroxene-clinopyroxene solvus continues to narrow.

Figure 7 is more complicated by the presence of protopyroxene at low pressures. At pressure of P_1 , all the four pyroxenes appear with two three-phase fields: protopyroxene/orthopyroxene/Ca-rich clinopyroxene and orthopyroxene/Ca-poor clinopyroxene/Ca-rich clinopyroxene. As pressure increases, the two three-phase fields move apart. The former converges into the En-Di join at P_2 and the latter reaches to a critical point at P_3 . Above P_3 , only the orthopyroxene-clinopyroxene solvus stretches from the En-Di join to Fs-Hd join. The orthopyroxene/Ca-rich clinopyroxene solvus widens with increasing pressure.

At 0 to 2 kbar

The experimental information is much restricted to the joins En-Di (Boyd and Schairer, 1964; Kushiro, 1972) and Fs-Hd (Lindsley and Munoz, 1969). In the former join, all the four pyroxenes appear at appropriate temperatures, but the latter join is characterized by wollastonite, fayalite and quartz

except at the Hd corner where clinopyroxene is stable at temperatures lower than 960°C. Experiments along the En-Fs join are scarce, but it is generally inferred that orthopyroxene inverts to Ca-free clinopyroxene at higher temperature. This inference is based on the classic work by Bowen and Schairer (1935) and high-temperature single crystal X-ray study by Smyth (1969), both of whom used natural orthopyroxenes with Wo content up to 3 mole percent instead of strictly Ca-free orthopyroxene.

The phase relations within the quadrilateral can be inferred by analogy with those in natural rock systems. Especially, Ross and Huebner's (1975) experimental study on natural orthopyroxenes containing augite lamellae established that there is a field where Ca-rich and Ca-poor clinopyroxenes and orthopyroxene coexist, and that this field moves towards the En-Di join as temperature increases. This feature is consistent with petrographical observation of coexisting three pyroxenes in nature (e.g. Nakamura and Kushiro, 1970). The field, however, would not stretch to the En-Di join at this pressure range, but be intercepted by appearance of protopyroxene (Warner, 1975; Mori and Green, 1975). Ross and Huebner's (1975) data give a temperature of first appearance of Ca-poor clinopyroxene from Ca-rich clinopyroxene/orthopyroxene assemblage as a function of the Mg/(Mg + Fe) ratio of orthopyroxene:

$$T^{\circ}\text{C} = 440 \times [\text{Mg}/(\text{Mg} + \text{Fe})]^{\text{opx}} + 860$$

However, since the temperature may be strongly affected by presence or absence of certain elements (c.f. Lindsley et al., 1974c), this equation could be different from the counterpart in the simple system.

At 15 to 20 kbar

15 kbar is the pressure where the phase relations have been best studied in the literature. Figure 8 illustrates a comparison of the present data at 1200°C to those at 980°C and 810°C (Lindsley et al., 1974 a and b). At 980°C, three-phase field occurs and some additional data from slightly different temperatures are available to confirm this: Smith (1972) indicated

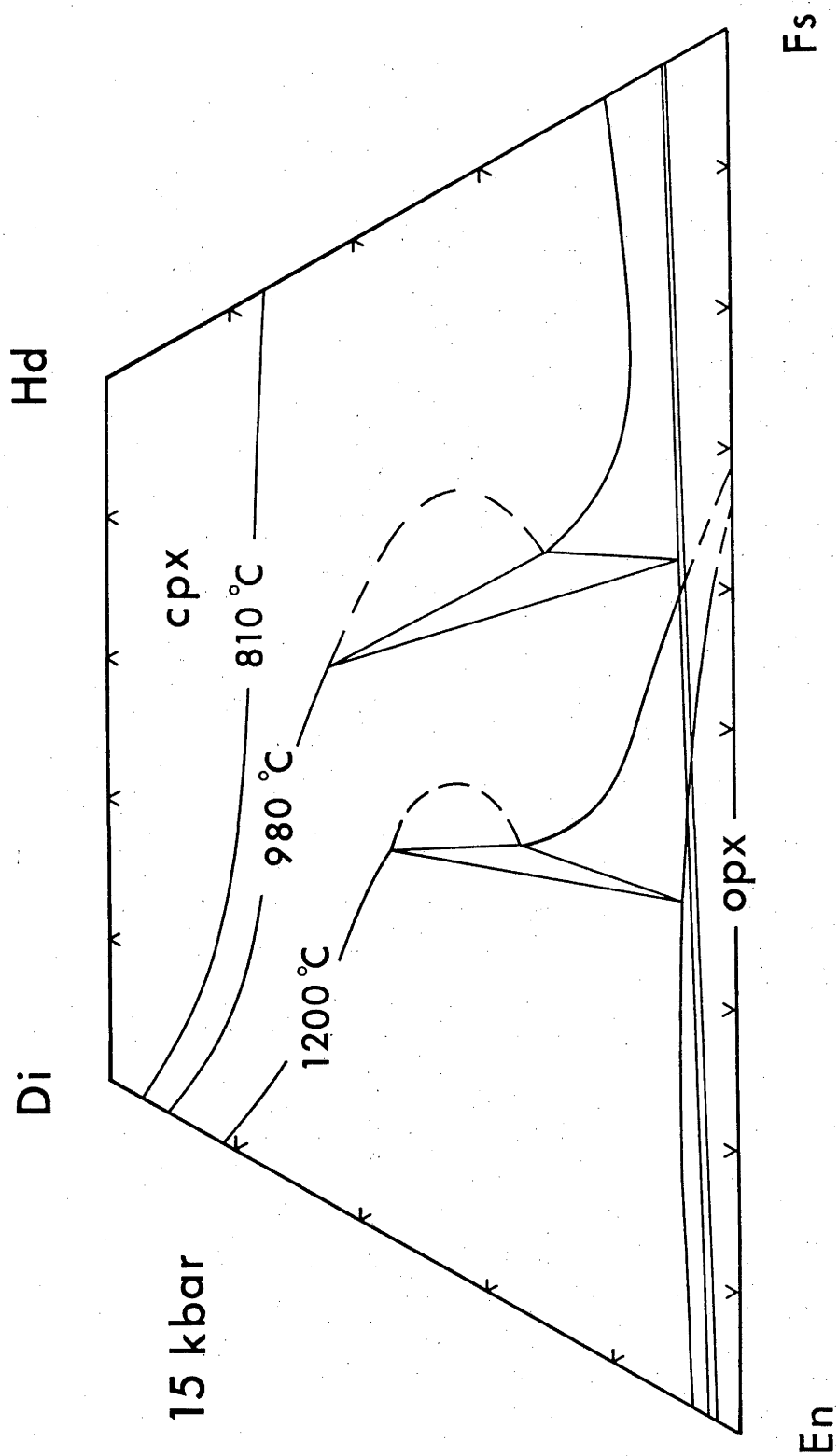


Fig. 8 Comparison of three isothermal sections at 15 kbar. The data at 810°C and 980°C are from Lindsley et al, (1974a and b).

its presence along the join of $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.85$ at 880°C and 15-16 kbar, and similarly, at 1000° and 900°C for the joins of $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.6$ and 0.75 , respectively (Grover et al., 1972). Thus, these data are consistent with the trend observed at low pressures, i.e. three-phase field moves towards the En-Di join as temperature increases. The Wo content of Ca-poor clinopyroxene at the apex of the three-phase field is much higher than those found in low-pressure natural rocks (8 to 10 mole percent). Therefore, as is depicted in Figure 7, Wo content is expected to increase with pressure.

The two-clinopyroxene solvus is narrower at 1200°C than at 980°C , and is expected to disappear at higher temperature before the solvus reaches at the En-Di join. This feature is depicted at T_2 in Figure 6.

The lack of the three-pyroxene field at 810°C would be explained in two ways: firstly, the three-phase field had already reached the Fs-Hd join at 810°C , or secondly, it converged somewhere in the Fe-rich part within the quadrilateral before reaching the Fs-Hd join thereby resulting single orthopyroxene-clinopyroxene solvus stretching between two joins En-Di and Fs-Hd.

At 20 kbar, no two-clinopyroxene solvus was found along the joins of $\text{Fe}/(\text{Fe} + \text{Mg}) = 1, 0.6$ and 0 (Lindsley and Munoz, 1969; Turnock, 1970; Howells and O'Hara, 1975; Lindsley and Dixon, 1975; Mori and Green, 1976). However, it is not clear whether this is so all over the quadrilateral or if the two-clinopyroxene solvus and also three-phase field appear in some restricted compositional range. The phase relations at 20 kbar would be depicted by sections just above or below P_3 in Figure 8, according to which of these alternatives is correct.

At 30 kbar

No Ca-poor clinopyroxene (Fe-free pigeonite) was found in the join En-Di (Mori and Green, 1976). The isothermal section at 1200°C (Figure 4) demonstrates the orthopyroxene-clinopyroxene solvus stretching between the two joins of En-Di and Fs-Hd. At 915°C along the join of $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.85$,

Smith (1972) reported a pair of Ca-rich clinopyroxene and orthopyroxene. The three-phase field has not been observed at 30 kbar. As is the case at 15 kbar, high temperature brings in clinopyroxene on the Fe-rich side of the En-Fs join (run 201, Table 1). Figure 7 between P_3 and P_4 gives pictorial basis for understanding the phase relations at 1200°C and 30 kbar.

Fe-Mg PARTITION BETWEEN PYROXENES

The chemical compositions of coexisting orthopyroxene and clinopyroxene in a wide range of Fe/(Mg + Fe) at 30 kbar and 1200°C yield suitable data to examine the Fe-Mg partition between the pyroxenes and test if this partition is independent of the bulk chemistry or not. Partition coefficient of Fe and Mg between phases or sites A and B is defined as

$$K^{A/B} = (Fe/Mg)^A / (Fe/Mg)^B$$

$K^{opx/cpx}$ at 30 kbar and 1200°C is plotted against Fe/(Mg + Fe) of orthopyroxene in Figure 9. $K^{opx/cpx}$ appears to decrease as orthopyroxene is enriched in Fe, and as Ca in clinopyroxene sympathetically decreases. The same tendency was reported from Broken Hill granulite pyroxenes (Binns, 1962), and was also suggested by Lindsley *et al.* (1974a) on experimental basis at 810°C and 15 kbar. Thus, both orthopyroxene and clinopyroxene cannot be ideal solution in terms of Fe and Mg. In fact, it is well known that Fe preferably enters into M2 site of pyroxenes resulting in deviation from ideality.

Alternatively, the ideally double-sited model (Banno and Matsui, 1966; Blander, 1972) assumes ideal Fe-Mg partition between M1 and M2 sites of pyroxenes. In this model, overall nonideality is caused solely by the intracrystalline partition of Fe and Mg. According to the model, three pairs of coexisting pyroxenes allow to calculate $K^{opx-M2/opx-M1}$ and $K^{cpx-M2/cpx-M1}$, if all Ca is assumed to be at M2. However, the calculation requires impractically high accuracy of the chemical data. Instead, these two coefficients at 1200°C can be estimated, based on Virgo and Hafner (1969),

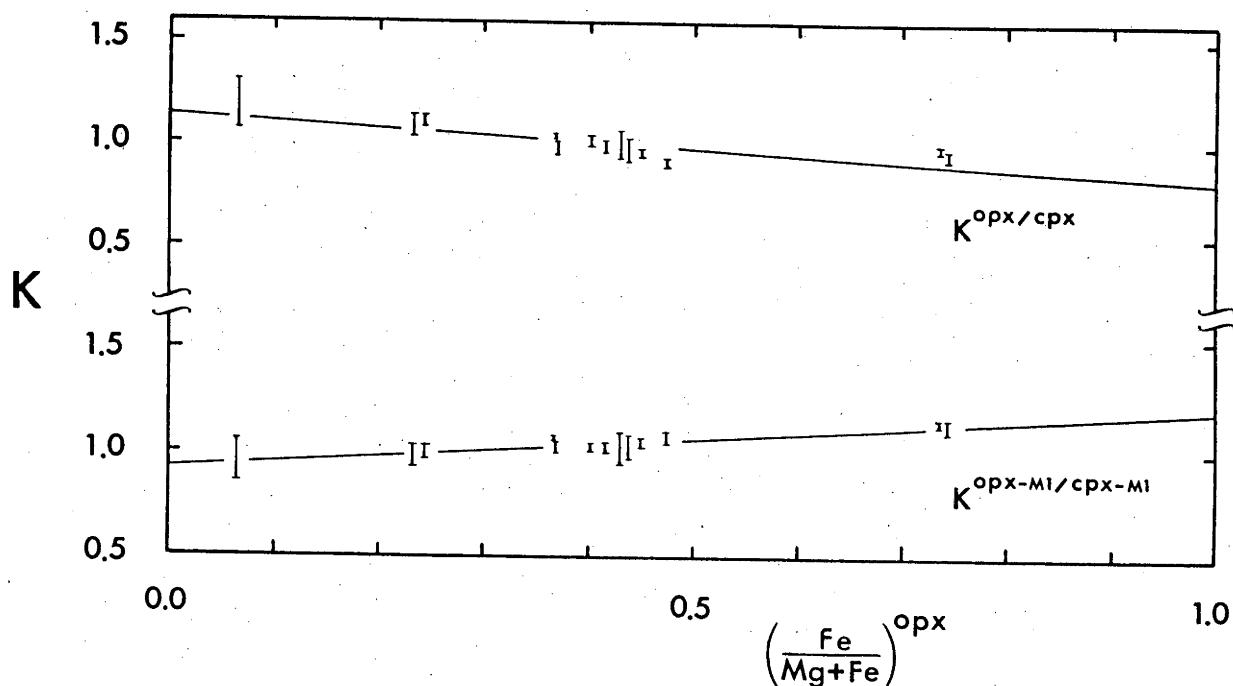


Fig. 9 Distribution of Fe and Mg between orthopyroxene and clinopyroxene (above) plotted against the $\text{Fe}/(\text{Mg} + \text{Fe})$ ratio of orthopyroxene. The Fe-Mg distribution between orthopyroxene-M1 and clinopyroxene-M1 is calculated on the basis of the ideally double-sited model of pyroxenes (see text). The error bars represent spreads due to the chemical differences within the three best-reacted compositions which are plotted in Figures 4 and 5.

Smyth (1973) and McCallister et al (1976), to be 2.48 and 4.35 respectively. One of the required properties of the model is constant $K^{\text{opx-Ml/cpx-Ml}}$ throughout entire range of Fe/Mg at constant pressure and temperature. Figure 9 also shows the coefficient as a function of overall Fe/(Mg + Fe) of orthopyroxene. The coefficient increases as orthopyroxene becomes enriched in Fe. Therefore, this model is not strictly satisfactory either.

SOME UNUSUAL NATURAL PYROXENES

Apart from the rapidly crystallized Ca-poor clinopyroxenes in basalts, almost every natural pyroxene fits in the generalized scheme of pyroxene phase equilibria described in the previous sections. However, there are a few exceptions which do not satisfactorily fit in the scheme. These pyroxenes along with some other unusual natural pyroxenes are referred to from the literature.

Cape Vogel protopyroxene

Dallwitz et al (1966) described phenocrysts of Ca-poor clinoenstatites coexisting with orthopyroxenes in a magnesian "andesite" from Cape Vogel, Papua. As has been discussed by them and by Nakamura (1971), there is every evidence that the clinoenstatite was primarily protopyroxene which later inverted to clinopyroxene upon cooling. Chemical compositions of coexisting protopyroxene and orthopyroxene are reproduced in Figure 10. Compositional relation between the two pyroxenes clearly corresponds to the inferred phase relation of pyroxenes at a pressure between P_1 and P_2 or slightly greater than P_2 in Figure 7. Dallwitz et al (1966) and Nakamura's (1971) inference that this andesite crystallized the protopyroxene and orthopyroxene at a very low pressure and high temperature is consistent to the generalized scheme of pyroxene equilibria.

Connecticut clinobronzite

The report of clinobronzite by Philpotts and Gray (1974) is noteworthy. The clinobronzite is phenocrysts in the chilled margins of a

Connecticut diabase dike. While optically they are now orthopyroxene, the morphology of the crystals clearly shows monoclinic form, indicating that the phenocrysts originally crystallized as clinopyroxene (pigeonite), then inverted to orthopyroxene upon cooling. The composition of the clinobronzite (Figure 10) is slightly higher in CaO and FeO than that of the orthopyroxene III used by Bowen and Schairer (1935) for the experiments to define orthopyroxene-clinopyroxene inversion at atmospheric pressure. The inversion took place at around 1130°C in Bowen and Schairer's experiments. Recent similar experiments by Ross et al (1973) and Ross and Huebner (1975), however, show that augite-bearing orthopyroxene with similar composition to Bowen and Schairer's (1935) orthopyroxene III reacted to form Ca-poor clinopyroxene (pigeonite) and liquid at 1240°C. Because of these conflicting experimental results, it is not clear if the Connecticut clinobronzite corresponds to the Bowen and Schairer's orthopyroxene-clinopyroxene inversion. However, this new occurrence of clinobronzite strongly suggests that orthopyroxene/Ca-poor clinopyroxene field reaches around $\text{Ca}_{0.05}\text{Mg}_{0.75}\text{Fe}_{0.20}\text{SiO}_3$ composition at low pressures and high temperatures, and that it will extend to the En-Fs join, as was found at 15 kbar and 1200°C.

Subcalcic clinopyroxene lamellae from Makrirkakhi, Greece

From the ultramafic and mafic rocks at Makrirkakhi, Greece, Menzies (1973) reported subcalcic clinopyroxene lamellae ($\sim\text{Wo}_{28}$) in calcic clinopyroxene ($\sim\text{Wo}_{50}$). Their compositions are reproduced in Figure 10. These lamellae, if equilibrated with the host pyroxenes, directly conflict with any experimentally determined two-clinopyroxene solvus. It is not well understood how these lamellae were formed from the very calcic host clinopyroxenes. One possibility is that the subcalcic clinopyroxenes are not equilibrium products exsolved from the calcic clinopyroxenes, and it is perhaps possible that they are in fact very thin amphibole lamellae, and not clinopyroxenes as reported by Menzies (1973).

REFERENCES

- AKIMOTO, S., KATSURA, T., SYONO, Y., FUJISAWA, H. & KOMADA, E., 1965.
Polymorphic transition of pyroxenes FeSiO_3 and CoSiO_3 at high pressures and temperatures. *J. Geophys. Res.* 70, 5269-78.
- BANNO, S., & MATSUI, Y., 1966. Intracrystalline exchange equilibrium in orthopyroxene. *Proc. Japan. Acad.* 42, 629-33.
- BINNS, R.A., 1962. Metamorphic pyroxenes from the Broken Hill district, New South Wales. *Mineral. Mag.* 33, 320-38.
- BLANDER, M., 1972. Thermodynamic properties of orthopyroxenes and clinopyroxenes based on the ideal two-site model. *Geochim. Cosmochim. Acta*, 36, 787-99.
- BORG, I.Y. & SMITH, D.K., 1969. Calculated X-ray powder patterns for silicate minerals. *Geol. Soc. Am. Memoir* 122.
- BOWEN, N.L., & SCHAIRER, J.F., 1935. The system, MgO-FeO-SiO_2 . *Am. J. Sci.* 229, 151-217.
- BOYD, F.R., & SCHAIRER, J.F., 1964. The system $\text{MgSiO}_3\text{-CaMgSi}_2\text{O}_6$. *J. Petrol.* 5, 275-309.
- BROWN, G.E., PREWITT, C.T., PAPIKE, J.J., & SUENO, S., 1972.
A comparison of the structures of low and high pigeonite. *J. Geophys. Res.* 77, 5778-89.
- CHEN, C-H., & PRESNALL, D., 1975. The system $\text{Mg}_2\text{SiO}_4\text{-SiO}_2$ at pressures up to 25 kilobars. *Am. Mineral.* 60, 398-406.
- DALLWITZ, W.B., GREEN, D.H., & THOMPSON, J.E., 1966.
Clinoenstatite in a volcanic rock from the Cape Vogel area, Papua. *J. Petrol.* 7, 375-403.
- GROVER, J., 1972. The stability of low-clinoenstatite in the system $\text{Mg}_2\text{Si}_2\text{O}_6\text{-CaMgSi}_2\text{O}_6$. *Trans. Am. Geophys. Union.* 53, 539.
- GROVER, J.E., LINDSLEY, D.H. & TURNOCK, A.C., 1972. Ca-Mg-Fe pyroxenes: subsolidus phase relations in iron-rich portions of the pyroxene quadrilateral. *Geol. Soc. Am. Abstracts with Programs* 4, 521-2.

- HENSEN, B.J., 1973. Pyroxenes and garnets as geothermometers and barometers. Carnegie Inst. Wash. Year Book, 72, 527-34.
- HOWELLS, S. & O'HARA, M.J., 1975. Palaeogeotherms and the diopside-enstatite solvus. Nature, 254, 406-8.
- KISS, A., 1974. Synthesis of a sulphonated ferroin reagent for chelating iron (II) in strong acid. Spectrophotometric determination of the oxidation state of iron in silicates. Analytica Chimica Acta, 72, 127-44.
- KUSHIRO, I., 1972. Determination of liquidus relations in synthetic silicate systems with electron probe analysis: the system forsterite-diopside-silica at 1 atmosphere. Am. Mineral. 57, 1260-71.
- LINDSLEY, D.H., 1965. Ferrosilite. Carnegie Inst. Wash. Year Book, 64, 148-50.
- LINDSLEY, D.H., 1967. The join hedenburgite-ferrosilite at high pressures and temperatures. Carnegie Inst. Wash. Year Book 65, 230-4.
- LINDSLEY, D.H. & BURNHAM, C.W., 1970. Pyroxferroite: stability and X-ray crystallography of synthetic $\text{Ca}_{0.15}\text{Fe}_{0.85}\text{SiO}_3$ pyroxenoid. Science 168, 364-7.
- LINDSLEY, D.H. & DIXON, S.A., 1975. Coexisting diopside and enstatite at 20 kbar 900°-1200°C. Geol. Soc. Am. Abstracts with Programs 7, 1171.
- LINDSLEY, D.H., KING, H.E. JR., & TURNOCK, A.C., 1974a. Compositions of synthetic augite and hypersthene coexisting at 810°C: Application to pyroxenes from lunar highland rocks. Geophys. Res. Lett. 1, 134-6.
- LINDSLEY, D.H., KING, H.E. JR., TURNOCK, A.C. & GROVER, J.E., 1974b. Phase relations in the pyroxene quadrilateral at 980°C and 15 kbar. Geol. Soc. Am. Abstracts with Programs, 6, 846.
- LINDSLEY, D.H. & MUNOZ, J.L., 1969. Subsolidus relations along the join hedenburgite-ferrosilite. Am. J. Sci. Schairer vol. 267-A, 295-324.
- LINDSLEY, D.H., TSO, J. & HEYSE, J.V., 1974c. Effect of Mn on the stability of pigeonite. Geol. Soc. Am. Abstracts with Programs 6, 846-7.

- McALLISTER, R.H., FINGER, L.W., & OHASHI, Y., 1976. Intracrystalline Fe^{2+} -Mg equilibria in three natural Ca-rich clinopyroxenes. *Am. Mineral.* 61, 671-676.
- MENZIES, M., 1973. Mineralogy and partial melt textures within an ultramafic-mafic body, Greece. *Contrib. Mineral. Petrol.* 42, 273-85.
- MORI, T., & GREEN, D.H., 1975. Pyroxenes in the system $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ at high pressure. *Earth Planet. Sci. Lett.* 26, 277-86.
- MORI, T., & GREEN, D.H., 1976. Subsolidus equilibria between pyroxenes in the CaO-MgO-SiO_2 system at high pressures and temperatures. *Am. Mineral.* 61, 616-25.
- NAKAMURA, Y., 1971. Equilibrium relations in Mg-rich part of pyroxene quadrilateral. *Mineral. J.* 6, 264-76.
- NAKAMURA, Y. & KUSHIRO, I., 1970. Equilibrium relations of hypersthene, pigeonite and augite in crystallizing magmas: microprobe study of pigeonite andesite from Weiselberg, Germany. *Am. Mineral.* 55, 1999-2015.
- PHILPOTTS, A.R., & GRAY, N.H., 1974. Inverted clinobronzite in eastern Connecticut diabase. *Am. Mineral.* 59, 374-7.
- ROSS, M. & HUEBNER, J.S., 1975. A pyroxene geothermometer based on composition-temperature relationships of naturally occurring orthopyroxene, pigeonite and augite. Extended abstracts, International Conference on Geothermometry and Geobarometry, Pennsylvania State Univ.
- ROSS, M., HUEBNER, J.S., & HICKLING, N., 1973. Delineation of the orthopyroxene-pigeonite transition and its bearing on pyroxene phase relations in lunar rocks. *Lunar Science* 3, 637-9.
- SIMMONS, E.C., LINDSLEY, D.H. & PAPIKE, J.J., 1974. Phase relations and crystallization sequence in a contact-metamorphosed rock from the Gunflint iron formation, Minnesota. *J. Petrol.* 15, 539-65.
- SMITH, D., 1971. Stability of the assemblage iron-rich orthopyroxene-olivine-quartz. *Am. J. Sci.* 271, 370-82.
- SMITH, D., 1972. Stability of iron-rich pyroxene in the system CaSiO_3 -

- FeSiO₃-MgSiO₃. Am. Mineral. 57, 1413-28.
- SMYTH, J.R., 1969. Orthopyroxene high-low clinopyroxene inversions. Earth Planet. Sci. Lett. 6, 406-7.
- SMYTH, J.R., 1973. An orthopyroxene structure up to 850°C. Am. Mineral. 58, 636-48.
- SMYTH, J.R., 1974. Low orthopyroxene from a lunar deep crustal rock: a new pyroxene polymorph of space group $P2_1ca$. Geophys. Res. Lett. 1, 27-9.
- TURNOCK, A.C., 1970. A pyroxene solvus section. Canadian Mineral. 10, 744-7.
- TURNOCK, A.C., LINDSLEY, D.H. & GROVER, J.E., 1973. Synthesis and unit cell parameters of Ca-Mg-Fe pyroxenes. Am. Mineral. 58, 50-9.
- VIRGO, D., & HAFNER, S.S., 1969. Fe²⁺, Mg order-disorder in heated orthopyroxenes. Mineral. Soc. Am. Spec. Pap. 2, 67-81.
- WARNER, R.D., 1975. New experimental data for the system CaO-MgO-SiO₂-H₂O and a synthesis of inferred phase relations. Geochim. Cosmochim. Acta, 39, 1413-21.
- YANG, H-Y, 1973. Crystallization of iron-free pigeonite in the system anorthite-diopside-enstatite-silica at atmospheric pressure. Am. J. Sci. 273, 488-97.
- YANG, H-Y, & FOSTER, W.R., 1972. Stability of iron-free pigeonite at atmospheric pressure. Am. Mineral. 57, 1232-41.

CHAPTER 5

GEOTHERMOMETRY OF SPINEL LHERZOLITES

TAKESHI MORI

ABSTRACT

Three methods of geothermometry, currently used for spinel lherzolites, are refined based on new experiments on subsolidus phase equilibria of olivine, pyroxenes and spinel in $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ and natural rock systems at 16 kb and 1200°C. Although quasi-thermodynamic modelling is employed, the methods are essentially based on the pyroxene solvus, alumina contents in clinopyroxene and orthopyroxene. Increasing alumina contents in pyroxenes reduce enstatite and diopside components in clinopyroxene and orthopyroxene, respectively. Thus, neglect of alumina in pyroxenes causes underestimates of temperatures by the solvus method.

The three geothermometers were tested by applying them to homogeneous spinel lherzolites which were especially selected for this purpose. Coincidence of the three temperatures thus estimated gives confidence in the effectiveness of the geothermometers.

They were also applied to spinel lherzolite nodules in basalts and intrusive lherzolites described in the literature. It was found that equilibration temperature of the nodules varies from 1000°C to 1300°C, i.e., temperatures somewhat higher than have been generally thought. In contrast to the nodules, the intrusive spinel lherzolites show extensive disequilibrium, which is probably due to retrogressive metamorphism suffered by the intrusives.

INTRODUCTION

In the last decade, ultramafic nodules in basalts and intrusive periodotites have been subjected to intensive studies by petrologists as one of the keys to understanding the earth's upper mantle. Particularly, the relatively constant whole rock chemistry and world-wide distribution of spinel lherzolite nodules in basalts in conjunction with the experimentally determined stability field for spinel lherzolite mineralogy [1, 2] established the concept of an uppermost mantle dominantly composed of spinel lherzolites. The petrographic and chemical information on spinel lherzolites has been

summarized [3]. A fundamental unsolved problem relating to spinel lherzolites is the estimation of the physical conditions of equilibration for individual nodules; this knowledge is fundamental because of its direct relevance to the geologic processes in the uppermost mantle, and it is unsolved because of the limited data available for phase equilibria between coexisting olivine, pyroxenes and spinel in natural rock systems.

Currently, there are two types of approach to temperature and pressure estimates for the spinel lherzolites:

- 1) Boyd-MacGregor grids [4, 5] in which estimates of temperature are based on the pyroxene solvus, more specifically, $\text{Ca}/(\text{Ca}+\text{Mg})$ ratio of clinopyroxene. Pressure is estimated by alumina solubility in orthopyroxene. The grids do not appear to survive a field test by Wilshire and Jackson [6].
- 2) Thermodynamic models which are constructed on the experimental data in simple systems but are intended for use for natural rocks [7, 8, 9].

This approach originated with Wood and Banno [10].

Unfortunately our knowledge of the phase equilibria of olivine, pyroxenes and spinel even in simple systems with at most four components ($\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$) is not well established and currently in debate. The most serious debate concerns alumina solubility in orthopyroxene coexisting with olivine and spinel in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system. According to MacGregor [5], the solubility increases with temperature and decreases with pressure. However, Presnall [11] suggests the opposite pressure effect. A third opinion suggests very small pressure effect [8, 12, 13] and is based on simple thermodynamic models of olivine, orthopyroxene and spinel. These models are inferred from garnet-orthopyroxene equilibria as experimentally determined by MacGregor [5] in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system but necessarily ignore the orthopyroxene-spinel equilibria data obtained in the same study [5]. Fujii and Takahashi [13] also experimented on orthopyroxene-spinel equilibria in the same system at 1400°C from 10 to 20 kb, and found no pressure effect on

Al_2O_3 solubility in orthopyroxene. Their experiments are, however, overwhelmed in quantity by those of MacGregor [5].

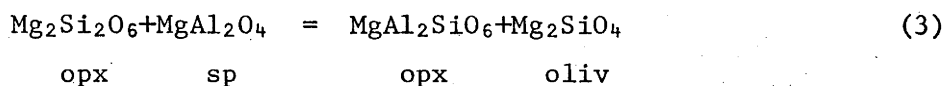
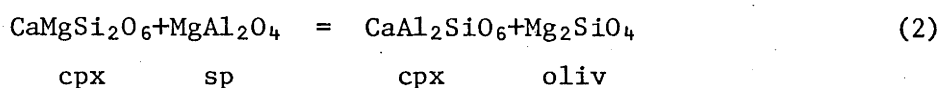
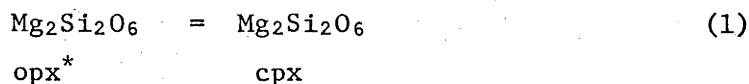
The other important phase relationship, i.e. the pyroxene solvus in the CaO-MgO-SiO_2 system, was recently redetermined [14, 15, 16] with the result that the solvus was shown to be a function of both temperature and pressure. Thus, if the solvus at any one pressure is used in geothermometry, some error in temperature estimates is expected from neglect of the pressure effect.

The thermodynamic approach is convenient in dealing with minerals in natural rock systems and ideally is superior to the first approach. A problem here is in the thermodynamic models themselves. Present knowledge is far from accurate in the assignment of cations to different sites in minerals. In addition, we know little of the thermodynamic properties of relevant solid solutions. Inevitably, many assumptions, some of which are highly unlikely have to be introduced. Overall errors in temperature and pressure estimates thereby caused are beyond our assessment.

This paper presents preliminary experimental data on equilibria between olivine, orthopyroxene, clinopyroxene and spinel in both simple and natural rock systems, proposes three methods of temperature estimates for spinel lherzolites, and examines the reliability of these methods by applying them to homogeneous natural spinel lherzolites. Temperatures of these rocks are estimated based on an assumed pressure of 16 kb, and the errors caused by this assumption are evaluated. This particular value of pressure was chosen because it is near the middle point of the experimentally determined stability field of spinel lherzolite, from about 8 kb to 24 kb at 1000 to 1300°C [1, 2, 17, 18].

THERMODYNAMIC MODELS

Three independent chemical reactions are used as the basis of the geothermometry. They involve two or three minerals among olivine, orthopyroxene, clinopyroxene and spinel. Because the methods are almost the same as those in the literature [7, 8, 9, 10], only brief descriptions are given. The three chemical reactions are as follows:



Equilibrium reaction coefficients for these reactions are:

$$K_1 = \frac{A_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{cpx}}}{A_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{opx}}} \quad (4)$$

$$K_2 = \frac{A_{\text{CaAl}_2\text{SiO}_6}^{\text{cpx}} \cdot A_{\text{Mg}_2\text{SiO}_4}^{\text{oliv}}}{A_{\text{CaMgSi}_2\text{O}_6}^{\text{cpx}} \cdot A_{\text{MgAl}_2\text{O}_4}^{\text{sp}}} \quad (5)$$

$$K_3 = \frac{A_{\text{MgAl}_2\text{SiO}_6}^{\text{opx}} \cdot A_{\text{Mg}_2\text{SiO}_4}^{\text{oliv}}}{A_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{opx}} \cdot A_{\text{MgAl}_2\text{O}_4}^{\text{sp}}} \quad (6)$$

In these equations, A_j^i represents the activity of component j in phase i .

The models assume:

- 1) ideal solid solutions where cations mix ideally in sites
- 2) Fe^{2+} and Mg in pyroxenes and olivine randomly distribute between the two cation sites (M1 and M2).

* Abbreviations used in this paper are: opx = orthopyroxene, cpx = clinopyroxene, oliv = olivine, sp = spinel.

- 3) Ca^{2+} , Na^{+} , and Mn^{2+} of pyroxenes are allocated to M2; Fe^{3+} , Ti^{4+} and Cr^{3+} are assigned to M1, tetrahedral $\text{Al}^{3+}(\text{x}_{\text{Al}}^{\text{T}})$ is identical to 2-Si, and the remaining Al^{3+} is assigned to M1.
- 4) Al^{3+} in tetrahedral and M1 sites are completely coupled to form tschermaks' components.

Thus, activities are calculated as follows:

$$\begin{aligned}
 A_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{cpx}} &= (\text{x}_{\text{Mg}}^{\text{M2}} \cdot \text{x}_{\text{Mg}}^{\text{M1}})^{\text{cpx}} \\
 A_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{opx}} &= (\text{x}_{\text{Mg}}^{\text{M2}} \cdot \text{x}_{\text{Mg}}^{\text{M1}})^{\text{opx}} \\
 A_{\text{CaAl}_2\text{SiO}_6}^{\text{cpx}} &= [\text{x}_{\text{Ca}}^{\text{M2}} \cdot \text{MIN}(\text{x}_{\text{Al}}^{\text{M1}}, \text{x}_{\text{Al}}^{\text{T}})]^{\text{cpx}} \\
 A_{\text{MgAl}_2\text{SiO}_6}^{\text{opx}} &= [\text{x}_{\text{Mg}}^{\text{M2}} \cdot \text{MIN}(\text{x}_{\text{Al}}^{\text{M1}}, \text{x}_{\text{Al}}^{\text{T}})]^{\text{opx}} \\
 A_{\text{CaMgSi}_2\text{O}_6}^{\text{cpx}} &= (\text{x}_{\text{Ca}}^{\text{M2}} \cdot \text{x}_{\text{Mg}}^{\text{M1}})^{\text{cpx}} \\
 A_{\text{Mg}_2\text{SiO}_4}^{\text{oliv}} &= [(\text{x}_{\text{Mg}})^2]^{\text{oliv}} \\
 A_{\text{MgAl}_2\text{O}_4}^{\text{sp}} &= [\text{x}_{\text{Mg}} \cdot (\text{x}_{\text{Al}})^2]^{\text{sp}}
 \end{aligned} \tag{7}$$

where MIN (i,j) represents the smaller value between i and j. Fe^{3+} of spinel, if not analytically determined and if the total cation is more than 3.0 per 4 oxygens, is estimated assuming stoichiometry of spinel, and the chemical formula is readjusted before the calculation of $A_{\text{MgAl}_2\text{O}_4}^{\text{sp}}$.

Substitutions of equations 4, 5 and 6 by 7 give:

$$K_1 = \frac{(\text{x}_{\text{Mg}}^{\text{M2}} \cdot \text{x}_{\text{Mg}}^{\text{M1}})^{\text{cpx}}}{(\text{x}_{\text{Mg}}^{\text{M2}} \cdot \text{x}_{\text{Mg}}^{\text{M1}})^{\text{opx}}} \tag{8}$$

$$K_2 = \frac{[X_{Ca}^{M2} \cdot \text{MIN}(X_{Al}^{M1}, X_{Al}^T)]^{cpx} \cdot [(X_{Mg})^2]^{oliv}}{(X_{Ca}^{M2} \cdot X_{Mg}^{M1})^{cpx} \cdot [X_{Mg} \cdot (X_{Al})^2]^{sp}} \quad (9)$$

$$K_3 = \frac{[X_{Mg}^{M2} \cdot \text{MIN}(X_{Al}^{M1}, X_{Al}^T)]^{opx} \cdot [(X_{Mg})^2]^{oliv}}{(X_{Mg}^{M2} \cdot X_{Mg}^{M1})^{opx} \cdot [X_{Mg} \cdot (X_{Al})^2]^{sp}} \quad (10)$$

These three coefficients are functions of temperature and pressure, and also of chemistry if the assumed simple models of the solid solutions are not adequate. They have been experimentally calibrated or can be calculated from the data in the literature. It should be noted that these calibrations are derived in simple chemical systems:-

K_1 can be calculated as a function of temperature and pressure by the experimental data on coexisting orthopyroxene and clinopyroxene in the CaO-MgO-SiO₂ system of Mori and Green [15, 16]. The function plotted in the $\ln K_1$ vs. $1/T^\circ K$ shows strong curvature at 30 kb, contrasting to the straight line obtained by Wood and Banno [10] who used Davis and Boyd's [19] data. Almost the same degree of curvature is also found in the data of pyroxenes in the same system at 30 kb [20] and 20 kb [21]. Interpolation of Mori and Green's [15] data at 16 kb gives an equation:

$$\frac{10^4}{T^\circ K} = 0.413 (\ln K_1)^2 - 0.0234 \ln K_1 + 5.61 \quad (11)$$

K_1 vs T relation at 16 kb has been presented also in the more complex system CaO-MgO-Al₂O₃-SiO₂ by Herzberg and Chapman [9]:

$$\frac{10^4}{T^\circ K} = -1.177 \ln K_1 + 4.215 \quad (12)$$

but, since Herzberg and Chapman did not directly determine compositions of orthopyroxenes, the equation 11 is preferred to 12.

K_2 has been calibrated in the system CaO-MgO-Al₂O₃-SiO₂ by Herzberg and Chapman [9]. Their equation at 16 kb is:

$$\frac{10^4}{T^\circ K} = -1.083 \ln K_2 + 4.80 \quad (13)$$

Temperature of their experiments ranges from 1100 to 1400°C.

K_3 can be calculated on the basis of experimental data of orthopyroxene which is coexisting with olivine and spinel in a wide range of temperature and pressure in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system by MacGregor [5]. Assuming both olivine and spinel are pure phases, his results at 16 kb give a curve of second degree:

$$\frac{10^4}{T^{\circ}\text{K}} = 0.357 (\ln K_3)^2 - 0.53 \ln K_3 + 5.2 \quad (14)$$

MacGregor's data are, however, currently being challenged [8, 12, 13] as mentioned in the introduction. An alternative scheme in the same system presented by Obata [8, his Fig. 2] gives an equation at 16 kb:

$$\frac{10^4}{T^{\circ}\text{K}} = -2.061 \ln K_3 + 3.454 \quad (15)$$

We can also obtain another equation from Obata's Fig. 6 which shows alumina content of orthopyroxene coexisting with olivine, spinel and clinopyroxene in $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system. Though the equation is very similar to the equation 15, the latter is preferred because his Fig. 6 shows spinel lherzolite facies boundary to garnet lherzolite facies much lower than the one experimentally determined in the same system [2].

EXPERIMENTAL METHODS

A piston-cylinder type high pressure apparatus was used for experiments with a pressure correction of -10% of nominal load pressure using piston-in technique. Thermometry was by Pt/Pt₉₀Rh₁₀ thermocouples with no correction applied for pressure effect on thermocouple emf. Possibly because of thermocouple drift [22] in long duration experiments, indicated temperature continuously decreased during the experiments. Thus it was necessary to maintain temperature by supplying constant electric power to the furnace assembly. The apparent temperature drop was about 70°C within 13 days for the experiments intended to be at 1200°C, and 35°C within 26 days for the one to be at 1000°C. It is believed, however,

accuracy of real temperature thus maintained was not worse than $\pm 40^{\circ}\text{C}$. The furnace assembly included a pyrex glass sleeve and an alumina thermocouple insulator. Run details are listed in Table 1. Starting material for the runs in the simple system was a mixture of synthetic forsterite (6.2 wt%), clinoenstatite (36.7%), diopside (37.2%) and MgAl_2O_4 spinel (19.9%), which were crushed down to < 4 microns. The clinoenstatite run at 30 kb and 1200°C for 4 minutes totally converted to orthoenstatite. Thus, use of clinoenstatite instead of orthoenstatite would have caused no problem of metastability in the experiments with much longer durations needed for chemical reactions.

For the natural rock system, olivine, orthopyroxene, clinopyroxene, and spinel were separated from a spinel lherzolite nodule (No. 2K) from Mt. Porndon, Victoria, which was 25 cm in diameter, free from alteration and without mineralogical banding. Examination by microscope and X-ray diffraction did not show exsolution in pyroxenes. Chemical compositions of the constituents (Table 2) are remarkably homogeneous. The separated minerals were crushed to 4 microns and remixed in almost equal proportions.

Run products were identified by microscope and X-ray diffraction, and analyzed by TPD-microprobe. Bulk analyses of the run products excluding the rims to capsules with defocussed beam showed no chemical contamination or iron loss to the capsules. Chemical compositions of the run products are listed in Tables 3 and 4.

EXPERIMENTAL RESULTS

At 16 kb and 1200°C in the simple system (run 2J), compositions of olivine and spinel are consistent with stoichiometry of pure end-member phases (Table 3). A search for the chemical range of pyroxenes detected a few clinopyroxenes almost free from alumina only at the places where no spinel was adjacent to the clinopyroxene. Only these analyses were discarded.

In the run 2L in the natural rock system at the same temperature

Table 1 Run details

Run no.	Starting material	P(Kb)	T(°C)	Hours	Capsule	Run products
2J	Mixture of synthetic forsterite (Mg_2SiO_4), clinoenstatite (Mg_2SiO_6), diopside ($\text{CaMgSi}_2\text{O}_6$) and spinel (MgAl_2O_4)	16	1200	210	Pt (sealed)	olivine, opx, cpx, spinel
2L	Mixture of natural olivine, orthopyroxene, clinopyroxene and spinel	16	1200	295	$\text{Ag}_{50}\text{Pd}_{50}$ (sealed)	olivine, opx, cpx, spinel
2M	Mixture of synthetic forsterite, clino- enstatite, diopside and spinel	16	1000	606	Pt (sealed)	olivine, opx, cpx, spinel Mineral chemistry is apparently disequilibrium.

Table 2 Microprobe analyses of natural minerals (2K) used in the high pressure experiment (2L)

	Olivine	Orthopyroxene	Clinopyroxene	Spinel
SiO ₂	40.72(15)	55.70(13)	52.87(22)	0.16(33)
Al ₂ O ₃	-	3.53(13)	5.14(26)	47.03(38)
Cr ₂ O ₅	-	0.42(4)	1.26(9)	21.40(20)
FeO*	8.87(10)	5.51(4)	2.32(6)	10.93(17)
MnO	-	-	-	0.13(13)
MgO	50.41(10)	34.15(11)	16.36(12)	19.90(18)
CaO	-	0.62(5)	20.58(14)	-
Na ₂ O	-	0.07(11)	1.47(9)	0.46(8)
Number of ions (pyroxenes: 0 = 6, olivine and spinel: 0 = 4)				
Si	0.993(3)	1.916(4)	1.910(8)	0.004(9)
Al	-	0.143(6)	0.219(12)	1.496(11)
Cr	-	0.011(1)	0.036(3)	0.457(5)
Fe	0.181(3)	0.159(2)	0.070(2)	0.247(5)
Mn	-	-	-	0.003(3)
Mg	1.833(5)	1.752(6)	0.881(7)	0.800(8)
Ca	-	0.023(2)	0.796(6)	-
Na	-	0.005(8)	0.103(7)	0.024(5)
Total	3.007(3)	4.009(6)	4.015(7)	3.031(5)
Ca		1.2(1)	45.6(3)	
Mg		90.6(1)	50.4(3)	
Fe		8.2(1)	4.0(2)	
Mg/(Mg+Fe)	0.910(1)			0.764(4)

Each column represents an average of 9 analyses (normalized to a total of 100). The numbers in parentheses are standard deviation and refer to the last decimal place(s).

*: Total Fe as FeO. -: not detected. TiO₂ and K₂O were analysed but not detected in any mineral.

Table 3 Microprobe analyses of the run products at 16 kb and 1200°C
in the CaO-MgO-Al₂O₃-SiO₂ system (run 2J)

	Olivine	Orthopyroxene	Clinopyroxene	Spinel
SiO ₂	42.52(14)	56.06(36)	52.36(27)	-
Al ₂ O ₃	-	5.91(65)	6.39(29)	73.37(35)
MgO	57.38(23)	36.97(24)	19.09(18)	28.88(15)
CaO	-	1.14(9)	22.07(32)	-
Total	99.90(36)	100.08(35)	99.91(47)	102.25(24)
Numbers of ions (pyroxenes: 0 = 6, olivine and spinel: 0 = 4)				
Si	0.997(1)	1.880(13)	1.869(8)	-
Al	-	0.234(25)	0.269(12)	2.002(5)
Mg	2.006(1)	1.848(13)	1.016(10)	0.997(7)
Ca	-	0.041(3)	0.844(10)	-
Total	3.003(1)	4.003(3)	3.998(4)	2.999(3)

Data are an average of 3, 14, 10 and 3 analyses for olivine, orthopyroxene, clinopyroxene and spinel, respectively. The numbers in parentheses represent standard deviations and refer to the last decimal place(s).

Table 4 Microprobe analyses of the run products at 16 Kb and 1200°C in the natural spinel
herzolite system (run 2L)

	Olivine	Orthopyroxene	Clinopyroxene	Spinel
SiO ₂	40.71(35)	55.52(48)	52.19(47)	-
Al ₂ O ₃	-	3.58(25)	5.02(2)	47.85(55)
Cr ₂ O ₃	0.25(8)	0.61(6)	1.45(6)	20.86(22)
FeO*	9.04(21)	5.54(9)	2.56(13)	10.49(15)
MgO	50.14(33)	33.74(47)	16.25(31)	19.93(25)
CaO	-	0.68(3)	19.93(28)	0.09(2)
Na ₂ O	-	-	1.32(14)	0.36(9)
Total	100.14(88)	99.67(73)	98.7(1.0)	99.58(94)
Number of ions (pyroxenes: 0 = 6, olivine and spinel: 0 = 4)				
Si	0.993(1)	1.917(4)	1.910(6)	-
Al	-	0.146(11)	0.216(4)	1.521(5)
Cr	0.005(2)	0.017(2)	0.042(3)	0.445(4)
Fe	0.184(3)	0.160(2)	0.079(4)	0.237(4)
Mg	1.823(6)	1.737(12)	0.886(12)	0.802(5)
Ca	-	0.025(2)	0.781(7)	0.003(1)
Na	-	-	0.094(10)	0.019(4)
Total	3.005(1)	4.002(4)	4.008(10)	3.027(2)
Ca		1.3(1)	44.7(5)	
Mg		90.4(1)	50.8(4)	
Fe		8.4(1)	4.5(2)	
Mg/(Mg+Fe)	0.908(2)			0.772(3)

Data are an average of 3, 4, 4 and 5 analyses for olivine, orthopyroxene, clinopyroxene and spinel, respectively. Standard deviations are in parentheses and refer to the last decimal place(s). TiO₂, MnO and K₂O were analyzed but not detected in any mineral.

*: Total Fe as FeO. Microchemical analysis of the bulk run product shows 0.31 wt % Fe₂O₃ (Analyst: E. Kiss).

and pressure, faster reaction might be expected. Conservatively, run duration was also prolonged by 40%. The compositions of the minerals after the run (Table 4) are very similar to those in the starting material (Table 2). Retrospectively, it was unfortunate that the spinel lherzolite nodule (No 2K) used as a starting material was in equilibrium at a temperature not far from 1200°C. This inference derives from substitution of the mineral compositions in equations 11-15, yielding temperature estimates of 990, 1160, 1280, 1020 and 1040°C respectively. The reality of chemical reaction can be seen in slight but definite changes in Cr of olivine, orthopyroxene and spinel, Al of spinel, Fe and Ca/(Ca+Mg+Fe) of clinopyroxene. These changes are beyond the compositional variations in the reactants and products and lead to the conclusion that the products have closely approached equilibrium under the experimental conditions. Comparison of Tables 3 and 4 (run products of 2J and 2L) shows a noteworthy difference of alumina content in orthopyroxenes in the simple and natural rock systems at the same temperature and pressure. The Al_2O_3 content dropped from 5.9 wt% in the simple system to 3.6% in the natural rock system apparently in accordance with a similar change of alumina in coexisting spinels. This sympathetic change in Al_2O_3 has been observed also in spinel lherzolite nodules [23, 24].

The run 2M in the simple system at 1000°C and 16 kb could not reach even local equilibrium, showing a sharp contrast to the run 2J at a temperature higher by only 200°C. Alumina content in pyroxenes contacting to spinel varied widely, some being below detection limits. Again olivine and spinel were of pure end member compositions. Knowing that equilibrium was not achieved at this temperature even within 26 days, the planned further experiments at this, and lower temperatures, were discontinued.

GEOOTHERMOMETRY

As has been shown, we know from the literature fundamental

relationship between temperature, and $\ln K_1$, $\ln K_2$ and $\ln K_3$ at 16 kb in three or four-component system. If the solid solution models were correct, the equations 11, 13 and 14 or 15 could be used to calculate accurate $\ln K_1$, $\ln K_2$ and $\ln K_3$, and consequently accurate temperatures of natural spinel lherzolites. However although these models are necessary at the present state of knowledge, it is known that they are approximations only to the real solid solution models. Thus, application of those equations inevitably causes systematic errors in $\ln K$ terms and eventually in temperatures.

The systematic errors can be seen in Fig. 1 and are discussed below:

$\ln K_1$: $\ln K_1$ decreases as chemical system becomes more complex. Even addition of only Al_2O_3 to the CaO-MgO-SiO_2 system causes significant change in $\ln K_1$. This change in terms of pyroxene compositions is better illustrated in Fig. 2.

$\ln K_2$: $\ln K_2$ in this paper in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system agrees well with Herzberg and Chapman's value [9] in the same system. Although the determined CaO contents of pyroxene differ in the two studies, the $X_{\text{Ca}}^{\text{M2}}$ terms in equation 9 cancel in the chosen system and as long as $X_{\text{Al}}^{\text{M1}}$ is the same in the two studies, the value of $\ln K_2$ is the same. $\ln K_2$ in the natural rock system is higher than in the simple system.

$\ln K_3$: Two reference curves in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system by MacGregor [5] and Obata [8] are almost the same at 16 kb and below 1200°C .

Presence of CaO results in lower $\ln K_3$ which, in turn, is the same as the value in the natural rock system within the estimated errors.

The errors in temperatures caused by difference of chemical system in conjunction with the inadequacy of the solid solution models are quite large: the reference curves for K_1 , K_2 and K_3 would give T_1^* of the run 2L about 150°C lower than real, T_2 higher by 70°C , and T_3 lower by 170°C . The desirable method for accurate temperature estimates is, of course, to construct satisfactory models of olivine, pyroxenes and spinel, but being far from such knowledge, we have to choose another approach. In this

* T_1 , T_2 and T_3 denote temperatures obtained by respective K_1 , K_2 and K_3 .

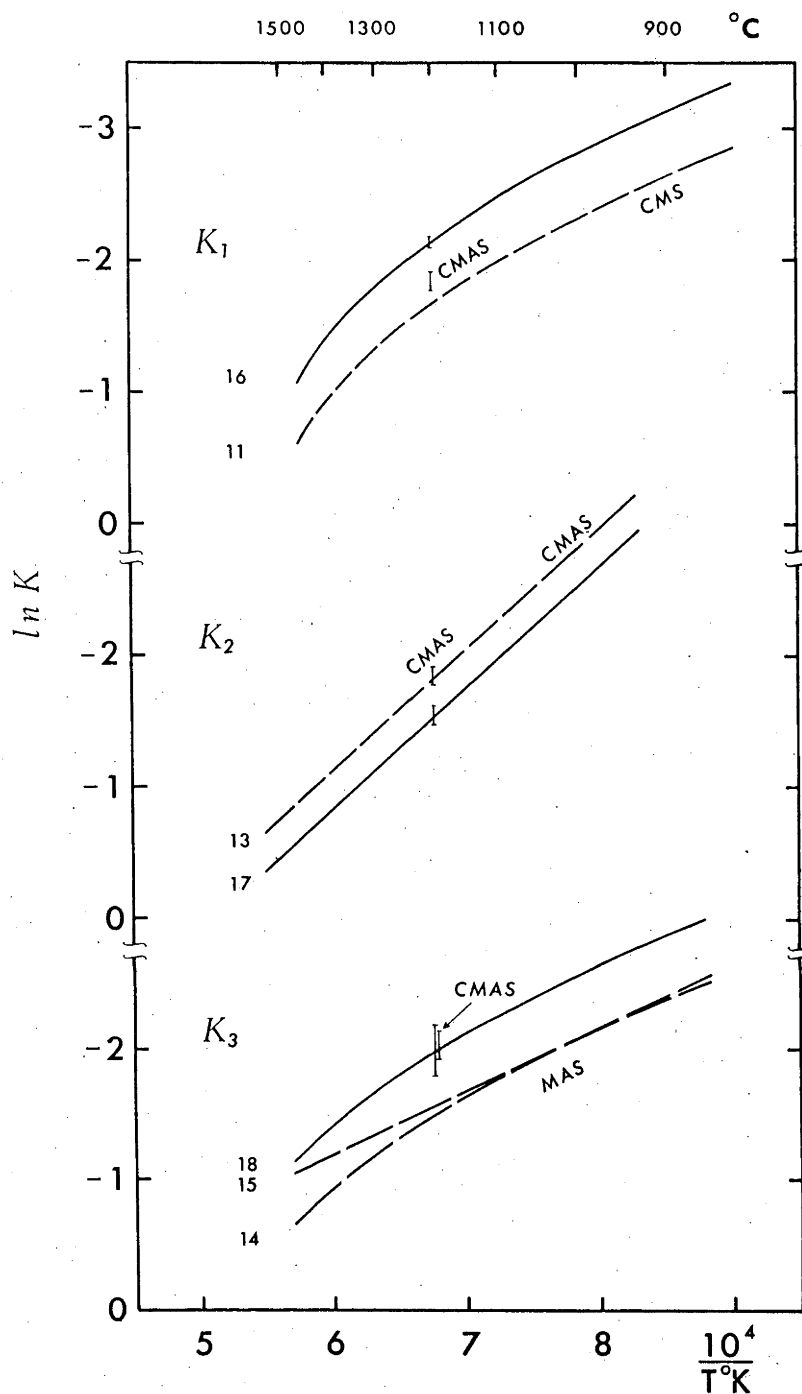


Fig. 1 K_1 , K_2 and K_3 geothermometers (16, 17 and 18). The others are reference curves in simple systems. The numbers refer to the equations in the text. Experimental data at 1200°C and 16 kb in simple and natural rock systems are also shown. C.M.A. and S represent CaO , MgO , Al_2O_3 and SiO_2 , respectively.

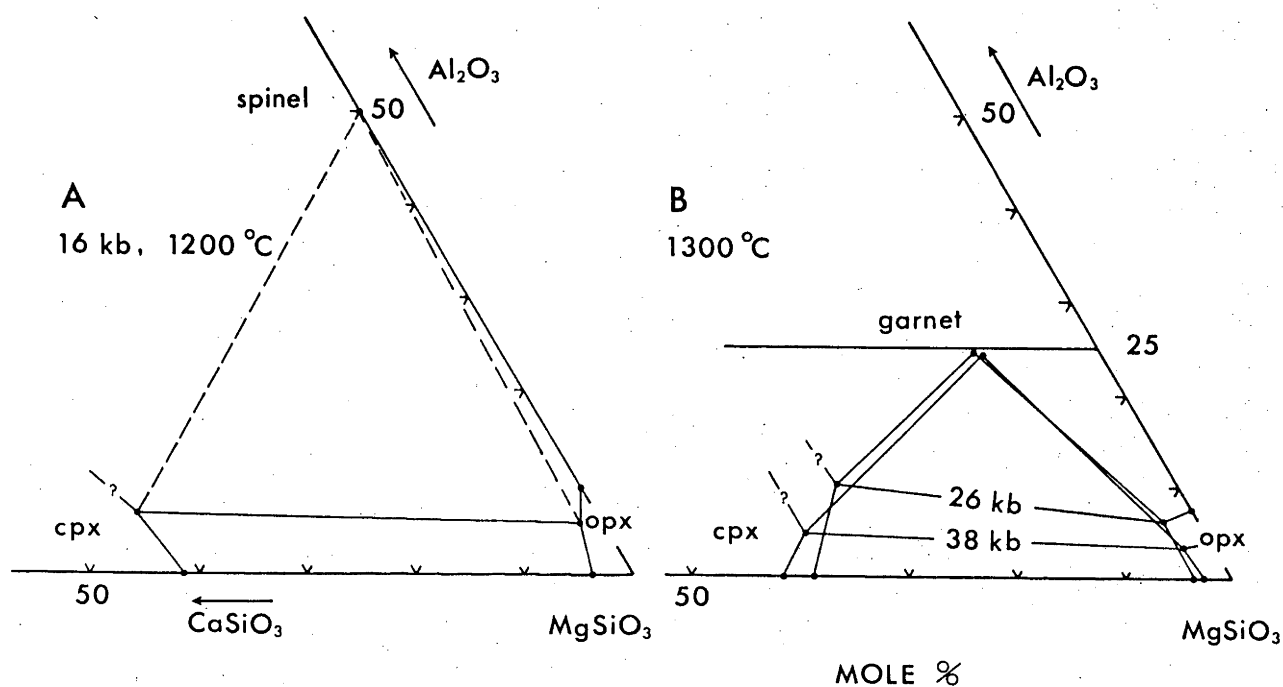


Fig. 2 Contrasted alumina effect on the pyroxene solvus in (A) spinel and (B) garnet lherzolite facies. Note the difference in the direction of the clinopyroxene phase boundary facing to orthopyroxene between the two facies. Data sources are Akella [25] for the coexisting garnet and pyroxenes, MacGregor [5] for Ca-free pyroxenes, Mori and Green [15] and Al-free pyroxenes (by interpolation), and this paper for coexisting spinel and pyroxenes.

alternative approach, the errors in temperature estimates can be minimized if empirical reference curves, drawn parallel to those of equations 11, 13 and 14, are made to pass through the experimental data point for the natural rock system (Table 4, Fig. 1). By using the new curves as geothermometers, more reliable temperatures can be obtained for natural spinel lherzolite insofar as their mineral chemistries are similar to the example chosen for experiments. It should be noted that in these 'empirical' $\ln K$ vs $\frac{1}{T}$ curves the $\ln K$ terms do not have the theoretical meaning of the original expressions. The new equations proposed as practical geothermometers are:

$$\frac{10^4}{T_1^{\circ}\text{K}} = 0.41 (\ln K_1)^2 + 0.37 \ln K_1 + 5.7 \quad (16)$$

$$\frac{10^4}{T_2^{\circ}\text{K}} = -1.08 \ln K_2 + 5.12 \quad (17)$$

$$\frac{10^4}{T_3^{\circ}\text{K}} = 0.357 (\ln K_3)^2 - 0.177 \ln K_3 + 5.04 \quad (18)$$

MacGregor's scheme [5] was tentatively employed for the equation 18 in preference to Obata's [8] which would have given an alternative equation:

$$\frac{10^4}{T_3^{\circ}\text{K}} = -2.06 \ln K_3 + 2.69 \quad (19)$$

It should be noted that these equations are based on empirical curve fitting using arbitrarily chosen form of function, and consequently that extrapolations to temperatures outside 900°C to 1400°C are unwarranted. Besides, the equation 16 should not be used for the rocks in garnet lherzolite facies where phase relations of alumina in pyroxenes are different (Fig. 2).

EVALUATION OF THE GEOTHERMOMETERS

Two lines of argument are introduced in this section in order to test and evaluate the equations 16, 17 and 18 as geothermometers. The first approach uses samples of natural spinel lherzolites which are considered to be frozen-in, equilibrated mineral assemblages. The three equations, if effective as geothermometers, should give the same temperatures within the error estimates for each rock. The second line of argument evaluates the errors in temperature estimates caused by various factors.

An unsuccessful literature search was made for spinel lherzolites for which chemical compositions of olivine, orthopyroxene, clinopyroxene and spinel had been obtained, homogeneity of minerals was tested for and established and in which there were no textural features suggesting disequilibrium. Because of this lack of success, a large collection of thin sections of spinel lherzolites from Eastern Australia were examined and two rocks selected: LJ7 occurring in olivine melilitite at Laughing Jack Marsh [26, 27], and SC4 occurring in olivine nephelinite at Scottsdale, Tasmania. Both rocks show exsolution of pyroxenes and trace spinel in some pyroxene grains. Distribution of exsolved lamellae in a single grain is also localized. The compositions of constituent minerals are listed in Table 5. Chemical homogeneity, apart from the exsolved phases, is comparable to or slightly worse than that in the rock 2K used as a starting material in the run 2L (Table 2).

Another set of data was supplied by J. Keller. The spinel lherzolite, L3, is a nodule in olivine nephelinite at Kaiserstuhl, Germany. Though the rock shows low temperature alteration on grain boundaries the relic minerals are quite homogeneous except for tiny secondary spinels around the primary discrete spinels.

Temperatures, T_1 , T_2 and T_3 , for these rocks were estimated by the equations, 16, 17 and 18 and for the nodule 2K as well. As is shown in Figure 3, the estimated three temperatures in each rock fall in a range of

Table 5 Microprobe analyses of minerals in spinel ilherzolite nodules from Tasmania

	LJ7, Laughing Jack, Tasmania				SC4, Scotsdale, Tasmania			
	Olivine	Opx	Cpx	Spinel	Olivine	Opx	Cpx	Spinel
SiO ₂	40.92	54.83	52.18	-	41.15	55.74	52.78	-
TiO ₂	-	-	0.23	0.12	-	-	0.14	-
Al ₂ O ₃	-	4.13	5.26	55.85	-	3.56	4.96	58.50
Cr ₂ O ₃	-	0.26	0.77	11.52	-	0.24	0.65	10.13
FeO*	10.13	6.45	2.80	11.84	10.56	6.62	2.49	11.41
MgO	48.84	32.78	15.55	20.51	48.67	33.28	15.42	20.48
CaO	-	0.58	20.51	-	-	0.38	21.57	-
Na ₂ O	-	-	1.16	0.20	-	-	0.99	0.34
Total	99.89	99.03	98.46	100.04	100.38	99.82	99.00	100.86
Number of cations (olivine and spinel: 0=4, pyroxenes: 0=6)								
Si	1.003	1.911	1.915	-	1.006	1.926	1.926	-
Ti	-	-	0.006	0.002	-	-	0.004	-
Al	-	0.170	0.228	1.718	-	0.145	0.214	1.770
Cr	-	0.007	0.022	0.238	-	0.007	0.019	0.206
Fe	0.208	0.188	0.086	0.258	0.216	0.191	0.076	0.245
Mg	1.785	1.703	0.851	0.798	1.773	1.715	0.839	0.784
Ca	-	0.022	0.806	-	-	0.014	0.843	-
Na	-	-	0.082	0.010	-	-	0.070	0.017
Total	2.996	4.001	3.996	3.024	2.995	3.998	3.991	3.022
Ca		1.2	46.3			0.7	48.0	
Mg		89.0	48.8			89.3	47.7	
Fe		9.8	4.9			10.0	4.3	
Mg/(Mg+Fe)	0.896			0.755	0.891			0.762

*: Total Fe as FeO. MnO and K₂O were not detected in any mineral.

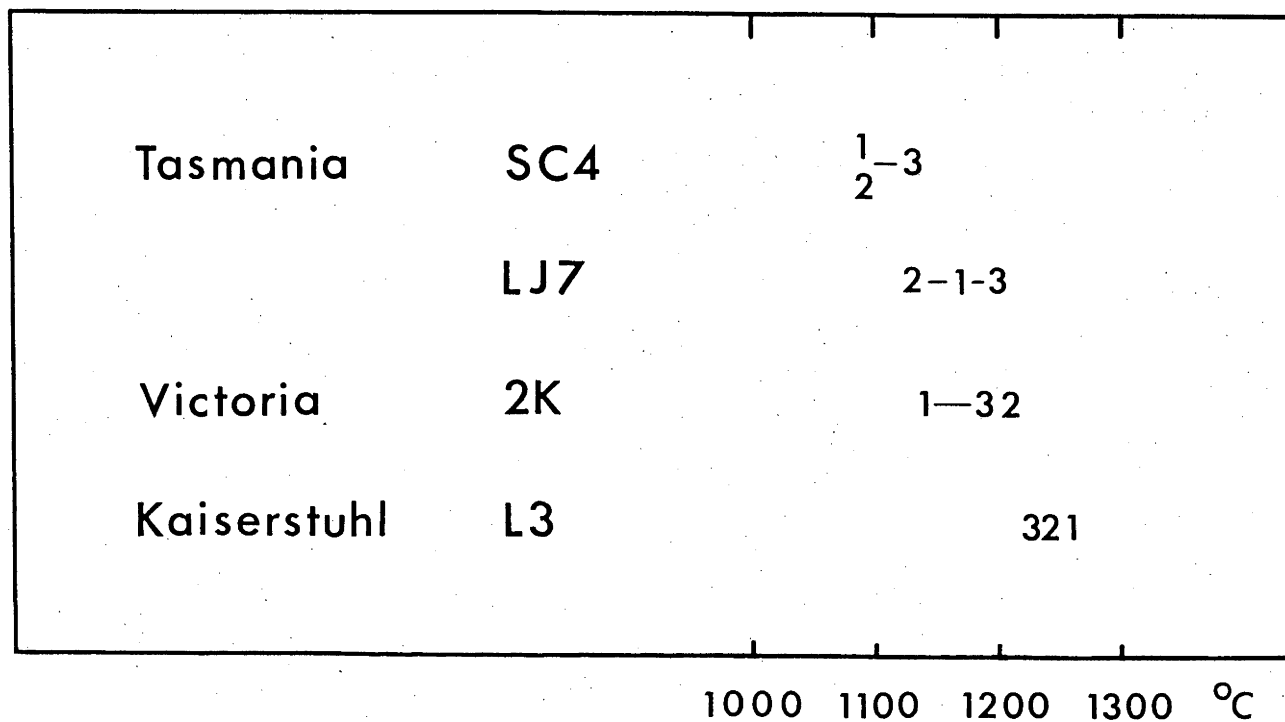


Fig. 3 Assessment of the geothermometers by using homogeneous spinel ilherzolites. The numbers 1, 2, 3 refer to independent temperature estimates based on K_1 , K_2 , K_3 respectively.

70°C for two rocks and 40°C for the others. Error of $\pm 35^\circ\text{C}$ is well within the estimated errors associated with the methods as will be discussed in the following paragraphs. Thus, we conclude that these three methods of temperature estimates can give consistent results for the rocks in which chemical equilibrium is considered to be frozen, at least in a temperature range between 1100 and 1300°C.

There are several major sources of error in temperature estimates. As was mentioned earlier, however, the application of inadequate solid solution models should not cause serious errors as long as the samples are spinel lherzolites chemically similar to the run products, 2L. In fact, the similarity in chemistry among natural spinel lherzolites has often been noted in the literature. If a problem exists, it should be most apparent in the equilibria involving spinel which varies in Cr_2O_3 content from ~50% to ~0% although the common range is 10-25 wt %. Because the spinel in the run, 2L, has 20 wt % Cr_2O_3 , the error in temperature should be minimal for rocks containing similar spinels. Among the examined samples shown in Fig. 3, 2K has ~20% Cr_2O_3 and L3, SC4 and LJ7 have 10-14% Cr_2O_3 . If the deviation of Cr_2O_3 content from 20 wt % is a serious problem, systematic errors will be caused, by their nature, in T_2 and T_3 , and not in T_1 for which spinel has no relevance. Thus, the data in Fig. 3 argue that this particular variable is not a source of error although application to spinels with >30% Cr_2O_3 (chromites) would not be justified.

The assumption of 16 kb pressure inevitably causes an error in temperature estimates. Because of their mineral assemblage of spinel lherzolite, the possible maximum deviation of pressure from 16 kb is 8 kb [1, 2, 17, 18]. The temperature error due to neglect of 8 kb difference can be estimated from the original experimental or calculated data [5, 9, 15] from which the reference equations, 11, 13 and 14, were derived: T_1 , T_2 and T_3 of rocks equilibrated at 24 kb will be underestimated by 60°C, 50°C and 150°C, respectively, near an apparent temperature of 1200°C. However, if

Obata's [8] scheme is used, T_3 is underestimated by 25°C.

Accuracy of chemical analyses of minerals is crucial for reliable temperature estimation. This is particularly true for calculation of T_2 and T_3 since calculations of $A_{\text{CaAl}_2\text{SiO}_6}^{\text{cpx}}$ and $A_{\text{MgAl}_2\text{SiO}_6}^{\text{opx}}$ are critically dependent on SiO_2 analyses. All the data used in Fig. 3 are obtained by TPD-microprobe which has good accuracy in SiO_2 determination [16, 28]. However, there are some pyroxene analyses in the literature in which Al is insufficient to fill the tetrahedral site unoccupied by Si. Consequently, activity of Tschermak's molecule in the pyroxene becomes 0, resulting in a temperature estimate of 0°K. However, as is described in the next section, such extreme cases can be avoided by selecting only the pyroxene analyses with good chemical formulae. It can be seen that inaccurate SiO_2 determination can result in remarkably underestimated temperature by the nature of the scheme of activity calculations. Also, T_1 is sensitive to chemical analyses as calculation of $A_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{cpx}}$ involves subtraction of Ca, Na and Mn from unity. Slight errors in analyses of these elements cause large error in T_1 , particularly if T_1 is lower than 900°C [15].

The overall error in temperature estimates is difficult to evaluate. If the minerals are proved to be very homogeneous, analyses are accurate enough, and if the three temperatures are within $\pm 50^\circ\text{C}$, then this range of temperature must be highly meaningful. If the minerals are heterogeneous, temperatures of local equilibrium may possibly be obtained.

Temperatures estimated by the methods developed herein deviate from those estimated by other methods. Three of these methods are directly based on experiments at high pressures and temperatures: the pyroxene solvus method [4, 5], Wood-Banno geothermometer [10], and Al-Cr partition between orthopyroxene and clinopyroxene [29].

The first method employs the pyroxene solvus as determined by Davis and Boyd [19] at 30 kb, and compares Ca/(Ca+Mg) ratio of clinopyroxene of sample to those experimentally obtained. Estimated

temperatures for the rocks in Fig. 3 are systematically lower than the estimates in Fig. 3 by about 200°C. Substitute of the Davis and Boyd's solvus by recent refinements [15, 20, 21] does not improve the situation. The prime reason for this discrepancy is, as was briefly pointed out earlier, that the pyroxene solvus is highly dependent on Al_2O_3 content in clinopyroxene (Fig. 2) at constant pressure and temperature within spinel lherzolite facies. Neglect of Al_2O_3 in clinopyroxene results in an underestimation of temperature.

The Al-Cr partition method [29] gives temperature estimates for the rocks in Fig. 3 which vary by up to 100°C from estimates using the Davis and Boyd solvus. This deviation is better than the reported deviation between the two methods of up to 350°C [30]. Successful use of the Al-Cr method is dependent on accurate determination of the low Cr_2O_3 content in orthopyroxene. Another source of error is the arbitrary assumption that half of all Al in pyroxenes is in M1 site. It is considered that experimental calibration of this method should be improved.

The Wood and Banno geothermometer [10] gives temperatures higher than the solvus temperatures [4, 5] by 100°C and lower than those in Fig. 3 by 100°C. This method should be revised and incorporate the recently refined pyroxene solvus and the strong alumina effect on the solvus. In fact the equation 16 is one of the possible revised versions of this method.

APPLICATION TO NATURAL SPINEL LHERZOLITES

The geothermometers have been applied to natural spinel lherzolites reported in the literature (Fig. 4) for which analyses of olivine, orthopyroxene, clinopyroxene and spinel are available. To exclude inferior analyses, only those samples with pyroxene analyses between 3.975 and 4.025 cations per 6 oxygens were included.

As is seen in Fig. 4, the three temperatures estimated for each rock show good coincidence in some rocks, but deviate widely in others.

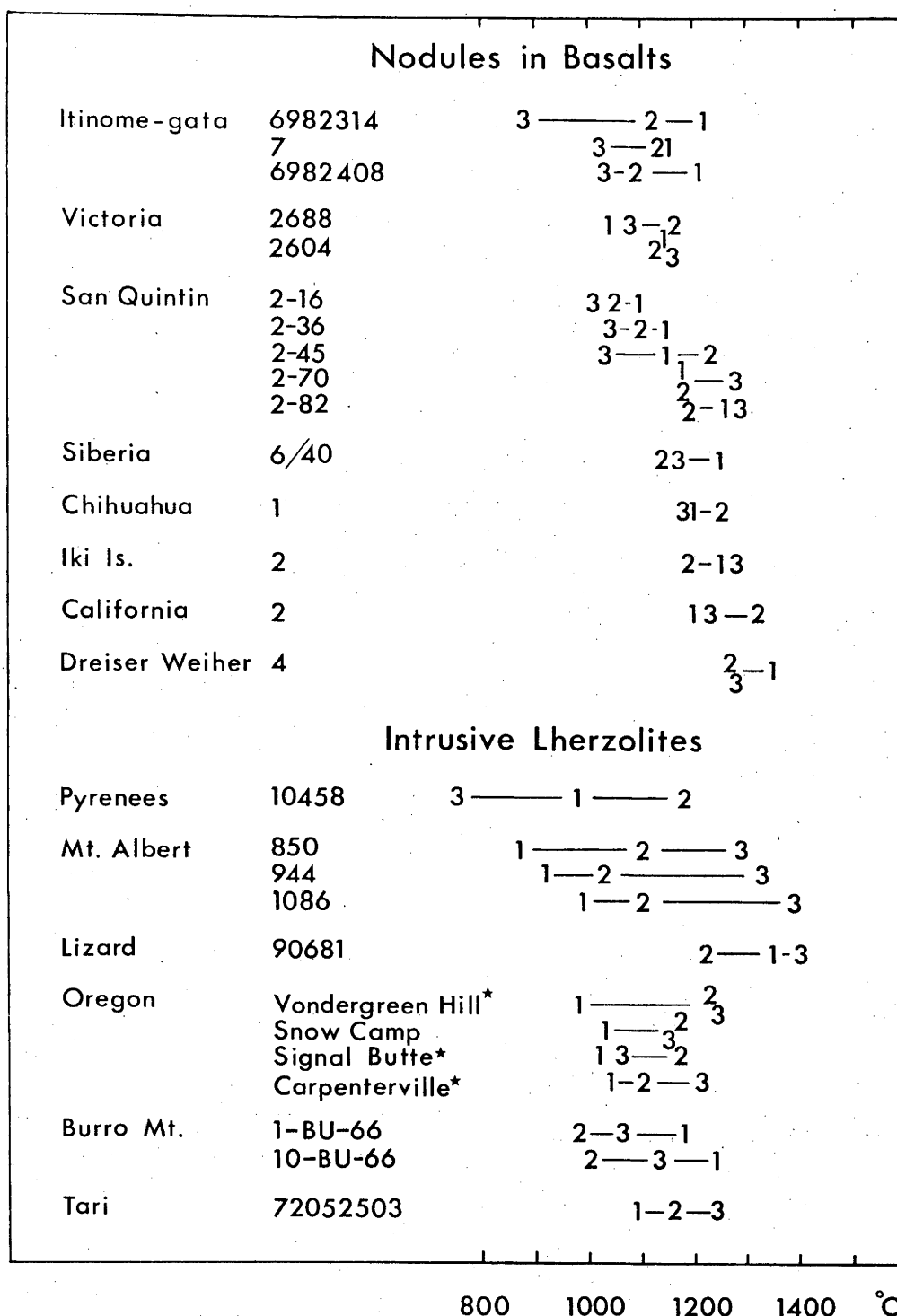


Fig. 4 Temperature estimates of spinel lherzolites reported in the literature [2, 31-43]. The numbers 1, 2, 3 refer to independent temperature estimates based on K_1 , K_2 , K_3 respectively. The star attached to the Oregon samples means that compositions used for pyroxenes were of augen.

If chemical equilibrium, at a particular P,T condition has been frozen-in within these rocks, the three estimated temperatures should be the same for each rock within the error estimates of the geothermometers. Since it is considered that the internal consistency of the geothermometers is demonstrated on the selected samples of the previous section, problem to be considered now is that of possible lack of equilibrium between minerals of the spinel lherzolites. Though no definite criterion exists to judge equilibrium, chemical homogeneity is a necessary condition for it. However, in the literature, it is common to find only one set of chemical analyses without any description of the homogeneities. Experience shows that spinel lherzolites with homogeneity similar to that of the sample 2K (Table 2) are uncommon.

Thus, without the detailed knowledge relating to chemistry and texture, it is quite difficult to understand if the estimated temperatures are meaningful. It is tentatively suggested that if three temperatures converge within $\pm 50^{\circ}\text{C}$ then this approximates to an equilibrium condition of the sample just prior to inclusion in the host magma. All the spinel lherzolite nodules in Fig. 3 and several nodules shown in Fig. 4 belong to this category.

All the intrusive spinel lherzolites have widely divergent temperatures in contrast to the nodules. This is probably a reflection of the less equilibrated nature of the intrusives. In fact, the intrusives generally show more chemical heterogeneity than the nodules, e.g. the former may show alumina gradient of even 6 wt % within a single orthopyroxene. This contrast in heterogeneity may be attributed to the likelihood of retrogressive metamorphism for the intrusives, while the recent measurements of viscosity of basaltic magmas at high pressures [44] would suggest that the nodules have been brought up by magmas from their source regions within a day, and are much less likely to have suffered partial

reequilibration in their movement to the surface.

The large divergency for the Mt. Albert rocks indicates disequilibrium (two rocks were omitted from Fig. 4 because of unrealistic T_3 temperatures $>1450^\circ\text{C}$). The order of the three temperatures in the mass is consistently T_1 - T_2 - T_3 . This could be due to differential degree of reequilibration for the reaction equations 1, 2 and 3, and may correlate with a particular temperature-pressure history for the Mt. Albert lherzolites. Systematic but different temperature trend is found also in such localities as Itinome-gata and Burro Mt. However, there is no overall tendency in the order of the three temperatures in the intrusive peridotites as a whole. T_1 and T_2 temperatures of the nodules are similar to those corresponding estimates by Herzberg and Chapman [9]. San Quintin nodules range from 1000 to 1300°C , and Victorian nodules from 1050 to 1200°C . These values are significantly higher than previous estimates by Frey and Green [36] and Basu [37]. These authors regarded their estimated low temperatures as consistent with and supportive of the geochemical and isotopic evidence for accidental, xenolithic origin of these nodules in relation to their host magmas. The temperature estimates in this paper are similar to or lower than estimated liquidus temperatures of water or water + CO_2 bearing undersaturated basanites, melilitites etc. [27, 45], and may suggest a closer physical proximity of the depth of magma segregation and depth of incorporation of lherzolite inclusions than envisaged in these earlier papers.

Temperatures of the spinel lherzolite nodules shown in Fig. 3 and 4 range from 1000 to 1300°C . These temperatures at assumed pressure between 8 and 24 kbar are higher than commonly used model oceanic geotherms and are definitely too high for estimates of the continental geotherm [46]. When, in future, a reliable geobarometer becomes available, it may, in conjunction to the geothermometers, give a temperature - pressure trend. It may, however, only reflect conditions in a thermally disturbed region related

to magma generation and have little or nothing to do with typical, steady state geotherms.

CONCLUDING REMARKS

So far in this paper, spinel lherzolite nodules have been discussed only from a view point of their temperature condition of equilibration. Other important features of the nodules are their mineral chemistries and textures. It is well recognized that ultramafic nodules in general can be divided by mineral chemistry, especially of clinopyroxene, into two categories: Cr-diopside and Ti-augite suites [47]. The former is further divided by their texture into protogranular, porphyroclastic and equigranular textures [48], while cumulate texture is common to the latter. Majority of spinel lherzolite nodules belong to the Cr-diopside suite, and the Ti-augite suite is comprised of wehrlites and pyroxenites. The Cr-diopside suite is commonly regarded as accidental xenoliths to the host magmas and as rocks composing the uppermost mantle. However, careful observation of textures have led Mercier and Nicholas [48] among others to suggest that these nodules have varied and complex histories of formation and tectonic and thermal events prior to their incorporation to basaltic magmas.

Mercier and Nicholas' preliminary experimental data suggest a temperature at an earlier stage of 1400°C at 18 kb for a texturally reconstructed Al, Cr-rich composition of orthopyroxene. Similar complexities and high temperature for a reconstructed clinopyroxene were also suggested for the chromium-spinel peridotite xenoliths at western Grand Canyon [49].

Among the nodules for which temperatures of the last equilibration were best estimated (Fig. 3), SC4 and LJ7 can be classified in protogranular type [48]. Probe analyses with an enlarged beam covering both host pyroxene and lamellae in it suggest K_1 temperature of 1260 and 1370°C, respectively, which are higher than their respective temperatures for

the last equilibration by nearly 200°C. Thus, we can conclude, in accordance with Mercier and Nicholas [48] and Best [49], that these nodules conceal their earlier histories in the textures. Common close association of spinel and clinopyroxene with orthopyroxene, in conjunction with more explicit texture of spinel and clinopyroxene which are in part lamellae in orthopyroxene and in part forming discrete grains outside the orthopyroxene, would suggest that the primary assemblage of many spinel lherzolites was olivine and orthopyroxene which were possibly formed at very high temperatures (say > 1400°C) by major igneous activities in the uppermost mantle. According to this inference, it is extensive superposition by later exolution, recrystallization and deformation processes which created the present spinel lherzolites.

REFERENCES

1. Green, D.H., Ringwood, A.E.: The stability fields of aluminous pyroxene periodotite and garnet peridotite and their relevance in upper mantle structure. *Earth Planet. Sci. Lett.* 3, 151-160, (1967).
2. O'Hara, M.J., Richardson, S.W., Wilson, G.: Garnet-periodotite stability and occurrence in crust and mantle. *Contrib. Mineral. Petrol.* 32, 48-68 (1971).
3. Wyllie, P.J. (ed): Ultramafic and related rocks. New York - London - Sydney: John Wiley and Sons, Inc.(1967).
4. Boyd, F.R.: A pyroxene geotherm. *Geochim. Cosmochim. Acta.* 37, 2533-2546 (1973).
5. MacGregor, I.D.: The system $MgO-Al_2O_3-SiO_2$: solubility of Al_2O_3 in enstatite for spinel and garnet peridotite compositions. *Am. Mineral.* 59, 110-119 (1974).
6. Wilshire, H.G., Jackson, E.D.: Problems in determining mantle geotherms from pyroxene compositions of ultramafic rocks. *J. Geol.* 83, 313-329 (1975).
7. Stroh, J.M.: Solubility of alumina in orthopyroxene plus spinel as a geobarometer in complex systems. Applications to spinel-bearing alpine-type peridotites. *Contrib. Mineral. Petrol.* 54, 173-188 (1976).
8. Obata, M.: The solubility of Al_2O_3 in orthopyroxenes in spinel and plagioclase peridotites and spinel pyroxenite. *Am. Mineral.* 61, 804-816 (1976).
9. Herzberg, C.T., Chapman, N.A.: Clinopyroxene geothermometry of spinel-lherzolites. *Am. Mineral.* 61, 626-637 (1976).
10. Wood, B.J., Banno, S.: Garnet-orthopyroxene and orthopyroxene - clinopyroxene relationships in simple and complex systems. *Contrib. Mineral. Petrol.* 42, 109-124 (1973)
11. Presnall, D.C.: Alumina content of enstatite as a geobarometer for spinel lherzolites. Extended abstracts, International Conference on Geothermometry and Geobarometry, The Pennsylvania State

University (1975).

12. Wood, J.B.: The application of thermodynamics to some subsolidus equilibria involving solid solutions. *Fortschr. Mineral.* 52, 21-45 (1975).
13. Fujii, T., Takahashi, E.: On the solubility of alumina in orthopyroxene coexisting with olivine and spinel in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$. *Mineral. J.* (in press).
14. Howells, S., O'Hara, M.J.: Palaeogeotherms and the diopside-enstatite solvus. *Nature* 254, 406-408 (1975).
15. Mori, T., Green, D.H.: Pyroxenes in the system $\text{Mg}_2\text{Si}_2\text{O}_6\text{-CaMgSi}_2\text{O}_6$ at high pressure. *Earth Planet. Sci. Lett.* 26, 277-286 (1975).
16. Mori, T., Green, D.H.: Subsolidus equilibria between pyroxenes in the CaO-MgO-SiO_2 system at high pressures and temperatures. *Am. Mineral.* 61, 616-625 (1976).
17. Green, D.H., Hibberson, W.O.: The instability of plagioclase in peridotite at high pressure. *Lithos* 3, 209-221 (1970).
18. Herzberg, C.T.: Stability fields of plagioclase and spinel-lherzolite. *Progress in Experimental Petrology*, 2, 145-148 (1972).
19. Davis, B.T.C., Boyd, F.R.: The join $\text{Mg}_2\text{Si}_2\text{O}_6\text{-CaMgSi}_2\text{O}_6$ at 30 kilobars and its application to pyroxenes from kimberlites. *J. Geophys. Res.* 71, 3567-3576 (1966).
20. Nehru, C.E., Wyllie, P.J.: Electron microprobe measurement of pyroxenes coexisting with H_2O - undersaturated liquid in the join $\text{CaMgSi}_2\text{O}_6\text{-Mg}_2\text{Si}_2\text{O}_6\text{-H}_2\text{O}$ at 30 kilobars, with applications to geothermometry. *Contrib. Mineral. Petrol.* 48, 221-228 (1974).
21. Lindsley, D.H., Dixon, S.E.: Coexisting diopside and enstatite at 20 kbar and $900^\circ\text{-}1200^\circ\text{C}$. *Geol. Soc. Am., Abstracts with Programs*, 1975. Annu. Meet., 1171 (1975).
22. Presnall, D.C., Brenner, N.L., O'Donnell, T.H.: Drift of Pt/Pt10Rh and W3Re/W25Re thermocouples in single stage piston-cylinder apparatus. *Am. Mineral.* 58, 771-777 (1973).

23. O'Hara, M.J., Mercy, E.L.P.: Petrology and petrogenesis of some garnetiferous peridotites. *Trans. Roy. Soc. Edin.* 65, 251-314 (1963).
24. Basu, A.R., MacGregor, I.D.: Chromite spinels from ultramafic xenoliths. *Geochim. Cosmochim. Acta*, 39, 937-945 (1975).
25. Akella, J.: Solubility of Al_2O_3 in orthopyroxene coexisting with garnet and clinopyroxene for compositions on the diopside-pyrope join in the system $CaSiO_3$ - $MgSiO_3$ - Al_2O_3 . *Carnegie Inst. Wash. Year Book* 73, 273-278 (1974).
26. Sutherland, L.V.: Igneous rocks, central plateau. In the lake country of Tasmania. *Roy. Soc. Tasmania. Symp.*, Nov. 1972, 43-54 (1973).
27. Brey, G., Green, D.H.: The role of CO_2 in the genesis of olivine melilitite. *Contrib. Mineral. Petrol.* 49, 93-103 (1975).
28. Bence, A.E., Papike, J.J., Ayuso, R.A.: Petrology of submarine basalts from the central Caribbean: DSDP Leg 15. *J. Geophys. Res.* 80, 4775-4804 (1975).
29. Mysen, B.O., Boettcher, A.L.: Melting of hydrous mantle: II Geoghemistry of crystals and liquids formed by anatexis of mantle peridotite at high pressures and high temperatures as a function of controlled activities of water, hydrogen, and carbon dioxide. *J. Petrol.* 16, 549-593. (1975).
30. Eggler, D.H.: A field test of geothermometers and barometers. Extended abstracts, International Conference on Geothermometry and Geobarometry, The Pennsylvania State University (1975).
31. Aoki, K., Shiba, I.: Pyroxenes from lherzolite inclusions of Itinome-gata, Japan. *Lithos*, 6, 41-51 (1973).
32. Aoki, K., Shiba, I.: Olivines from lherzolite inclusions of Itinome-gata, Japan. *Mem. Geol. Soc. Japan*, 11, 1-10, (1974).
33. Aoki, K., Prinz, M.: Chromian spinels in lherzolite inclusions from Itinome-gata, Japan. *Contrib. Mineral. Petrol.* 46, 249-256 (1974).

34. Ross, C.S., Foster, M.D., Myers, A.T.: Origin of dunite and of olivine-rich inclusions in basaltic rocks. *Am. Mineral.* 39, 693-737 (1954).
35. Irving, A.J.: Pyroxene-rich ultramafic xenoliths in the Newer Basalts of Victoria, Australia. *N. Jahrbuch f. Mineralogie. Abhandlungen.* 120, 147-167 (1974).
36. Frey, F.A., Green, D.H.: The mineralogy, geochemistry and origin of lherzolite inclusions in Victorian basanites. *Geochim. Cosmochim. Acta*, 38, 1023-1059 (1974).
37. Basu, A.R.: Hot-spots, mantle plumes and model for the origin of ultramafic xenoliths in alkali basalts. *Earth Planet. Sci. Lett.* 28, 261-274 (1975).
38. Kutolin, V.A., Frolova, V.M.: Petrology of ultrabasic inclusions from basalts of Minusa and Transbaikalian regions (Siberia, USSR). *Contrib. Mineral. Petrol.* 29, 163-179 (1970).
39. Aoki, K.: Petrogenesis of ultrabasic and basic inclusions in alkali basalts, Iki Island, Japan. *Am. Mineral.* 53, 241-256 (1968).
40. Green, D.H.: The petrogenesis of the high-temperature peridotite intrusion in the Lizard area, Cornwall. *J. Petrol.* 5, 134-188 (1964).
41. Medaris, L.G. Jr.: High-pressure peridotite in southwestern Oregon. *Geol. Soc. Am. Bull.* 83, 41-58 (1972).
42. Loney, R.A., Himmelberg, G.R., Coleman, R.G.: Structure and petrology of the alpine type peridotite at Burro Mountain, California, U.S.A. *J. Petrol.* 12, 245-309 (1971).
43. Arai, S.: Contact metamorphosed dunite - harzburgite complex in the Chugoku district, western Japan. *Contrib. Mineral. Petrol.* 52, 1-16 (1975).
44. Kushiro, I., Yoder, H.S. Jr., Mysen, B.O.: Viscosity of basalt and andesite magmas at high pressures. *Transactions, American Geophysical Union*, 57, 354 (1976).
45. Green, D.H.: Condition of melting of basanite magma from garnet

- peridotite. *Earth Planet. Sci. Lett.* 17, 456-465 (1973).
46. Clark, S.P., Ringwood, A.E.: Density distribution and constitution of the mantle. *Rev. Geophys.* 2, 35-88 (1964).
47. Wilkinson, J.F.G.: Ultramafic inclusions and high pressure megacrysts from a nephelinite sill, Nandewar Mountains, north-east New South Wales, and their bearing on the origin of certain ultramafic inclusions in alkaline volcanic rocks. *Contrib. Mineral. Petrol.* 51, 235-262. (1975).
48. Mercier, J-C. C., Nicholas, A.: Textures and fabrics of uppermantle peridotites as illustrated by xenoliths from basalts. *J. Petrol.* 16, 454-487 (1975).
49. Best, M.G.: Contrasting types of chromium-spinel peridotite xenoliths in basaltic lavas, western Grand Canyon, Arizona, *Earth Planet. Sci. Lett.* 23, 229-237 (1974).

CHAPTER 6

LABORATORY DUPLICATION OF PHASE EQUILIBRIA OBSERVED IN
NATURAL GARNET LHERZOLITES

TAKESHI MORI and DAVID H. GREEN

ABSTRACT

High pressure experiments have been carried out on two synthetic ultramafic compositions and also on natural mineral mixes at 30-40 kbar and 950-1500°C. Olivine, orthopyroxene, clinopyroxene and garnet coexist in the majority of runs. Equilibria among the four minerals are examined in detail. Because of the close similarity in chemical systems, the experimental results can be directly applied to natural garnet lherzolites. The natural garnet lherzolites show wider variety in mineral chemistry than the run products, indicating very wide ranges of pressure-temperature for their equilibration. However, mineral compositions found in some runs closely reproduce the compositions of coexisting phases in some natural garnet lherzolites from Lesotho and Montana kimberlites and from Alpe Arami lherzolite. Thus, the phase equilibria observed in natural lherzolites can be successfully duplicated in laboratory at appropriate P-T conditions.

INTRODUCTION

The first full analyses of coexisting olivine, orthopyroxene, clinopyroxene and garnet experimentally produced in a natural lherzolite system under known pressure and temperature were published in 1972 (Kushiro et al., 1972). Previous studies of compositional variations among these phases were studies in simple systems such as $\text{SiO}_2\text{-MgO-CaO}$, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaO}$ (e.g., Davis and Boyd, 1966; Boyd, 1970) or had yielded partial analyses of minerals in multicomponent systems (e.g., Al_2O_3 content in orthopyroxene, Green and Ringwood, 1970). The knowledge of the simple systems has now substantially increased while accumulation of data for natural rock and synthetic multicomponent systems has been rather slow in spite of the high demands for such data. Study of natural ultramafic rocks, especially of garnet lherzolite which is believed to be a major rock type in the mantle, desirably requires experimentally determined phase relations

among orthopyroxene, clinopyroxene and garnet, and preferably olivine as well in natural rock systems and/or in synthetic systems containing at least SiO_2 , Al_2O_3 , FeO , MgO and CaO . Such data available at present are from Kushiro et al. (1972), Akella and Boyd (1972, 1973) and Akella (1976). The first authors present a set of chemical compositions of the four phases at 30 kbar and 1450°C , and the second and third authors present 11 sets but without olivine in a P-T range of 25-45 kbar and 1050 - 1300°C .

Experiments in the simple systems may not be directly comparable to natural rocks but reveal essential features of phase relations among the relevant minerals. They are much easier to perform compared to those in the multicomponent systems. By contrast, experiments in complex systems are directly comparable to the natural counterparts, but are technically difficult to carry out. Therefore, these two lines of experiments are complementary and could be best understood together.

This paper is an extension of the previous experimental study in Ca-Mg-Fe pyroxenes (Mori, in preparation), and presents chemical compositions of coexisting olivine, orthopyroxene, clinopyroxene and garnet both in natural rock and synthetic multicomponent systems. Most experiments used the composition of pyrolite III minus 40% olivine with variable water content. Phase boundaries, but not mineral chemistry, for this series of experiments, were reported by Green (1973). For the purpose of this paper, appropriate run products were selected among the earlier experiments and their minerals were analysed by TPD-microprobe. Additional high pressure experiments and probe analyses of their run products were carried out on another synthetic composition and also on natural mineral mixes.

The data obtained are compared with those in the literature, and chemical relations among phases are examined in detail. Some of the experimental runs closely duplicate the phase relations observed in some natural garnet lherzolites occurring both as inclusions in kimberlites and

as intrusives. Mineral chemistries of the majority of garnet lherzolites are, however, not matched with those in any run, indicating they were in equilibrium outside the experimental ranges of 30-40 kbar and 950-1500°C.

EXPERIMENTAL METHODS AND RESULTS

Starting materials used in the high pressure experiments are A) sintered oxides of pyrolite III minus 40% olivine composition, B) a synthetic glass rich in pyroxene components, or its sintered equivalent (at 950°C for 24 hours in an evacuated silica tube), C) a mechanical mixture of olivine, orthopyroxene, clinopyroxene and garnet separated from Norwegian garnet lherzolites (ANU No. 2506, 2501) in an equal weight proportion and D) a mechanical mixture of the orthopyroxene and clinopyroxene in an equal weight proportion. Chemical compositions of these materials are listed in Table 1.

Temperature measurement in all the experiments was by Pt/Pt₉₀Rh₁₀ thermocouples without correction of pressure effect on the thermocouple emf.

The other details of the methods of high pressure experiments, identification of the run products, and TPD-probe analysis are the same as those described by Green (1973).

Run details are summarized in Table 2. Chemical compositions of olivine, orthopyroxene, clinopyroxene, garnet and ilmenite are listed in Tables 3-7. Because of space limitations only part of the data is listed. Full data are obtainable from the authors on request.

COMPARISON OF THE DATA WITH THOSE IN THE LITERATURE

Our data in this paper are most easily compared with those in the literature by plotting them in the ACF-diagram. It should be noted, however, that although olivine-orthopyroxene-clinopyroxene-garnet is an invariant assemblage in the SiO₂-Al₂O₃-MgO-CaO system at fixed temperature and pressure, this does not hold true in more complex systems including

Table 1. Chemical compositions of starting materials.

	Pyrolite III -40% olivine	Pyroxene-rich composition	Minerals from Norwegian garnet lherzolites			
			olivine	orthopyroxene	clinopyroxene	garnet
SiO ₂	47.8	49.46	41.35	57.65	54.61	41.70
TiO ₂	1.2	1.02	—	—	—	—
Al ₂ O ₃	5.9	7.64	—	0.36	2.69	21.90
Fe ₂ O ₃	0.8	0.26	—	—	—	—
FeO	8.2	5.51	7.71*	4.97*	1.33*	9.66*
MnO	0.1	—	—	—	—	0.51
MgO	28.7	23.86	50.44	35.28	15.34	18.69
CaO	5.1	9.60	—	0.09**	21.56	4.92
Na ₂ O	0.95	1.31	—	—	1.90	—
K ₂ O	0.22	0.08	—	—	—	—
Cr ₂ O ₃	0.7	1.06	—	—	1.55	2.92
NiO	0.2	—	0.22	—	—	—
Total	99.9	99.80	99.72	98.35	98.98	100.30

The composition of pyrolite III minus 40% olivine was referred from Green (1973). Fe₂O₃ was determined by E. Kiss. The other analyses were by TPD-probe or ARL-probe (marked **).

*: Total Fe as FeO.

Table 2. Run details

Experiment No.	Reactants with H ₂ O content in wt. %	Pressure (kbar)	Temperature (°C)	Time (hour)	Capsule	Products
DD4	A 0.3	40	1300	1	Pt	oliv, opx, cpx, gar, gl
DD3	A 0.3	40	1250	1	Pt	oliv, opx, cpx, gar, gl
DD2	A 0.3	40	1200	1.5	Ag ₅₀ Pd ₅₀	oliv, opx, cpx, gar, ilm, phlog, gl
DD1	A 0.3	40	1100	4	Ag ₇₅ Pd ₂₅	oliv, opx, cpx, gar, ilm, phlog
DD7	A 0.3	30	1250	1	Ag ₅₀ Pd ₅₀	oliv, opx, cpx, gar, gl
X6	A 0.3	30	1200	1.25	Ag ₅₀ Pd ₅₀	oliv, opx, cpx, gar, ilm, phlog, gl
X7	A 0.3	30	1150	1	Ag ₅₀ Pd ₅₀	oliv, opx, cpx, gar, ilm, phlog, gl
X8	A 0.3	30	1100	6.75	Ag ₇₅ Pd ₂₅	oliv, opx, cpx, gar, ilm, phlog, gl
X9	A 0.3	30	1050	1	Ag ₇₅ Pd ₂₅	oliv, opx, cpx, gar, ilm, phlog, gl
X11	A 0.3	30	1000	7.5	Ag ₇₅ Pd ₂₅	oliv, opx, cpx, gar, ilm, phlog
FF8	A 2	30	1250	2	Ag ₅₀ Pd ₅₀	oliv, opx, cpx, gar, gl
T10	A 2	30	1200	1	Ag ₅₀ Pd ₅₀	oliv, opx, cpx, gar, gl
T11	A 2	30	1150	1	Ag ₅₀ Pd ₅₀	oliv, opx, cpx, gar, ilm, gl
T12	A 2	30	1100	1.5	Ag ₇₅ Pd ₂₅	oliv, opx, cpx, gar, ilm, phlog, gl
FF7	A 2	30	1050	4.75	Ag ₇₅ Pd ₂₅	oliv, opx, cpx, gar, ilm, phlog, gl
FF6	A 2	30	1000	29	Ag ₇₅ Pd ₂₅	oliv, opx, cpx, gar, ilm, phlog(?)
T6	A 10	30	1050	4.75	Ag ₇₅ Pd ₂₅	oliv, opx, cpx, gar, sp(Cr ₂ O ₃ ~48 wt.%), gl
T7	A 10	30	1020	4	Ag ₇₅ Pd ₂₅	oliv, opx, cpx, gar, ilm
T8	A 10	30	1000	4	Ag ₇₅ Pd ₂₅	oliv, opx, cpx, gar, ilm, sp(Cr ₂ O ₃ ~46 wt.%)
T9	A 10	30	950	6	Ag ₇₅ Pd ₂₅	oliv, opx, cpx, gar, ilm
A2	B(Xst) 0	30	1500	0.33	Pt	opx, cpx, gar, oliv(?)
A7	B(glass) 0	30	1450	0.5	Pt	oliv(tr), opx, cpx, gar
A4	B(Xst) 0	30	1400	0.75	Pt	opx, cpx, gar, oliv(?)
A5	B(Xst) 0	30	1350	1	Pt	opx, cpx, gar, oliv(?)
C2	C tr	30	1200	2.5	Pt	oliv, opx, cpx, gar
C4	D tr	30	1450	1	Pt	opx, cpx

Abbreviations: oliv - olivine, opx - orthopyroxene, cpx - clinopyroxene, gar - garnet, ilm - ilmenite, sp - spinel, phlog - phlogopite, gl - glass.

Table 3. Olivine analyses with structural formulae (cations per 4 oxygens).

Run No.	DD4	DD2	DD1	X6	X8	X11	T10	T12	FF6	T8	A7	C2
kbar	40	40	40	30	30	30	30	30	30	30	30	30
O _C	1300	1200	1100	1200	1100	1000	1200	1100	1000	1000	1450	1200
SiO ₂	41.12	41.15	40.66	40.30	41.12	40.96	40.45	39.93	40.04	40.68	42.28	41.76
Al ₂ O ₃	0.29	—	—	—	—	0.18	0.54	0.52	—	—	0.45	—
FeO	8.44	12.59	12.50	12.22	13.18	13.29	11.90	12.98	12.73	12.22	6.56	9.16
MgO	50.08	46.96	46.91	46.46	46.52	46.63	47.10	46.34	46.27	46.95	49.62	49.14
CaO	0.13	0.16	0.08	—	0.19	—	0.22	—	—	—	0.75	0.21
Na ₂ O	—	—	—	—	—	—	—	—	—	—	0.48	0.24
Cr ₂ O ₃	—	—	—	—	—	—	—	—	—	—	0.15	—
NiO	0.23	0.48	0.29	n.a.	n.a.	n.a.	0.22	0.40	0.31	n.a.	—	0.42
Total	100.29	101.34	100.44	98.98	101.01	101.06	100.43	100.17	99.35	99.85	100.29	100.93
Si	0.998	1.007	1.004	1.007	1.010	1.006	0.996	0.992	1.001	1.007	1.017	1.011
Al	0.008	—	—	—	—	0.005	0.016	0.015	—	—	0.013	—
Fe	0.171	0.258	0.258	0.255	0.271	0.273	0.245	0.270	0.266	0.253	0.132	0.185
Mg	1.812	1.714	1.726	1.731	1.704	1.707	1.729	1.716	1.725	1.733	1.780	1.773
Ca	0.003	0.004	0.002	—	0.005	—	0.006	—	—	—	0.019	0.005
Na	—	—	—	—	—	—	—	—	—	—	0.022	0.011
Cr	—	—	—	—	—	—	—	—	—	—	0.003	—
Ni	0.004	0.009	0.006	—	—	—	0.004	0.008	0.006	—	—	0.008
Total	2.996	2.992	2.996	2.993	2.990	2.991	2.996	3.001	2.998	2.993	2.986	2.993

n.a.: not analyzed

Table 4. Orthopyroxene analyses with structural formulae (cations per 6 oxygens).

Run No.	DD4	DD2	DD1	X6	X8	X11	T10	T12	FF6	T8	A7	C2
kbar	40	40	40	30	30	30	30	30	30	30	30	30
O _C	1300	1200	1100	1200	1100	1000	1200	1100	1000	1000	1450	1200
SiO ₂	56.50	56.69	57.17	53.46	55.86	55.21	54.90	55.31	56.14	56.22	56.56	56.36
TiO ₂	0.25	0.27	—	0.35	0.24	—	0.22	0.16	—	—	—	—
Al ₂ O ₃	2.43	1.82	1.33	3.91	2.92	1.89	3.76	2.92	1.44	2.16	3.50	2.69
FeO	4.82	7.44	7.32	7.74	7.95	7.92	6.84	7.71	7.77	7.53	3.98	5.95
MgO	32.66	31.50	32.52	30.65	31.14	32.75	31.80	31.88	32.47	32.11	32.48	32.84
CaO	1.56	1.62	0.99	1.58	1.05	0.78	1.60	1.14	0.66	0.61	2.20	1.41
Na ₂ O	0.29	0.31	0.19	0.44	—	—	0.18	0.18	—	—	—	0.22
Cr ₂ O ₃	0.35	0.32	—	0.44	0.28	0.25	0.76	0.44	0.39	0.56	0.63	0.88
Total	98.86	99.97	99.52	98.57	99.44	98.80	100.06	99.74	98.87	99.19	99.35	100.35
Si	1.962	1.971	1.988	1.896	1.951	1.945	1.907	1.930	1.971	1.964	1.949	1.941
Ti	0.007	0.007	—	0.009	0.006	—	0.006	0.004	—	—	—	—
Al	0.099	0.075	0.055	0.163	0.120	0.078	0.154	0.120	0.060	0.089	0.142	0.109
Fe	0.140	0.216	0.213	0.230	0.232	0.233	0.199	0.225	0.228	0.220	0.115	0.171
Mg	1.691	1.632	1.686	1.621	1.622	1.720	1.647	1.659	1.699	1.672	1.668	1.686
Ca	0.058	0.060	0.037	0.060	0.039	0.029	0.060	0.043	0.025	0.023	0.081	0.052
Na	0.020	0.021	0.013	0.030	—	—	0.012	0.012	—	—	—	0.015
Cr	0.010	0.009	—	0.012	0.008	0.007	0.021	0.012	0.011	0.015	0.017	0.024
Total	3.987	3.991	3.992	4.021	3.978	4.012	4.006	4.005	3.994	3.983	3.972	3.998

Table 5. Clinopyroxene analyses with chemical formulae (cations per 6 oxygens).

Run No.	DD4	DD2	DD1	X6	X8	X11	T10	T12	FF6	T8	A7	C2
kbar	40	40	40	30	30	30	30	30	30	30	30	30
O _C	1300	1200	1100	1200	1100	1000	1200	1100	1000	1000	1450	1200
SiO ₂	54.66	53.52	53.57	53.33	53.98	53.89	53.22	52.37	54.28	54.37	52.45	53.87
TiO ₂	0.54	0.84	0.66	0.86	0.85	0.63	0.34	0.46	0.29	0.28	0.91	—
Al ₂ O ₃	3.85	4.54	4.51	5.04	4.91	3.64	3.62	3.97	2.52	2.10	7.14	3.04
FeO	3.17	4.39	4.17	4.43	4.38	3.78	4.41	4.27	3.31	3.70	3.73	3.20
MgO	19.18	16.85	15.37	16.79	16.13	16.02	18.12	17.36	16.71	17.35	21.31	18.64
CaO	15.75	15.56	16.23	16.72	17.57	19.44	17.86	18.32	19.48	20.71	11.70	18.47
Na ₂ O	1.89	2.66	3.07	2.07	2.08	1.89	1.39	1.27	1.47	0.93	1.55	0.92
Cr ₂ O ₃	0.97	0.96	1.08	1.15	0.86	1.26	1.11	1.00	1.27	0.87	1.23	1.40
Total	100.01	99.32	98.66	100.39	100.76	100.55	100.07	99.02	99.33	100.31	100.02	99.54
Si	1.952	1.940	1.958	1.917	1.934	1.944	1.925	1.917	1.975	1.966	1.859	1.948
Ti	0.014	0.023	0.018	0.023	0.023	0.017	0.009	0.013	0.008	0.008	0.024	—
Al	0.162	0.194	0.194	0.214	0.207	0.155	0.154	0.171	0.108	0.089	0.298	0.130
Fe	0.095	0.133	0.127	0.133	0.131	0.114	0.133	0.131	0.101	0.112	0.111	0.097
Mg	1.021	0.911	0.838	0.900	0.861	0.861	0.977	0.947	0.906	0.935	1.126	1.005
Ca	0.603	0.604	0.636	0.644	0.674	0.751	0.692	0.718	0.759	0.802	0.444	0.716
Na	0.131	0.187	0.218	0.144	0.144	0.132	0.097	0.090	0.104	0.065	0.107	0.065
Cr	0.027	0.028	0.031	0.033	0.024	0.036	0.032	0.029	0.037	0.025	0.034	0.040
Total	4.005	4.020	4.020	4.008	3.998	4.010	4.019	4.016	3.998	4.002	4.003	4.001

Table 6. Garnet analyses with chemical formulae (cations per 12 oxygens).

Run No.	DD4	DD2	DD1	X6	X8	X11	T10	T12	FF6	T8	A7	C2
kbar	40	40	40	30	30	30	30	30	30	30	30	30
°C	1300	1200	1100	1200	1100	1000	1200	1100	1000	1000	1450	1200
SiO ₂	41.87	40.31	41.49	40.85	41.52	41.31	41.69	41.05	41.00	41.16	43.41	42.91
TiO ₂	0.92	1.63	0.90	1.13	0.86	0.68	0.53	0.94	0.48	0.73	1.06	—
Al ₂ O ₃	22.06	21.51	22.10	22.03	21.63	21.95	22.18	20.85	22.06	21.65	20.99	21.24
FeO	7.05	10.19	9.86	9.91	10.03	10.92	8.28	9.97	10.58	9.98	5.62	7.10
MnO	—	0.25	—	—	0.23	0.21	0.15	0.20	0.26	0.23	—	0.14
MgO	20.91	18.47	19.46	18.66	18.32	18.30	19.48	17.75	17.85	17.47	21.39	20.36
CaO	5.24	5.58	4.82	5.82	5.71	5.96	5.88	7.06	5.86	6.98	6.35	6.39
Na ₂ O	—	—	—	—	—	—	—	—	—	—	0.42	0.35
Cr ₂ O ₃	2.07	1.86	2.25	2.50	1.85	1.53	2.56	2.55	2.36	1.99	2.23	3.64
Total	100.12	99.80	100.88	100.90	100.15	100.86	100.75	100.37	100.45	100.19	101.47	102.13
Si	2.968	2.922	2.955	2.924	2.987	2.964	2.963	2.969	2.955	2.973	3.029	3.006
Ti	0.049	0.089	0.048	0.061	0.047	0.037	0.028	0.051	0.026	0.040	0.056	—
Al	1.843	1.838	1.855	1.858	1.834	1.856	1.858	1.777	1.874	1.843	1.726	1.754
Fe	0.418	0.618	0.587	0.593	0.604	0.655	0.492	0.603	0.638	0.603	0.328	0.416
Mn	—	0.015	—	—	0.014	0.013	0.009	0.012	0.016	0.014	—	0.008
Mg	2.210	1.996	2.066	1.991	1.965	1.958	2.064	1.914	1.918	1.881	2.225	2.127
Ca	0.398	0.433	0.368	0.446	0.440	0.458	0.448	0.547	0.453	0.540	0.475	0.480
Na	—	—	—	—	—	—	—	—	—	—	0.057	0.048
Cr	0.116	0.107	0.127	0.141	0.105	0.087	0.144	0.146	0.134	0.114	0.123	0.202
Total	8.002	8.018	8.006	8.014	7.996	8.028	8.006	8.019	8.014	8.008	8.019	8.041

Table 7. Ilmenite analyses with chemical formulae (cations per 12 oxygens).

Run No.	DD2	DD1	X8	X11	T12	FF6
kbar	40	40	30	30	30	30
°C	1200	1100	1100	1000	1100	1000
SiO ₂	0.20	1.60	1.20	0.32	1.51	0.47
TiO ₂	57.96	54.90	54.61	55.40	55.15	55.55
Al ₂ O ₃	0.53	0.56	0.74	0.29	0.74	0.26
FeO	26.27	26.93	27.88	28.59	27.78	28.21
MnO	0.16	0.16	0.22	0.23	0.26	0.25
MgO	13.46	12.84	12.73	12.01	13.60	12.32
CaO	0.24	0.35	0.27	0.32	0.27	0.32
Cr ₂ O ₃	1.77	1.52	1.66	1.54	2.99	2.53
NiO	0.21	0.26	n.a.	0.43	0.48	0.41
Total	100.80	99.12	99.31	99.13	102.78	100.32
Si	0.018	0.147	0.110	0.030	0.134	0.043
Ti	3.927	3.783	3.774	3.875	3.680	3.833
Al	0.056	0.060	0.080	0.032	0.077	0.028
Fe	1.979	2.064	2.143	2.224	2.062	2.165
Mn	0.012	0.012	0.017	0.018	0.020	0.019
Mg	1.808	1.754	1.744	1.666	1.799	1.685
Ca	0.023	0.034	0.027	0.032	0.026	0.031
Cr	0.126	0.110	0.121	0.113	0.210	0.184
Ni	0.015	0.019	—	0.032	0.034	0.030
Total	7.964	7.983	8.016	8.022	8.042	8.018

TiO₂, FeO, Na₂O, Cr₂O₃, etc. Among these elements, the most influential is FeO, and it is therefore preferable to compare the data within a range of limited Mg/(Mg + Fe) ratio of, for example, orthopyroxene. The range chosen is from 0.8 to 0.95 which encompasses the majority of orthopyroxenes in natural ultramafic rocks. Our data are compared with such data available from the literature in four small T-P ranges (Fig. 1).

Orthopyroxenes show compositional convergence in any T-P field, indicating relatively quick approach to the equilibrium of this mineral, and also higher reliability of probe analysis due to its relatively larger grain sizes obtainable in the high pressure experiments. Clinopyroxenes at 30-31 kbar and 1100°C also show good convergence and this may be related to the small range of Mg/(Mg + Fe) (0.88-0.93) for these data. By contrast, clinopyroxenes in the other three T-P ranges show wide divergence. It should be noted that A-component of Hensen's (1973) clinopyroxenes might be overestimated due to the lack of Na₂O analyses. Among the three ranges, the divergence of clinopyroxene compositions at 27-30 kbar and 1410-1450°C is most discouraging. The difference between two data by Hensen (1973) and ours may be partly due to the difference in the Mg/(Mg + Fe) ratio of clinopyroxene which are 0.85 and 0.91 respectively. Akella's (1976) data in a FeO-free system indicate by interpolation, a clinopyroxene composition of $A_{11}C_{30}F_{59}$ at 31 kbar and 1450°C. Thus, these three data are reasonably consistent and suggest that the equilibrium clinopyroxene composition in the Kushiro et al.'s (1972) experiment should be higher in A and F components than that reported. If so, the reported datum may only represent a transitional composition during partial reaction from the starting composition of $A_1C_{43}F_{56}$.

Garnets also show compositional spread in all the P-T ranges, possibly because garnet is most sluggish in reaction to a new equilibrium composition. Our datum at 30 kbar and 1450°C and all the data of Akella and Boyd (1973) and Akella (1976) plotted in Figure 1 show garnet

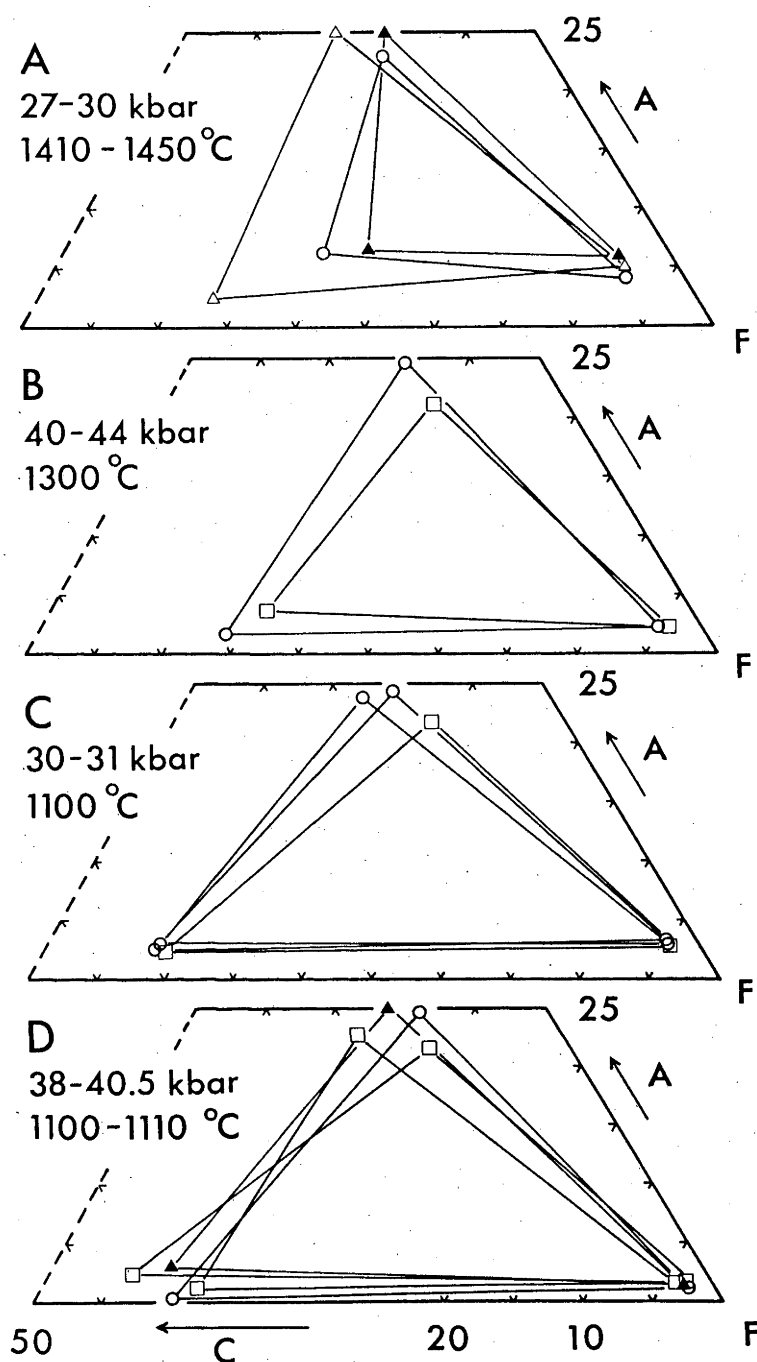


FIG. 1 ACF-plots (in mole percent) to compare our analyses of garnet, orthopyroxene and clinopyroxene with experimental data from the literature. Data sources: square - Akella and Boyd (1973) and Akella (1976), filled triangle - Hensen (1973), open triangle - Kushiro et al. (1972) and circle - this paper. $A = (Al,Cr)_2O_3-Na_2O$, $C = CaSiO_3$, $F = (Mg,Fe,Mn)SiO_3$. All the analyses are by microprobe, thus Fe is treated as entirely in the ferrous state.

compositions which deviate considerably from the stoichiometric join ($A = 25$). Unless garnet has solid solution towards pyroxenes in those T-P ranges, they possibly imply either inferior analyses or presence of Fe_2O_3 (all the iron was assumed to be in the ferrous state in constructing Figure 1).

Olivine can be compared only at 30 kbar and 1450°C between Kushiro et al.'s (1972) and our data. Fe-Mg partition coefficient between olivine and orthopyroxene is the same between these two sets of data. Consistency is observed in this regard, but our datum shows CaO content of 0.75 wt.% compared with Kushiro et al.'s 0.10. High CaO and also high Na_2O may be due to possible contamination of clinopyroxene in our probe analysis.

In summary, consistency within the published data and between our new data and the published data is not very good except for orthopyroxene analyses. However, because of the effects of such elements as TiO_2 , FeO , Na_2O , Cr_2O_3 , etc., the consistency is not so bad as Figure 1 may suggest. The following sections should be read with cautionary allowance for the inconsistency among all the data discussed above.

OLIVINE, ORTHOPYROXENE, CLINOPYROXENE, GARNET EQUILIBRIA

Pyroxene solvus

Chemical compositions of coexisting orthopyroxene and clinopyroxene at known temperatures and pressures have been eagerly sought after. Our data are comprehensive in the P-T ranges of 950 – 1500°C and 30–40 kbar. Figure 2 shows compositions of the alumina-saturated pyroxenes plotted in a temperature vs. wollastonite content diagram. The spread of data, especially of clinopyroxene, is due to experimental errors, to the pressure range (30–40 kbar) of the data and to the arbitrary projection of compositions in the multi-component systems to the plane. The shaded boundaries of the solvus are directly comparable with pyroxene

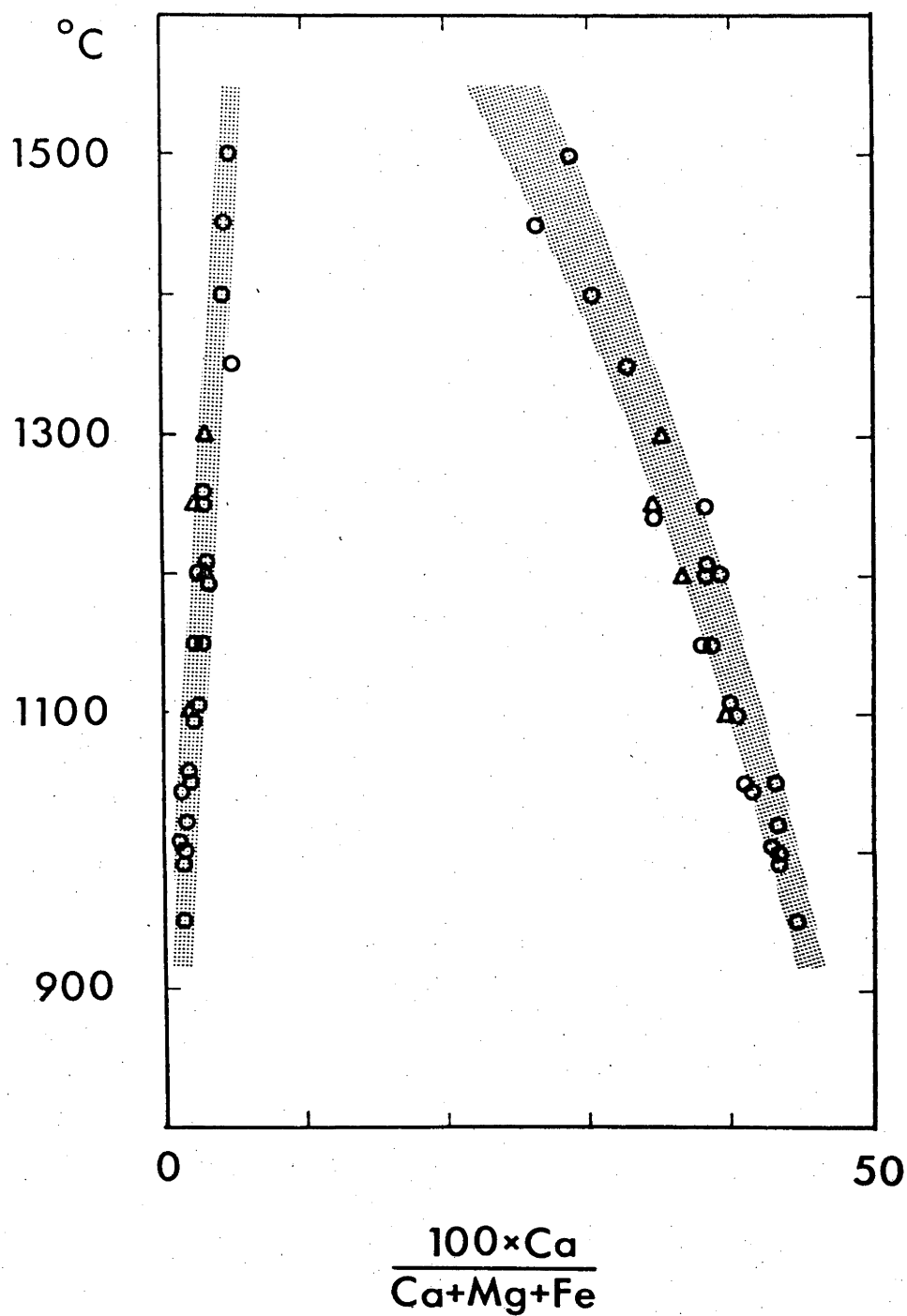


FIG. 2 Orthopyroxene-clinopyroxene solvus from data of tables 4 and 5 projected to the wollastonite (mole percent) - temperature plane at 30-40 kbar. Triangle-40 kbar, circle - 30 kbar.

compositions for natural garnet-orthopyroxene-clinopyroxene rocks with the $\text{Mg}/(\text{Mg} + \text{Fe})$ ratio of orthopyroxene between about 0.87 and 0.96.

The data are consistent with those of Akella (1976) at 1100–1300°C and 31–44 kbar in a natural rock system with the similar $\text{Mg}/(\text{Mg} + \text{Fe})$ ratio.

The pressure effect on the solvus (Howells and O'Hara, 1975; Mori and Green, 1975) is not seen in the figure probably because the uncertainty of the data is large enough to conceal the effect. If the analogy to the Al, Fe-free system is valid, this effect would be only 0.8 mole percent wollastonite from 30 to 40 kbar at 1200°C but would be 5 percent at 1500°C (Mori and Green, 1976).

Another method of expressing the pyroxene solvus in a more sophisticated way has been developed by Wood and Banno (1973). Activity ratio of $\text{Mg}_2\text{Si}_2\text{O}_6$ in clinopyroxene and orthopyroxene (K) is plotted against temperature. This has been done for the new data (Fig. 3) but with one difference from Wood and Banno's (1973) method of activity calculation. For this paper, Fe and Mg are assigned to M1 and M2 sites in accordance with the experimental determination of Fe-Mg intracrystalline partitions in pyroxenes (Virgo and Hafner, 1969; Smyth, 1973; McCallister et al., 1976) rather than by assuming equal Fe/Mg ratio in the two sites. Their data above 500°C give, by linear regression:

$$\ln K^{\text{opx-M2/opx-M1}} = 3080/T^\circ\text{K} - 1.181$$

$$\ln K^{\text{cpx-M2/cpx-M1}} = 2410/T^\circ\text{K} - 0.139$$

where $K^{i/j} = (\text{Fe}/\text{Mg})^i/(\text{Fe}/\text{Mg})^j$, and i and j are sites in these cases, but later may also represent whole minerals.

The recent determinations of pyroxene solvus in the $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ system (Nehru and Wyllie, 1974; Mori and Green, 1975; Lindsley and Dixon, 1975) show that the $\ln K$ vs. $1/T^\circ\text{K}$ relation is not approximated by a straight line. The spread of the data in Figure 3, however, does not allow us to judge if or not the relation is linear in the complex systems.

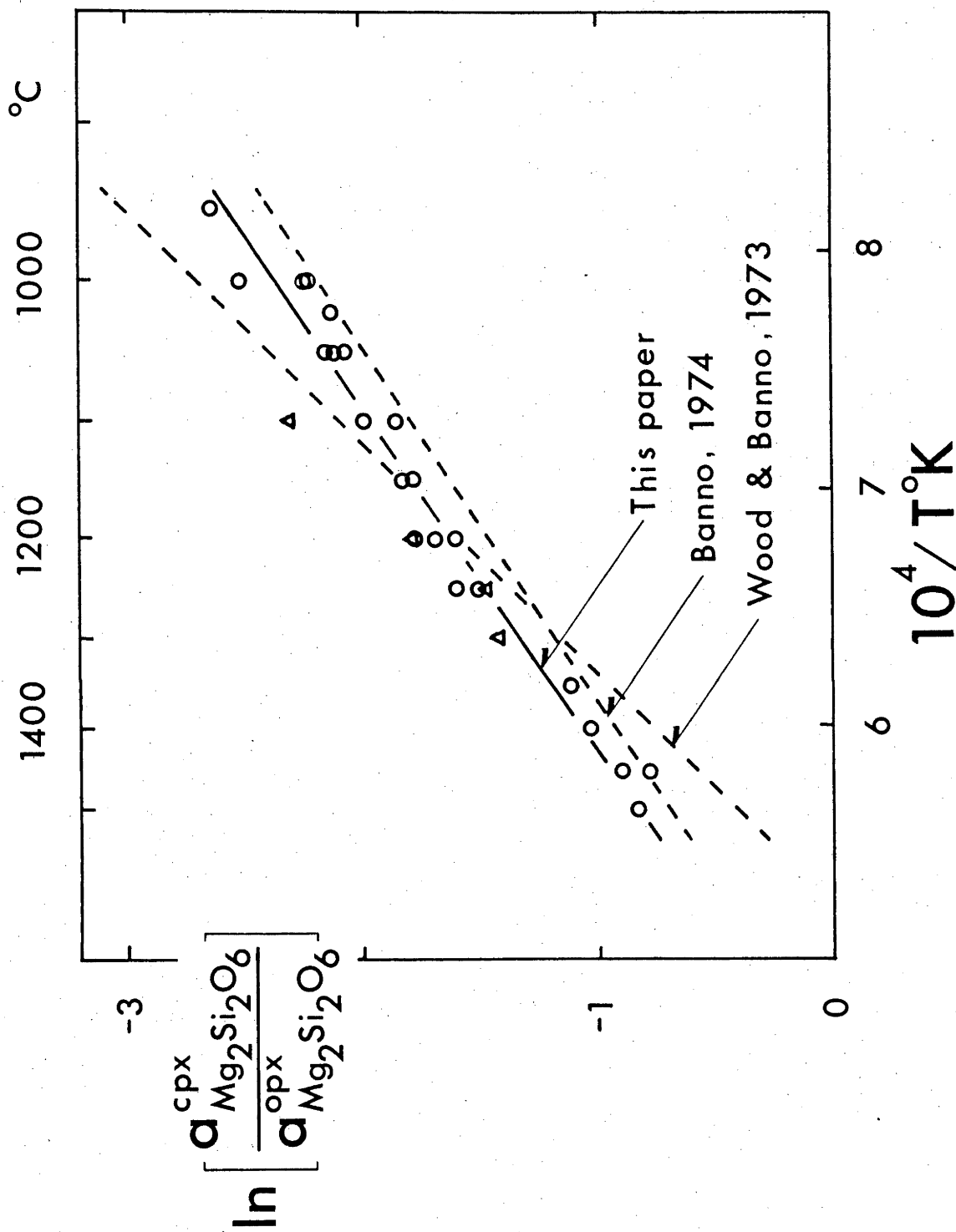


FIG. 3 Activity ratio of $\text{Mg}_2\text{Si}_2\text{O}_6$ in clinopyroxene and orthopyroxene (Tables 4, 5) plotted against temperature. Wood and Banno's equation was obtained by assuming the $\text{Fe}/(\text{Mg}+\text{Fe})$ ratio in orthopyroxene is 0.1. Triangle-40 kbar, circle-30 kbar.

Though the linear relationship is less likely, it would give an equation by regression analysis:

$$\ln K = -6860/T^{\circ}\text{K} + 3.03$$

The error associated with the temperature is about 100°C within the P-T ranges of 950–1500°C and 30–40 kbar. The equation should not be used outside these ranges. In addition, the oversimplified nature of the solid solution models employed is illustrated since $\ln K$ also strongly depends on the Mg/(Mg + Fe) ratio of pyroxenes. This is apparent when our data are compared with those of Akella and Boyd (1973) which show higher $\ln K$ in more Fe-rich systems.

Figure 3 also shows the relationships obtained by Wood and Banno (1973) and Banno (1974). Our data are on the slightly higher temperature side of Banno's equation. Wood and Banno's equation considerably deviates from either of the others. This is because it was obtained mainly on the basis of Davis and Boyd's (1966) experiments of pyroxenes in the $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ at 30 kbar, which has been later revised (e.g., Mori and Green, 1975). Thus, Wood and Banno geothermometer yields considerable overestimation in temperature for the rocks equilibrated below 1000°C and underestimation of temperature for rocks equilibrated above 1300°C.

Alumina contents in pyroxenes

Compositions of orthopyroxene and clinopyroxene coexisting with garnet are plotted in the ACF-diagram (Fig. 4). Both pyroxenes define compositional trends at 30 and 40 kbar. It is well known that the pyroxene solvus narrows and both pyroxenes become enriched in A-component with increasing temperature (e.g., O'Hara, 1967; Akella, 1976). Our data in the multicomponent systems generally follow these sequences but with some local reversals.

Al_2O_3 content and A-component (i.e. $\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 - \text{Na}_2\text{O}$) should now be clearly distinguished, particularly for clinopyroxene. In fact, Al_2O_3

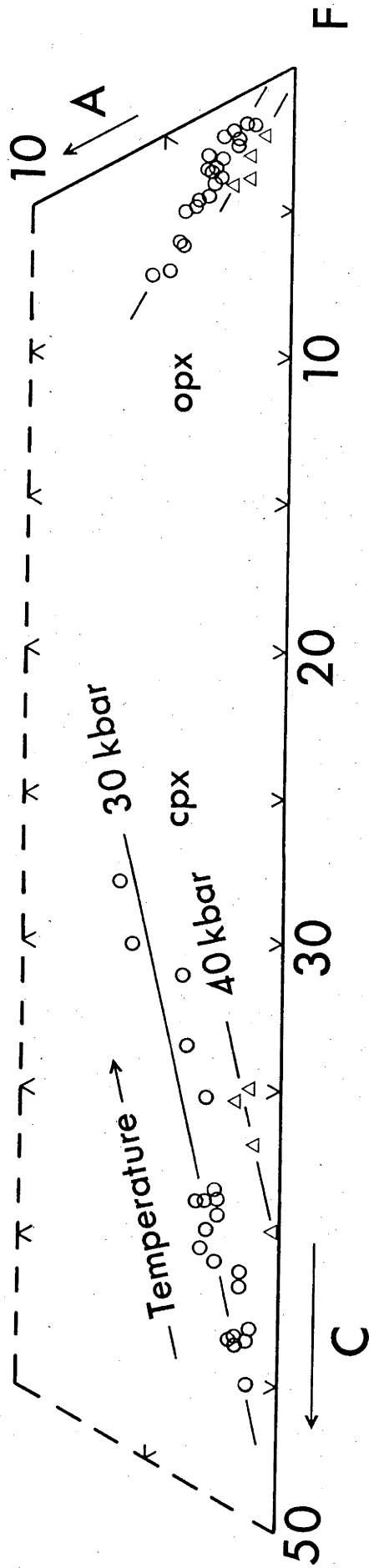


FIG. 4 Compositions of pyroxenes coexisting with garnet in a part of ACF-diagram. Triangle - 40 kbar, circle - 30 kbar.

content of clinopyroxene would show less correlation with temperature and pressure than A-component. For example, Al_2O_3 content changes irregularly from 1300 to 1100°C at 40 kbar (3.9 - 3.6 - 4.5 - 4.5 wt. percent, showing rather higher Al_2O_3 content at lower temperature), while A-component monotonously decreases from 1.7 to 0.2 percent. More examples are seen at 1200°C and 1000°C at 30 kbar where the 3 sets of clinopyroxene composition (Table 5), show spreads in Al_2O_3 content but rather convergent values of A-component. These effects are, of course, mainly due to the different content of Na_2O in clinopyroxenes.

By contrast, the distinction between A-component and Al_2O_3 content is less important for orthopyroxene since Na_2O and Cr_2O_3 contents are much less than in coexisting clinopyroxene. Therefore, Al_2O_3 content in orthopyroxene should be a better indicator of physical conditions of equilibration than that in clinopyroxene. Figure 5 shows the T-P effects on Al_2O_3 content of orthopyroxene coexisting with clinopyroxene and garnet. Scattered nature of Al_2O_3 in orthopyroxene is a general problem in experiments and is further documented by Howells (1975).

Garnet compositions

All the garnets in our runs are coexisting with at least orthopyroxene and clinopyroxene. Compositions of garnet (Table 6) show A-component ($\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3 - \text{Na}_2\text{O}$) of 24.5 ± 0.7 percent which is consistent with stoichiometry of garnet (A = 25 percent) within the error. This suggests that Fe_2O_3 content in the garnet is insignificant.

Grossular contents are shown in Figure 6. In spite of the spread of data, it is apparent that compositions in all the four runs at 40 kbar are poorer in grossular content than in any composition at 30 kbar. That is, when garnet is coexisting with orthopyroxene and clinopyroxene, grossular content decreases with increasing pressure. The same tendency has been already shown experimentally and theoretically in the system $\text{MgSiO}_3\text{-CaSiO}_3\text{-Al}_2\text{O}_3$ by Kushiro et al. (1967). The pressure effect on

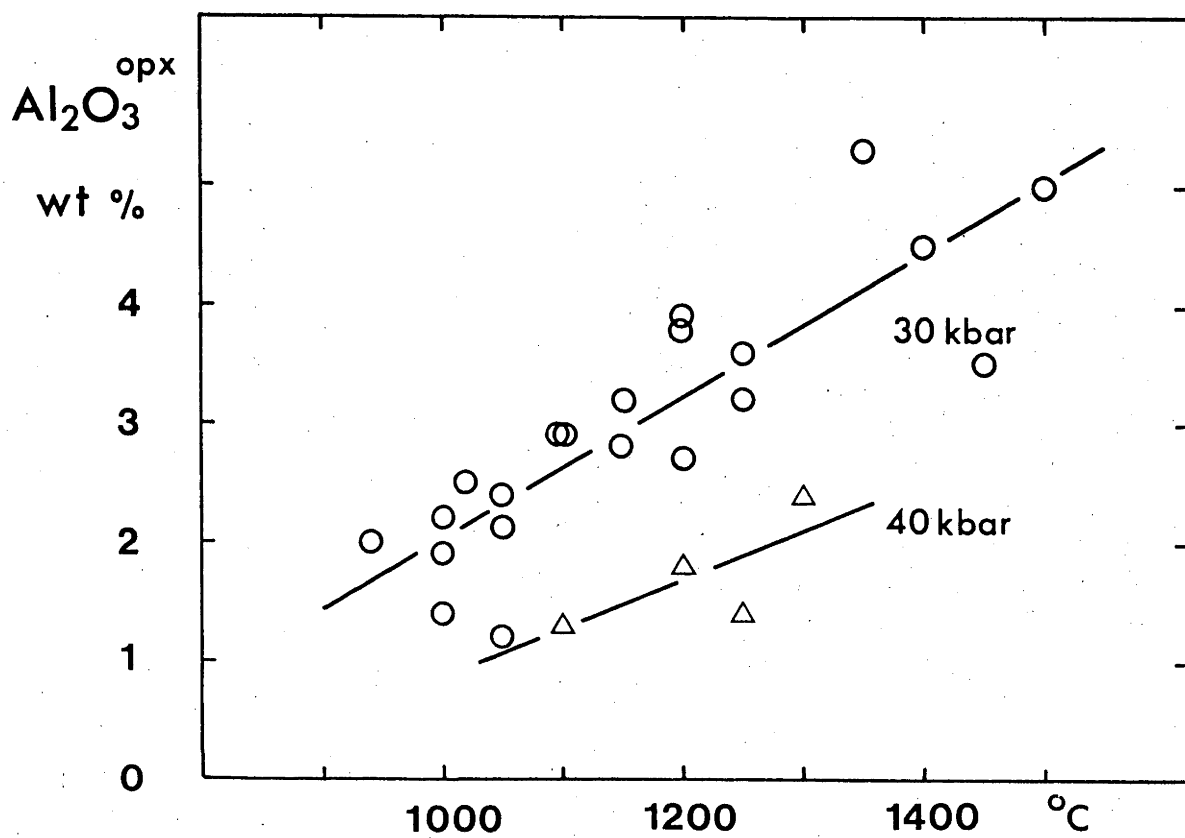


FIG. 5 Al_2O_3 content in orthopyroxene coexisting with at least clinopyroxene and garnet.

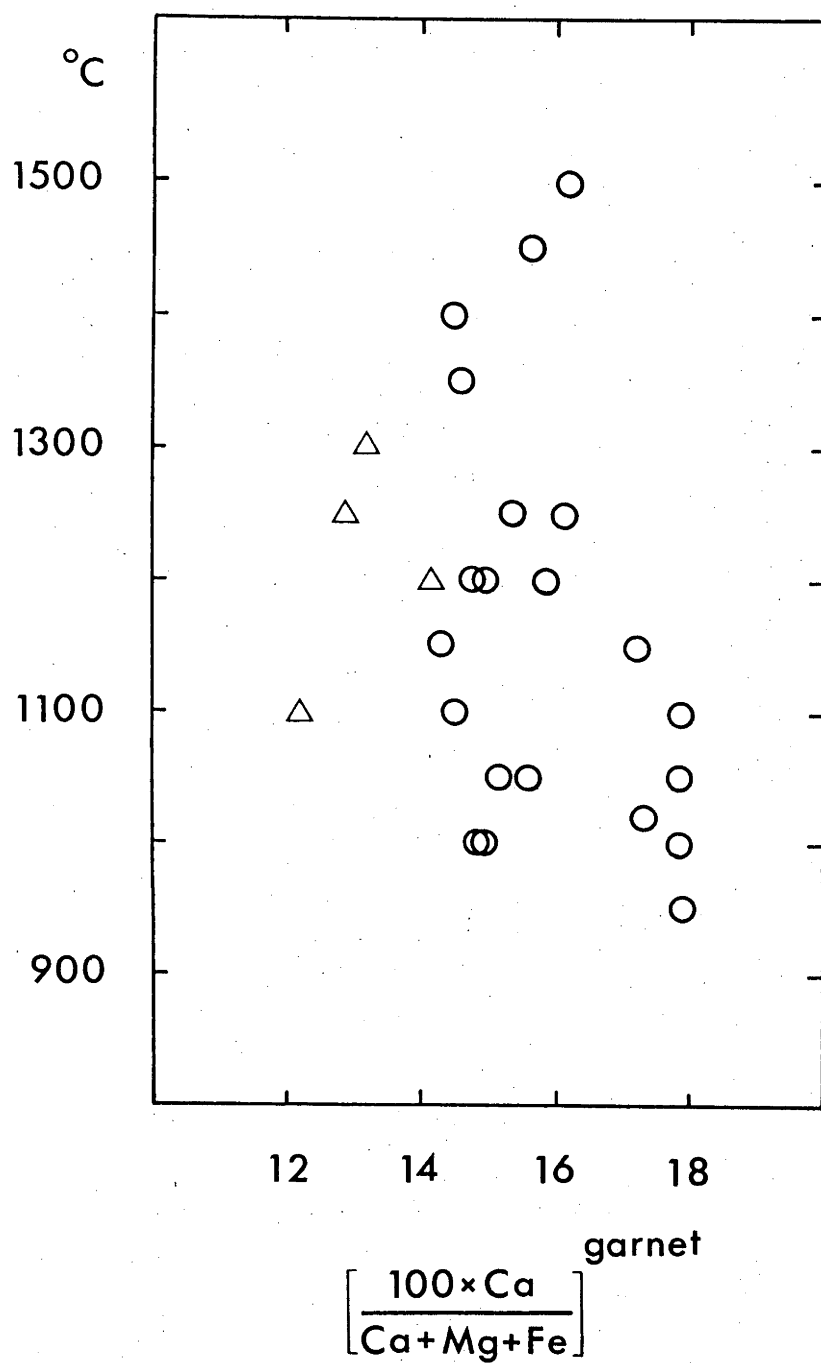


FIG. 6 Grossular content in garnet coexisting with orthopyroxene and clinopyroxene. Triangle - 40 kbar, circle - 30 kbar.

grossular content probably explains the distinction between the lower grossular content of garnets of sheared lherzolites in kimberlites and the higher grossular content of garnets of the granular lherzolites (data from Boyd, in Nixon, 1973). Temperature effect, which is the opposite to the pressure effect in Kushiro et al.'s experiments, cannot be assessed from the data in Figure 6.

The contents of TiO_2 and Cr_2O_3 in minerals of the garnet lherzolite assemblage decrease in the order garnet- clinopyroxene- orthopyroxene. Both TiO_2 and Cr_2O_3 in olivine are at the limit of detection for our analytical methods. Ti concentration ratio on the 6 oxygen basis is roughly 0.7 for clinopyroxene/garnet and 0.2 for orthopyroxene/garnet. Corresponding Cr ratios are roughly 0.5 and 0.2, respectively. These ratios do not show any systematic change with temperature or pressure.

Ilmenite compositions

Ilmenite, when present in our runs, always coexists with at least olivine, orthopyroxene, clinopyroxene and garnet. Because of the tiny grain size of this mineral, probe analysis is not as good as those of the silicate minerals. The composition does not widely vary within the experimental T-P conditions. The $\text{Mg}/(\text{Mg} + \text{Fe})$ ratio slightly increases above solidus temperature within a single series of runs at 40 kbar, and at 30 kbar with different H_2O content. MgO content is characteristically high (12-14 wt. percent). Al_2O_3 and Cr_2O_3 contents are respectively within ranges of 0.3-0.8 and 1.5-3.0 wt. percent. All these features are remarkably similar to those of the ilmenites associated with some garnet lherzolite nodules in southern African and Siberian kimberlites (Boyd, in Nixon, 1973; Green and Sobolev, 1975).

Fe-Mg partition between olivine, orthopyroxene, clinopyroxene and garnet

Among the four silicate phases of olivine, orthopyroxene, clinopyroxene and garnet, there are six different mineral pairs. However, only three pairs among them are independent. We have chosen garnet/

clinopyroxene, orthopyroxene/clinopyroxene and garnet/olivine as such pairs (Fig. 7). All the iron was assumed to be in the ferrous state. The chemical formulae of the minerals (Tables 3-6), calculated on this assumption, do not show much deviation from the ideal stoichiometry of these minerals.

Again the data spread does not allow discrimination of the 40 kbar data from 30 kbar, and linear regression analysis was carried out including all the data at 40 and 30 kbar. The equations obtained are valid at this pressure range:

$$\ln K^{\text{gar/cpx}} = 2800/T^{\circ}\text{K} - 1.19$$

$$\ln K^{\text{opx/cpx}} = 1500/T^{\circ}\text{K} - 1.07$$

$$\ln K^{\text{gar/oliv}} = 900/T^{\circ}\text{K} + 0.09$$

The similar equations for the other pairs can be calculated from the equations above:

$$\ln K^{\text{gar/opx}} = 1300/T^{\circ}\text{K} - 0.12$$

$$\ln K^{\text{oliv/cpx}} = 1900/T^{\circ}\text{K} - 1.28$$

$$\ln K^{\text{oliv/opx}} = 400/T^{\circ}\text{K} - 0.21$$

This paper is, to our knowledge, the first to present simultaneous temperature calibrations of these six Fe-Mg distribution coefficients from a single series of experiments. The six equations show that temperature sensitivity varies from pair to pair. Geothermometry is best in garnet/clinopyroxene pair, and becomes less sensitive in the order olivine/clinopyroxene, orthopyroxene/clinopyroxene, garnet/orthopyroxene, garnet/olivine, olivine/orthopyroxene. The last pair would be practically meaningless as a geothermometer. This conclusion is the same as that of Matsui and Nishizawa (1974) who studied Fe-Mg partition between this pair of minerals in a Ca-free system.

The individual $K^{\text{gar/cpx}}$ values for bulk composition $\text{Mg}/(\text{Mg} + \text{Fe}) = 0.85$ of Raheim and Green (1974) fall within the spread of our data but those for $\text{Mg}/(\text{Mg} + \text{Fe}) = 0.93$ fall at lower $K^{\text{gar/cpx}}$ values. Our linear

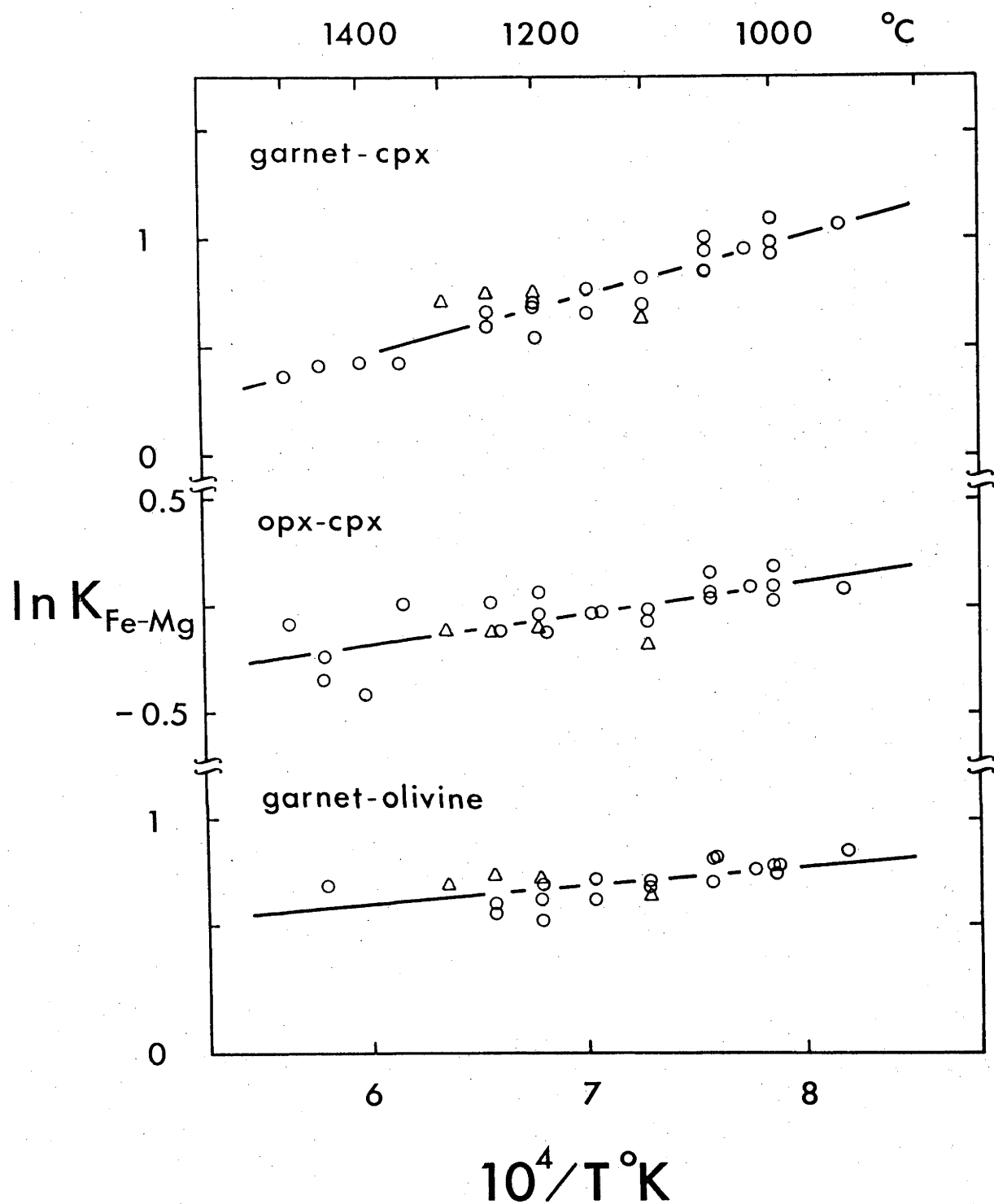


FIG. 7 Fe-Mg partition coefficients between garnet and clinopyroxene, orthopyroxene and clinopyroxene, and garnet and olivine. Triangle - 40 kbar, circle - 30 kbar.

regression curve differs from that of Raheim and Green for their data in bulk compositions $0.06 < \text{Mg}/(\text{Mg} + \text{Fe}) < 0.85$ and from that for $\text{Mg}/(\text{Mg} + \text{Fe}) = 0.93$. These differences may possibly result from the different chemical compositions of minerals (e.g., Al_2O_3 and Na_2O in clinopyroxene) reflecting the difference in bulk chemistry.

DUPLICATION OF PHASE EQUILIBRIA OBSERVED IN NATURAL GARNET LHERZOLITES

Chemical compositions of minerals presented in this paper can be directly compared with those in natural garnet lherzolites. Our experimental compositions were not however designed to investigate differences in such minor elements as Na_2O , TiO_2 , Cr_2O_3 in pyroxenes nor NiO in olivine between natural rocks and the experimental charges. At this stage of investigation, we are concerned with the major solid solution components of the four phases and we therefore use ACF-diagram as well as Fe-Mg partition coefficients for comparison of the data. If Fe_2O_3 analyses are available for the natural minerals, they are included in A-component. Otherwise, all Fe is assumed to be in the ferrous state. It should be noted that the $\text{Mg}/(\text{Mg} + \text{Fe})$ ratio in experimental run products is comparable to or only slightly lower than in the natural rocks. Therefore, the direct comparison in the ACF-diagram should be valid.

Nodules in Lesotho and Montana kimberlites

All the chemical analyses of minerals from nodules in Lesotho kimberlites used in this subsection are by F.R. Boyd and the data are published in various chapters in Nixon (1973). The detailed chemical aspects of minerals have been discussed by Boyd (e.g., 1973), and our unpublished probe analyses of minerals from garnet lherzolites in Lesotho kimberlites have confirmed his observations.

We have compared characteristics of our experimental assemblages at known P and T with the individual nodules analyzed by Boyd. Among

Boyd's samples, PHN2273 and PHN1591 are very closely matched by the run products DD1 (40 kbar and 1100°C) and DD2 (40 kbar and 1200°C), respectively (Table 8). A, C, F components of the natural pyroxenes and garnet are very similar to those of the experimental counterparts. In addition, Fe-Mg partition coefficients are almost the same in the two sets of data. To our knowledge, no experimental phase relations have ever achieved this degree of resemblance with those in natural garnet lherzolites.

Boyd (1973) classified garnet lherzolite nodules into granular and sheared types on the basis of texture, and he has clearly established that the sheared type nodules show equilibration at higher temperature and pressure than those of the granular type. Both PHN2273 and PHN1591 are relatively low temperature rocks from within the group of sheared lherzolite nodules. It was previously shown that use of the $\text{Ca}/(\text{Ca} + \text{Mg})$ ratio of clinopyroxene and Al_2O_3 content of orthopyroxene to estimate T-P conditions of PHN2273 gave an estimate of about 1430°C and 62 kbar (Mori and Green, 1976).

A shortcoming of this method of T-P estimates is the lack of a firm basis for the direct comparison of the $\text{Ca}/(\text{Mg} + \text{Ca})$ ratio between natural complex clinopyroxene and the clinopyroxene limb of the pyroxene solvus in the system $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$. Therefore we considered that very large uncertainties might be associated with our earlier estimates. This pessimism is strikingly confirmed by the data obtained for the complex system. The present estimate of about 40 kbar and 1100°C for PHN2273 was obtained by directly comparing compositions of olivine, orthopyroxene, clinopyroxene and garnet, and consequently the estimate should be quite accurate.

The highest T-P nodule among Boyd's samples is PHN1597. The relationship between temperature and activity ratio of $\text{Mg}_2\text{Si}_2\text{O}_6$ (Fig. 3) gives an apparent temperature of about 1450°C for this rock at an assumed pressure between 30 and 40 kbar. Similarly the relationship between

Table 8. Comparison between natural garnet lherzolites and experimental run products

	Orthopyroxene			Clinopyroxene			Garnet			K ^{gar} /cpx	K ^{opx} /cpx	K ^{gar} /oliv
	<u>A</u> <u>C</u> <u>F</u>			<u>A</u> <u>C</u> <u>F</u>			<u>A</u> <u>C</u> <u>F</u>					
	A	C	F	A	C	F	A	C	F			
Lesotho, PHN2273	0.9	1.8	97.3	0.4	38.8	60.8	23.4	10.6	66.0	2.1	0.92	2.0
DD1, 40 kbar, 1100°C	1.1	1.9	97.0	0.2	39.6	60.2	24.7	9.2	66.1	1.9	0.83	1.9
Lesotho, PHN1591	1.0	2.7	96.3	0.8	35.4	63.8	24.0	11.2	64.8	2.0	0.92	1.9
DD2, 40 kbar, 1200°C	1.6	3.1	95.3	1.0	36.3	62.7	24.1	10.7	65.2	2.1	0.90	2.1
Montana, H69-15F	1.5	2.4	96.1	1.2	35.8	63.0	23.0	11.3	65.7	1.9	0.90	1.9
Lesotho, PHN1597	0.9	3.2	95.9	0.7	26.4	72.9	23.2	8.2	68.6	1.6	0.88	1.6
A7, 30 kbar, 1450°C	4.1	4.2	91.7	6.3	24.8	68.9	22.8	12.1	65.1	1.5	0.70	2.0
Lesotho, PHN1595	1.1	0.6	98.3	0.8	46.5	52.7	24.7	13.8	61.5	4.1	1.4	2.6
T9, 30 kbar, 950°C	2.3	1.2	96.5	1.2	44.3	54.5	25.5	13.3	61.2	2.9	1.1	2.4
Mt. Higasi-Akaisi, G103	0.7	0.2	99.1	0.3	48.5	51.2	24.4	10.7	64.9	6.2	1.9	3.1
Alpe Arami, A2	2.3	0.9	96.8	1.9	42.2	55.9	24.2	9.1	66.7	3.9	1.2	3.5
PF6, 30 kbar, 1000°C	1.8	1.2	97.0	1.1	42.5	56.4	24.9	11.2	63.9	3.0	1.2	2.2

See text for data sources.

$K^{\text{gar/cpx}}$ and temperature indicates a temperature of $\sim 1400^\circ\text{C}$ for an assumed pressure between 30 and 40 kbar. Thus, the run A7 (30 kbar and 1450°C) was chosen to compare with PHN1597 (Table 8). A-component of orthopyroxene and clinopyroxene and C-component of garnet are distinctively lower in PHN1597 than in A7, suggesting the pressure of this rock would be much higher than 30 kbar. If the pressure effect in Al_2O_3 solubility in the complex pyroxene is similar in magnitude to that in the $\text{Al}_2\text{O}_3\text{-MgSiO}_3$ system (MacGregor, 1974) then the estimated pressure for PHN1597 would be higher than for A7 by about 30 kbar. This high pressure, in turn, causes a shift of the temperature-activity ratio equation (Fig. 3) and of $K^{\text{gar/cpx}}$ vs. T relationship, resulting in temperature estimates much higher than 1450°C .

The lowest T-P nodule: PHN1595 is compared with the lowest T-P run: T9 (30 kbar and 950°C) in Table 8. The difference of C-component in both orthopyroxene and clinopyroxene is small, but indicates temperature of this nodule substantially lower than 950°C since the limbs of pyroxene solvus at the low temperature region are very steep (Mori and Green, 1975). The systematic difference in Fe-Mg partition coefficients also supports the temperature substantially lower than 950°C .

Garnet lherzolite nodules in a Montana kimberlite also define a P-T trend of equilibration (Hearn and Boyd, 1975). Again, a sheared type nodule: H69-15F is, as is shown in Table 8, closely matched by the run DD2 (40 kbar and 1200°C). However, the highest T-P nodule: H67-28K-3 and the lowest T-P nodule: H68-16B are not matched by any experimental run product.

In summary, among the garnet lherzolite nodules with wide P-T ranges, some have very similar phase relations with those produced in our experiments, but many of them show equilibration conditions outside the experimental P-T ranges of 30-40 kbar and $950\text{-}1500^\circ\text{C}$. The inferred range of T,P conditions extends to both higher pressure and temperature and

lower pressure and temperature than the experimental range.

Intrusive garnet lherzolites

Equilibrium temperatures of intrusive garnet lherzolites are generally so low that it is difficult to find close similarities of mineral chemistry between natural rocks and experimental products. The most comparable examples are the Alpe Arami garnet lherzolite (A3, O'Hara and Mercy, 1963) and FF6 (30 kbar and 1000°C). The slight difference in A- and C-components in pyroxenes and also in Fe-Mg partition coefficients (Table 8) suggest that the real temperature and pressure for the Alpe Arami rock were slightly lower than 1000°C and 30 kbar. This particular rock shows the highest pressure and temperature among the intrusive garnet lherzolites we have examined so far.

The lowest T-P rock is probably G103 from Mt. Higasi-Akaisi (Mori and Banno, 1973). This is an orthopyroxene, garnet bearing wehrlite occurring as lenses within a dunite-wehrlite mass. Table 8 also compares G103 with the lowest T-P run T9 (30 kbar and 950°C). The low temperature nature of G103 is clearly seen in its very low C-component in orthopyroxene, high C-component in clinopyroxene and high Fe-Mg partition coefficients.

Garnet lherzolites from Norway (O'Hara and Mercy, 1963; Carswell, 1968) and Bohemian Massif (Fiala, 1966) seem to fall between these two extremities found at Alpe Arami and Mt. Higasi-Akaisi.

CONCLUDING REMARKS

It is a common assumption that deep-seated rocks attain equilibrium in mineral assemblages at high temperature, high pressure conditions and that this equilibrium can in some cases be preserved and brought to the surface.

On the other hand, experimental petrologists lean to the assumption that equilibrium in polymineralic assemblages can be easily

achieved in the laboratory at high pressures and temperatures. Both these assumptions must be treated with caution but it is nevertheless encouraging that in our experiments on complex peridotite compositions we have been able to closely duplicate the compositions of four coexisting phases, olivine, orthopyroxene, clinopyroxene and garnet, of some natural lherzolites.

The practical results of our study are Figures 1-7 themselves, providing empirical calibrations applicable to garnet lherzolite mineralogy within a limited, T, P range. The application of these calibration relationships to natural garnet lherzolite inclusions in kimberlites shows that some sheared lherzolites crystallized at 1100-1200°C and ~40 kbar but others (sheared varieties) crystallized at much higher temperatures and higher pressures while granular lherzolites crystallized at lower temperatures and pressures than our experimental range. We particularly draw attention to the large differences between estimates of T, P conditions based on complex systems and on simplistic deductions from the MgO-CaO-SiO₂-Al₂O₃ system. Much of our data was obtained on experiments designed primarily to determine the solidus and major aspects of phase relationships for the pyrolite composition. The extent to which systematic relationships amongst minerals can be observed in these experiments encourages us to the view that further experiments in which there is more rigorous evaluation of Fe-loss, use of longer run times, reversal of equilibria, etc. will greatly reduce the scatter in Figures 1-7 and provide high quality calibration data for natural garnet lherzolites. These experiments should proceed in parallel with studies in which the data of the simple CaO-MgO-Al₂O₃-SiO₂ system are extended into increasingly more complex compositions.

REFERENCES

- AKELLA, J., 1976, Garnet pyroxene equilibria in the system $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ and in a natural mineral mixture: *Am. Mineralogist*, v. 61, p. 589-598.
- _____, and BOYD, F.R., 1972, Partitioning of Ti and Al between pyroxenes, garnets, and oxides: *Carnegie Inst. Washington Yearbook*, v. 71, p. 378-384.
- _____, and _____, 1973, Effect of pressure on the composition of coexisting pyroxenes and garnet in the system $\text{CaSiO}_3\text{-MgSiO}_3\text{-FeSiO}_3\text{-CaAlTi}_2\text{O}_6$: *Carnegie Inst. Washington Yearbook*, v. 72, p. 523-526.
- BANNO, S., 1974, Use of partial solution of multi-component equilibria. Case study on pyroxene-bearing assemblages: *Bull. Soc. fr. Mineral. Cristallogr.*, v. 97, p. 108-116.
- BOYD, F.R., 1970, Garnet peridotites and the system $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$: *Mineral. Soc. America, Special Paper* 3, p. 63-75.
- _____, 1973, A pyroxene geotherm: *Geochim. et Cosmochim. Acta*, v. 37, p. 2533-2546.
- CARSWELL, D.A., 1968, Picritic magma - residual dunite relationships in garnet peridotite at Kalskaret near Tafjord, south Norway: *Contr. Mineralogy and Petrology*, v. 19, p. 97-124.
- DAVIS, B.T.C., and BOYD, F.R., 1966, The join $\text{Mg}_2\text{Si}_2\text{O}_6\text{-CaMgSi}_2\text{O}_6$ at 30 kilobars pressure and its application to pyroxenes from kimberlites: *Jour. Geophys. Research*, v. 71, p. 3567-3576.
- FIALA, J., 1966, The distribution of elements in mineral phases of some garnet peridotites from the Bohemian massif: *Krystalinikum*, v. 4, p. 31-53.
- GREEN, D.H., 1973, Experimental melting studies on a model upper mantle composition at high pressure under water-saturated and water-undersaturated conditions: *Earth and Planetary Sci. Letters*, v. 19, p. 37 - 53.

- _____, and RINGWOOD, A.E., 1970, Mineralogy of peridotitic compositions under upper mantle conditions: *Physics Earth and Planetary Interiors*, v. 3, p. 359-371.
- _____, and SOBOLEV, N.V., 1975, Coexisting garnets and ilmenites synthesized at high pressures from pyrolite and olivine basanite and their significance for kimberlitic assemblages: *Contr. Mineralogy and Petrology*, v. 50, p. 217-229.
- HEARN, B. C. JR., and BOYD, F.R., 1975, Garnet peridotite xenoliths in a Montana, U.S.A., kimberlite: *Physics and Chemistry of the Earth*, v. 9, p. 247-255.
- HENSEN, B.J., 1973, Pyroxenes and garnets as geothermometers and barometers, *Carnegie Inst. Washington Yearbook*, v. 72, p. 527-534.
- HOWELLS, S., 1975, Discrepancies in the apparent solubility of Al_2O_3 in enstatite at high pressure: Extended abstracts, International Conference on Geothermometry and Geobarometry, The Pennsylvania State University.
- _____, and O'HARA, M.J., 1975, Palaeogeotherms and the diopside-enstatite solvus: *Nature*, v. 254, p. 406-408.
- KUSHIRO, I.; SYONO, Y.; and AKIMOTO, S., 1967, Effect of pressure on garnet-pyroxene equilibrium in the system MgSiO_3 - CaSiO_3 - Al_2O_3 : *Earth and Planetary Sci. Letters*, v. 2, p. 460-464.
- _____, SHIMIZU, N.; NAKAMURA, Y.; and AKIMOTO, S., 1972, Compositions of coexisting liquid and solid phases formed upon melting of natural garnet and spinel lherzolites at high pressures: a preliminary report: *Earth and Planetary Sci. Letters*, v. 14, p. 19-25.
- LINDSLEY, D.H., and DIXON, S.A., 1975, Coexisting diopside and enstatite at 20 kbar and 900°-1200°C: *Geol. Soc. America, Abs. with Programs*, v. 7, p. 1171.
- MACGREGOR, I.D., 1974, The system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$: solubility of Al_2O_3 in

enstatite for spinel and garnet peridotite compositions:

Am. Mineralogist, v. 59, p. 110-119.

MATSUI, Y., and NISHIZAWA, O., 1974, Iron (II)-magnesium exchange equilibrium between olivine and calcium-free pyroxene over a temperature range 800°C to 1300°C: Bull. Soc. fr. Mineral. Cristallogr., v. 97, p. 122-130.

MCCALLISTER, R.H.; FINGER, L.W.; and OHASHI, Y., 1976, Intracrystalline Fe^{2+} -Mg equilibria in three natural Ca-rich clinopyroxenes: Am. Mineralogist, v. 61, p. 671-676.

MORI, T., and BANNO, S., 1973, Petrology of peridotite and garnet clinopyroxenite of the Mt. Higasi-Akai mass, central Shikoku, Japan - subsolidus relation of anhydrous phases: Contr. Mineralogy and Petrology, v. 41, p. 301-323.

_____, and GREEN, D.H., 1975, Pyroxenes in the system $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$ at high pressure: Earth and Planetary Sci. Letters, v. 26, p. 277-286.

_____, and _____, 1976, Subsolidus equilibria between pyroxenes in the CaO-MgO-SiO_2 system at high pressures and temperatures: Am. Mineralogist, v. 61, p. 616-625.

NEHRU, C.E., and WYLLIE, P.J., 1974, Electron microprobe measurement of pyroxenes coexisting with H_2O -undersaturated liquid in the join $\text{CaMgSi}_2\text{O}_6$ - $\text{Mg}_2\text{Si}_2\text{O}_6$ - H_2O at 30 kilobars, with applications to geothermometry: Contr. Mineralogy and Petrology, v. 48, p. 221-228.

NIXON, P.H., ed., 1973, Lesotho kimberlites: Maseru, Lesotho, Lesotho National Development Corp. 350 p.

O'HARA, M.J., 1967, Mineral parageneses in ultrabasic rocks in Wyllie, P.J., ed., Ultramafic and related rocks: New York, Wiley, p. 393-403.

_____, and MERCY, E.L.P., 1963, Petrology and petrogenesis of some garnetiferous peridotites: Trans. Royal Soc. Edinburgh, v. 65, p. 251-314.

- RAHEIM, A., and GREEN, D.H., 1974, Experimental determination of the temperature and pressure dependence of the Fe-Mg partition coefficient for coexisting garnet and clinopyroxene: Contr. Mineralogy and Petrology, v. 48, p. 179-203.
- SMYTH, J.R., 1973, An orthopyroxene structure up to 850°C: Am. Mineralogist, v. 58, p. 636-648.
- VIRGO, D., and HAFNER, S.S., 1969, Fe²⁺, Mg order-disorder in heated orthopyroxenes: Mineral. Soc. America, Special Paper 2, p. 67-81.
- WOOD, B.J., and BANNO, S., 1973, Garnet-orthopyroxene and orthopyroxene-clinopyroxene relationships in simple and complex systems: Contr. Mineralogy and Petrology, v. 42, p. 109-124.

CHAPTER 7

CONCLUSIONS

It has been commonly accepted that the orthopyroxene-clinopyroxene solvus in the system CaO-MgO-SiO_2 is almost independent of pressure, and consequently that the pyroxene solvus is a good geothermometer. However, new experiments on pyroxene equilibria in the same system revealed the non-negligible effect of pressure on the solvus. Thus, estimates of temperature based on pyroxene compositions must be based on a pressure estimate as well. Compositions of pyroxenes in this system can slightly deviate from the ideal stoichiometry, i.e., orthopyroxene and clinopyroxene have limited solid solutions towards olivine and quartz in addition to the mutual solid solutions between the En-Di end members. Therefore the mutual solubility can be influenced by coexisting phases other than pyroxenes. The experimental study, however, showed that the influence is practically negligible.

The pressure effect on the orthopyroxene - clinopyroxene solvus was also found in the system CaO-MgO-FeO-SiO_2 . However, pressure plays a more important role in other aspects of pyroxene equilibria in this system. Low pressure is a favourable condition for protopyroxene and Ca-rich clinopyroxene / Ca-poor clinopyroxene (pigeonite) solvus. Temperature has also very large effects. The three phase field of orthopyroxene/Ca-rich clinopyroxene/Ca-poor clinopyroxene at 15 kbar moves towards the En-Di join with increasing temperature. The three phase field was not found at 30 kbar. Ca-free clinopyroxene was found to be stable at relatively high temperatures at 15-30 kbar for Fe-rich compositions. The synthesis of the topology of pyroxene equilibria is consistent with any one of the recent experimental studies in the literature, and is also almost perfectly consistent with assemblages and chemistry of natural pyroxenes, in relation to geologically-based inferences on their conditions of crystallization.

Coexisting olivine, orthopyroxene, clinopyroxene and spinel at 1200°C and 16 kbar in the system $\text{CaO - MgO - Al}_2\text{O}_3 - \text{SiO}_2$ yield basic knowledge in understanding of natural spinel lherzolites. Olivine and spinel

are of stoichiometric pure end member compositions. The pyroxenes are as aluminous as those in the natural spinel lherzolites. The $\text{Ca}/(\text{Ca} + \text{Mg})$ ratio of aluminous clinopyroxene coexisting with orthopyroxene, olivine and spinel is much higher than the ratio of clinopyroxene coexisting with orthopyroxene in Al_2O_3 -free system.

The experiments in multicomponent systems yield chemical compositions of coexisting olivine, orthopyroxene, clinopyroxene and garnet or spinel. These data are directly comparable with those in natural lherzolites. Various kinds of geothermometer were calibrated from the data. Geothermometers based on equilibrium constants between orthopyroxene and clinopyroxene; orthopyroxene, olivine and spinel; and olivine, clinopyroxene and spinel are fairly accurate in temperature estimates for spinel lherzolites. Six Fe-Mg partition coefficients among olivine, orthopyroxene, clinopyroxene and garnet have been calibrated against temperature at 30-40 kbar, Garnet-clinopyroxene pair was found to be the most sensitive to temperature.

The experimental results for phase equilibria lead us to better understanding of natural ultramafic rocks. For example, the new estimates of equilibrium temperature for spinel lherzolites are higher than have been generally thought. The temperatures are as high as those of basaltic liquids and this must be considered alongside geochemical arguments on xenolithic vs. cognate origin in relation to basaltic host magma. Some garnet lherzolites in Lesotho and Montana kimberlites were successfully duplicated in the laboratory. As a consequence, T-P conditions for these rocks could be most accurately estimated. In addition, the success indicates that the deep-seated natural rocks retain their primary equilibria among the minerals, and that similar equilibria can be attained also in the laboratory under a wider P,T range than that investigated up to this time.

This thesis is my presentation of experiments starting from the pyroxenes in the simple system and reaching to natural ultramafic rocks at the end.

APPENDIX 1

A List of Whole Pyroxene Analyses Used in Chapter 2

<u>Correlation table between run numbers</u>	
<u>Chapter 2</u>	<u>This list</u>
1	E5
2	T2
3	T3
4	E4
5	G
6	E3
7	E1
8	F1
9	F2
10	E6
11	H1
12	H2
13	H4
14	J
15	H3
16	I

Due to the rounding-off conventions adopted, the 'total' column may differ by 0.01 from the sum of SiO_2 , MgO and CaO.

			SI02	MGO	CAO	TOTAL	SI	MG	CA	TOTAL CATION	WO %
E5	OPX	21	60.82	38.81	1.21	100.84	2.018	1.920	.043	3.982	2.2
E5	OPX	22	60.82	39.13	1.03	100.97	2.015	1.933	.037	3.985	1.9
E5	OPX	23	60.47	38.60	1.53	100.60	2.014	1.917	.055	3.986	2.8
E5	OPX	232C	60.41	39.18	.90	100.49	2.012	1.945	.032	3.988	1.6
E5	OPX	24	59.86	38.78	1.15	99.79	2.009	1.940	.041	3.991	2.1
E5	OPX	25	60.31	38.89	1.09	100.30	2.013	1.935	.039	3.987	2.0
E5	OPX	27	60.22	39.05	1.11	100.38	2.009	1.942	.040	3.991	2.0
E5	OPX	28	59.63	38.74	1.26	99.63	2.006	1.943	.045	3.994	2.3
E5	OPX	30	59.58	38.15	1.40	99.13	2.014	1.922	.051	3.986	2.6
E5	OPX	31	60.21	38.62	1.17	100.01	2.015	1.927	.042	3.985	2.1
E5	OPX	32	60.19	38.72	1.12	100.03	2.014	1.932	.040	3.986	2.0
E5	OPX	33	60.10	38.55	1.40	100.06	2.013	1.925	.050	3.987	2.5
E5	OPX	34	60.31	38.80	.85	99.96	2.017	1.935	.030	3.983	1.6
E5	OPX	35	60.16	38.69	.71	99.56	2.019	1.936	.026	3.981	1.3
E5	CPX	10	56.78	20.92	23.40	101.10	2.006	1.102	.886	3.994	44.6
E5	CPX	11	56.02	20.96	23.14	100.12	2.000	1.115	.885	4.000	44.2
E5	CPX	12	55.97	20.96	23.12	100.05	1.999	1.116	.885	4.001	44.2
E5	CPX	13	55.88	20.97	23.01	99.86	2.000	1.119	.882	4.000	44.1
E5	CPX	14	55.74	20.71	23.20	99.65	2.000	1.108	.892	4.000	44.6
E5	CPX	15	55.72	20.79	23.35	99.86	1.997	1.111	.896	4.003	44.7
E5	CPX	16	56.37	20.87	23.40	100.65	2.002	1.105	.891	3.998	44.6
E5	CPX	17	56.19	21.12	23.08	100.38	2.000	1.121	.880	4.000	44.0
E5	CPX	18	55.87	20.78	23.08	99.73	2.002	1.110	.886	3.998	44.4
E5	CPX	19RI	56.09	20.93	23.12	100.14	2.001	1.113	.884	3.999	44.3
E4	OPX	A13	59.99	38.47	1.36	99.82	2.013	1.925	.049	3.987	2.5

			SI02	MGO	CAO	TOTAL	SI	MG	CA	TOTAL CATION	WO 8
E4	OPX	A14	59.63	38.56	1.31	99.50	2.038	1.936	.047	3.992	2.4
E4	OPX	A15	60.16	38.87	1.32	100.35	2.039	1.935	.047	3.991	2.4
E4	OPX	A16R	59.90	38.49	1.48	99.87	2.010	1.926	.053	3.990	2.7
E4	OPX	A17C	60.10	38.28	1.35	99.74	2.018	1.916	.049	3.982	2.5
E4	OPX	A181	60.30	38.36	1.78	100.43	2.013	1.909	.064	3.987	3.2
E4	OPX	A182	60.34	38.86	1.31	100.51	2.011	1.931	.047	3.989	2.4
E4	OPX	A191	60.05	38.37	1.60	100.02	2.013	1.917	.057	3.987	2.9
E4	OPX	A192	60.22	38.51	1.34	100.07	2.015	1.921	.048	3.985	2.4
E4	OPX	A21	60.08	38.71	1.36	100.14	2.010	1.931	.049	3.990	2.5
E4	CPX	A1	55.94	21.17	23.04	100.15	1.996	1.126	.881	4.004	43.9
E4	CPX	A2	56.30	21.18	22.86	100.34	2.003	1.123	.871	3.997	43.7
E4	CPX	A3	56.14	20.95	22.95	100.04	2.004	1.115	.878	3.996	44.1
E4	CPX	A5	55.55	20.99	22.60	99.15	2.001	1.127	.872	3.999	43.6
E4	CPX	A6	55.52	21.21	22.38	99.11	1.999	1.139	.863	4.001	43.1
E4	CPX	A7	56.25	20.94	23.07	100.26	2.004	1.112	.881	3.996	44.2
E4	CPX	A8	56.12	21.52	22.48	100.12	1.999	1.143	.858	4.001	42.9
E4	CPX	A9	55.82	21.18	22.69	99.69	1.999	1.131	.871	4.001	43.5
E4	CPX	A11	55.58	21.22	22.52	99.33	1.998	1.137	.867	4.002	43.3
E4	CPX	A12	55.35	20.78	22.52	98.64	2.003	1.121	.873	3.997	43.8
E4	CPX	A222	56.10	21.22	22.45	99.77	2.005	1.131	.860	3.995	43.2
E4	CPX	A23	55.18	20.93	22.52	98.63	1.998	1.130	.874	4.002	43.6
E4	CPX	A24	55.73	21.23	22.34	99.30	2.002	1.137	.860	3.998	43.1
G	OPX	B4	60.20	38.37	1.14	99.71	2.020	1.919	.041	3.980	2.1
G	OPX	D3	60.52	38.57	1.38	100.47	2.017	1.916	.049	3.983	2.5
G	OPX	F2	60.66	38.83	1.59	101.08	2.012	1.920	.057	3.988	2.9

			SI02	MGO	CAO	TOTAL	SI	MG	CA	TOTAL CATION	WO %
G	OPX	G2	60.57	38.45	1.45	100.47	2.019	1.911	.052	3.981	2.6
G	OPX	J2	59.90	37.98	1.67	99.55	2.017	1.906	.060	3.983	3.1
G	OPX	K2	60.33	39.07	.60	100.00	2.016	1.946	.021	3.984	1.1
G	OPX	L2	60.71	38.64	.96	100.31	2.023	1.920	.034	3.977	1.8
G	OPX	M2	60.77	38.75	.97	100.49	2.022	1.922	.035	3.978	1.8
G	OPX	S2	60.52	38.19	.89	99.60	2.029	1.909	.032	3.971	1.6
G	OPX	T2	60.64	38.86	1.18	100.68	2.016	1.926	.042	3.984	2.1
G	OPX	BB2	60.59	38.50	1.17	100.27	2.022	1.915	.042	3.978	2.1
G	OPX	EE2	60.53	38.62	1.15	100.31	2.019	1.921	.041	3.981	2.1
G	OPX	FF7	60.10	38.50	1.16	99.76	2.016	1.926	.042	3.984	2.1
G	OPX	HH2	60.26	38.65	.95	99.86	2.018	1.930	.034	3.982	1.7
G	OPX	II2	59.94	38.49	.98	99.41	2.017	1.931	.035	3.983	1.8
G	CPX	BB	56.47	20.61	22.25	99.33	2.023	1.101	.854	3.977	43.7
G	CPX	DI	56.00	21.30	21.92	99.22	2.009	1.139	.843	3.991	42.5
G	CPX	FI	55.87	20.53	23.60	100.00	2.000	1.095	.905	4.000	45.2
G	CPX	GI	55.78	20.70	22.90	99.38	2.005	1.109	.882	3.995	44.3
G	CPX	JI	55.82	20.75	22.67	99.24	2.007	1.112	.873	3.993	44.0
G	CPX	KI	56.02	21.44	21.74	99.20	2.009	1.146	.835	3.991	42.2
G	CPX	LI	55.62	21.36	21.62	98.60	2.007	1.149	.836	3.993	42.1
G	CPX	M1	55.95	20.45	23.16	99.56	2.008	1.094	.890	3.992	44.9
G	CPX	S1	56.05	20.83	21.83	98.71	2.019	1.119	.843	3.981	43.0
G	CPX	T1	56.21	21.17	22.20	99.58	2.010	1.129	.851	3.990	43.0
G	CPX	BB1	56.37	21.10	21.94	99.41	2.017	1.125	.841	3.983	42.8
G	CPX	EE1	55.89	21.33	21.61	98.83	2.011	1.144	.833	3.989	42.1
G	CPX	FF5	55.92	20.73	22.24	98.90	2.014	1.113	.858	3.986	43.5

			SI02	MGO	CAO	TOTAL	SI	MG	CA	TOTAL CATION	WO %
G	CPX	I11	55.76	20.84	21.58	98.18	2.019	1.125	.837	3.981	42.7
G	CPX	C3-2	55.43	18.41	25.59	99.43	2.007	.994	.993	3.993	50.0
E3	OPX	A13	60.23	38.37	2.03	100.63	2.009	1.908	.073	3.991	3.7
E3	OPX	A15	59.76	37.40	2.68	99.84	2.013	1.878	.097	3.987	4.9
E3	OPX	A16	59.49	36.89	2.71	99.08	2.018	1.866	.098	3.982	5.0
E3	OPX	A17	59.87	37.35	2.51	99.73	2.017	1.876	.091	3.983	4.6
E3	OPX	A18	59.89	38.03	2.03	99.94	2.011	1.904	.073	3.989	3.7
E3	OPX	A19	60.15	37.74	2.30	100.19	2.016	1.886	.083	3.984	4.2
E3	OPX	A20	59.66	37.81	2.14	99.61	2.011	1.900	.077	3.989	3.9
E3	OPX	A22	59.72	37.47	2.40	99.59	2.014	1.884	.087	3.986	4.4
E3	OPX	A23	60.13	37.30	2.73	100.15	2.018	1.866	.098	3.982	5.0
E3	OPX	A25	60.25	37.81	2.22	100.28	2.017	1.887	.080	3.983	4.0
E3	CPX	A1	56.46	21.72	21.21	99.38	2.016	1.156	.811	3.984	41.2
E3	CPX	A2	56.59	22.56	20.85	100.00	2.007	1.193	.792	3.993	39.9
E3	CPX	A3-2	56.87	22.07	21.04	99.99	2.017	1.167	.799	3.983	40.7
E3	CPX	A4	56.33	22.75	20.51	99.60	2.005	1.207	.782	3.995	39.3
E3	CPX	A5	56.43	22.52	20.87	99.82	2.006	1.193	.795	3.994	40.0
E3	CPX	A7	56.47	22.33	21.22	100.02	2.005	1.182	.807	3.995	40.6
E3	CPX	A8	56.52	22.30	20.62	99.44	2.014	1.185	.787	3.986	39.9
E3	CPX	A10	56.03	22.42	20.70	99.15	2.005	1.196	.794	3.995	39.9
E3	CPX	A11	56.20	22.74	20.55	99.48	2.003	1.208	.785	3.997	39.4
E3	CPX	A12	56.09	22.67	20.48	99.24	2.004	1.208	.784	3.996	39.4
F1	OPX	B29	59.53	37.00	3.14	99.66	2.011	1.864	.114	3.989	5.7
F1	OPX	B30	59.11	36.44	3.39	98.94	2.013	1.850	.124	3.987	6.3
F1	OPX	B31	59.70	37.06	3.04	99.80	2.013	1.863	.110	3.987	5.6

		SI02	MGO	CAO	TOTAL	SI	MG	CA	TOTAL CATION	WO %	
F1	OPX	B32	60.20	37.58	2.75	100.54	2.014	1.874	.099	3.986	5.0
F1	OPX	B33	59.41	36.85	2.58	98.83	2.019	1.867	.094	3.981	4.8
F1	OPX	B34	59.74	36.73	3.20	99.67	2.017	1.849	.116	3.983	5.9
F1	OPX	B35	59.62	37.39	2.60	99.61	2.012	1.881	.094	3.988	4.8
F1	OPX	B36	59.79	37.47	2.63	99.88	2.012	1.880	.095	3.988	4.8
F1	OPX	B37	59.14	36.42	3.12	98.68	2.017	1.852	.114	3.983	5.8
F1	OPX	B38	60.69	37.89	2.67	101.24	2.015	1.875	.095	3.985	4.8
F1	CPX	B15	56.48	22.14	20.50	99.12	2.018	1.179	.785	3.982	40.0
F1	CPX	B16	56.57	23.04	20.07	99.67	2.009	1.220	.763	3.991	38.5
F1	CPX	B17	56.21	22.65	19.82	98.68	2.014	1.210	.761	3.986	38.6
F1	CPX	B18	55.95	23.02	19.87	98.84	2.004	1.229	.763	3.996	38.3
F1	CPX	B20	58.02	22.94	20.83	101.78	2.017	1.189	.776	3.983	39.5
F1	CPX	B21	56.64	22.97	19.98	99.59	2.012	1.216	.760	3.988	38.5
F1	CPX	B22	55.84	22.79	20.39	98.71	2.004	1.219	.773	3.996	38.8
F1	CPX	B24	56.66	23.34	19.44	99.44	2.012	1.236	.740	3.988	37.4
F1	CPX	B27	56.19	22.92	19.44	98.55	2.014	1.225	.747	3.986	37.9
F1	CPX	B28	56.73	22.15	20.41	99.29	2.022	1.177	.779	3.978	39.8
F2	CPX	A1-2	57.83	28.80	12.93	99.56	2.012	1.494	.482	3.988	24.4
F2	CPX	A2	57.61	27.83	14.03	99.48	2.013	1.449	.525	3.987	26.6
F2	CPX	A4	57.64	28.61	13.37	99.62	2.008	1.486	.499	3.992	25.1
F2	CPX	A5	57.85	29.32	12.07	99.24	2.014	1.522	.450	3.986	22.8
F2	CPX	A6	57.21	27.37	14.41	98.99	2.011	1.435	.543	3.989	27.5
F2	CPX	A7	57.82	28.65	13.14	99.62	2.012	1.486	.490	3.988	24.8
F2	CPX	A8	57.55	28.21	13.71	99.48	2.009	1.468	.513	3.991	25.9
F2	CPX	A9	57.86	28.94	12.80	99.60	2.012	1.500	.477	3.988	24.1

			SI02	MGO	CAO	TOTAL	SI	MG	CA	TOTAL CATION	WO %
F2	CPX	A10	57.77	28.27	13.91	99.94	2.008	1.465	.518	3.992	26.1
F2	CPX	A11	57.79	29.26	12.26	99.31	2.012	1.519	.457	3.988	23.1
F2	CPX	A12	57.87	28.78	12.93	99.58	2.013	1.492	.482	3.987	24.4
F2	CPX	A13	57.52	28.06	13.86	99.44	2.010	1.462	.519	3.990	26.2
E6	OPX	A2	59.29	37.41	2.65	99.36	2.008	1.889	.096	3.992	4.8
E6	OPX	A4	59.36	37.16	2.69	99.22	2.012	1.878	.098	3.988	4.9
E6	OPX	A6	59.34	37.86	2.02	99.22	2.008	1.910	.073	3.992	3.7
E6	OPX	A8	59.29	37.59	2.72	99.61	2.004	1.894	.098	3.996	4.9
E6	OPX	A11	59.60	38.04	1.96	99.60	2.009	1.911	.071	3.991	3.6
E6	OPX	A14	59.38	37.84	2.18	99.40	2.007	1.907	.079	3.993	4.0
E6	OPX	A20	59.56	38.06	2.12	99.74	2.006	1.911	.077	3.994	3.8
E6	OPX	A22R	59.58	37.81	2.31	99.71	2.008	1.900	.083	3.992	4.2
E6	OPX	A23	59.66	37.97	1.76	99.38	2.013	1.910	.064	3.987	3.2
E6	OPX	A29R	59.27	37.67	2.51	99.44	2.005	1.900	.091	3.995	4.6
E6	OPX	A30C	59.38	37.34	2.78	99.53	2.008	1.883	.101	3.992	5.1
E6	CPX	A1	56.93	26.31	15.96	99.20	2.007	1.383	.603	3.993	30.4
E6	CPX	A3	56.28	25.49	16.68	98.45	2.005	1.354	.637	3.995	32.0
E6	CPX	A5	57.57	26.92	15.14	99.62	2.014	1.404	.568	3.986	28.8
E6	CPX	A7	56.36	26.52	15.85	98.73	1.998	1.402	.602	4.002	30.0
E6	CPX	A10	56.51	26.39	15.90	98.79	2.002	1.393	.603	3.998	30.2
E6	CPX	A12	57.16	27.33	14.56	99.05	2.010	1.432	.548	3.990	27.7
E6	CPX	A13	56.73	26.15	16.35	99.22	2.003	1.376	.618	3.997	31.0
E6	CPX	A15	56.64	25.77	16.45	98.87	2.007	1.361	.625	3.993	31.4
E6	CPX	A19	56.77	26.04	16.50	99.30	2.003	1.370	.624	3.997	31.3
E6	CPX	A21	56.60	25.91	16.52	99.03	2.003	1.367	.626	3.997	31.4

			SI02	MGO	CAO	TOTAL	SI	MG	CA	TOTAL CATION	WO %
E6	CPX	A24	56.32	25.00	17.78	99.10	2.000	1.324	.676	4.000	33.8
E6	CPX	A25	56.88	25.51	17.59	99.99	2.000	1.337	.663	4.000	33.1
E6	CPX	A26	56.67	26.20	16.60	99.47	1.998	1.377	.627	4.002	31.3
E6	CPX	A27	57.01	27.30	14.57	98.88	2.008	1.434	.550	3.992	27.7
E6	CPX	A28	56.77	26.66	15.62	99.05	2.003	1.403	.591	3.997	29.6
E6	CPX	A31	57.22	26.70	15.71	99.62	2.007	1.396	.590	3.993	29.7
H1	OPX	A11	60.24	37.20	2.90	100.33	2.019	1.858	.104	3.981	5.3
H1	OPX	A13	60.24	37.20	2.91	100.35	2.019	1.858	.104	3.981	5.3
H1	OPX	A16	60.37	37.23	3.00	100.60	2.018	1.856	.107	3.982	5.5
H1	OPX	A17	60.36	37.27	3.10	100.73	2.016	1.856	.111	3.984	5.6
H1	OPX	A18	60.36	37.32	3.00	100.68	2.017	1.859	.107	3.983	5.5
H1	OPX	A19	61.12	37.83	3.11	102.06	2.015	1.860	.110	3.985	5.6
H1	OPX	A22	60.50	37.59	2.93	101.02	2.015	1.866	.105	3.985	5.3
H1	OPX	A27	60.27	37.31	2.86	100.44	2.018	1.862	.103	3.982	5.2
H1	OPX	A28	60.68	37.27	3.07	101.02	2.020	1.850	.110	3.980	5.6
H1	OPX	A30	60.54	37.22	3.20	100.96	2.018	1.850	.114	3.982	5.8
H1	CPX	A1	58.81	27.50	15.12	101.44	2.018	1.407	.556	3.982	28.3
H1	CPX	A2	58.10	28.61	13.11	99.82	2.016	1.480	.487	3.984	24.8
H1	CPX	A3	58.37	27.82	14.55	100.73	2.015	1.432	.538	3.985	27.3
H1	CPX	A4	58.25	28.07	13.09	99.41	2.028	1.457	.488	3.972	25.1
H1	CPX	A5	58.09	27.16	15.01	100.26	2.018	1.406	.559	3.982	28.4
H1	CPX	A6	57.94	27.72	14.17	99.83	2.017	1.438	.528	3.983	26.9
H1	CPX	A7	58.23	27.83	14.20	100.26	2.018	1.438	.527	3.982	26.8
H1	CPX	A8	57.85	27.66	14.60	100.11	2.011	1.434	.544	3.989	27.5
H1	CPX	A9	57.71	27.48	14.59	99.78	2.013	1.429	.545	3.987	27.6

			SI02	MGO	CAO	TOTAL	SI	MG	CA	TOTAL CATION	WO %
H1	CPX	A10	57.60	26.94	15.15	99.69	2.014	1.404	.568	3.986	28.8
H2	OPX	A4	58.93	36.81	2.62	98.36	2.014	1.876	.096	3.986	4.9
H2	OPX	A6 R	60.31	37.13	2.61	100.05	2.024	1.858	.094	3.976	4.8
H2	OPX	A8 R	60.65	36.93	2.51	100.09	2.032	1.845	.090	3.968	4.7
H2	OPX	A9 C	60.44	37.53	2.55	100.52	2.020	1.870	.091	3.960	4.7
H2	OPX	A11R	59.96	37.47	2.48	99.91	2.016	1.878	.089	3.984	4.5
H2	OPX	A14R	60.86	37.64	2.73	101.23	2.020	1.863	.097	3.980	5.0
H2	CPX	A1	57.59	27.01	15.28	99.88	2.011	1.406	.572	3.989	28.9
H2	CPX	A2	57.66	26.14	16.32	100.12	2.014	1.361	.611	3.986	31.0
H2	CPX	A3	57.63	26.15	16.20	99.98	2.015	1.363	.607	3.985	30.8
H2	CPX	A7	58.10	26.95	15.71	100.76	2.013	1.392	.583	3.987	29.5
H2	CPX	A10	57.34	24.97	17.67	99.98	2.014	1.307	.665	3.986	33.7
H2	CPX	A13	57.67	26.35	16.23	100.25	2.012	1.370	.607	3.988	30.7
H2	CPX	A15	58.15	26.28	16.45	100.88	2.016	1.358	.611	3.984	31.0
H2	CPX	A17	56.90	24.81	17.83	99.54	2.010	1.306	.675	3.990	34.1
H4	OPX	A8	60.60	39.18	.73	100.51	2.016	1.943	.026	3.984	1.3
H4	OPX	A29	60.58	39.07	.72	100.37	2.017	1.940	.026	3.983	1.3
H4	OPX	A10	60.91	39.22	.50	100.63	2.021	1.940	.018	3.979	.9
H4	OPX	A11	60.78	39.35	.56	100.68	2.017	1.947	.020	3.983	1.0
H4	OPX	A12	60.55	39.51	.46	100.52	2.013	1.958	.016	3.987	.8
H4	OPX	B19	60.36	39.34	.53	100.23	2.013	1.956	.019	3.987	1.0
H4	OPX	B20	60.90	39.56	.50	100.96	2.015	1.952	.018	3.985	.9
H4	OPX	B21	61.05	39.59	.57	101.22	2.016	1.949	.020	3.984	1.0
H4	OPX	B22	60.88	39.63	.75	101.26	2.011	1.952	.027	3.989	1.3
H4	OPX	B23	60.65	39.27	.64	100.56	2.016	1.946	.023	3.984	1.2

			SI02	MGO	CAO	TOTAL	SI	MG	CA	TOTAL CATION	WO %
H4	OPX	B25	60.83	39.28	.74	103.85	2.016	1.941	.026	3.984	1.3
H4	OPX	B26	60.86	39.45	.57	100.88	2.016	1.948	.020	3.984	1.0
H4	CPX	A1	54.85	19.63	23.49	97.96	2.005	1.070	.929	3.995	46.2
H4	CPX	A5	56.37	19.63	23.33	99.33	2.025	1.051	.898	3.975	46.1
H4	CPX	B10	55.44	19.93	23.28	98.65	2.039	1.077	.904	3.991	45.6
H4	CPX	B11	55.51	19.74	23.76	99.01	2.008	1.064	.921	3.992	46.4
H4	CPX	B17	54.87	19.78	23.27	97.92	2.005	1.078	.911	3.995	45.8
H4	CPX	B18	56.18	20.02	23.21	99.42	2.018	1.072	.893	3.982	45.5
H4	CPX	K5	55.83	19.89	23.82	99.54	2.008	1.066	.918	3.992	46.3
J	OPX	G 6	61.36	39.00	.44	100.81	2.030	1.924	.016	3.970	.8
J	OPX	G12	61.27	39.60	.29	101.15	2.021	1.947	.010	3.979	.5
J	OPX	G11	60.46	39.11	.21	99.78	2.022	1.949	.008	3.978	.4
J	OPX	H3	61.42	39.92	.07	101.41	2.020	1.957	.002	3.980	.1
J	OPX	H11	61.61	39.33	.21	101.15	2.030	1.932	.007	3.970	.4
J	CPX	F1-2	56.54	19.09	24.69	100.32	2.019	1.016	.945	3.981	48.2
J	CPX	F3	56.01	19.20	24.44	99.65	2.014	1.029	.942	3.986	47.8
J	CPX	F4	54.27	19.56	23.89	97.72	1.994	1.071	.940	4.006	46.7
J	CPX	F4-1	56.17	19.41	24.21	99.79	2.015	1.038	.931	3.985	47.3
J	CPX	G3-1	56.18	18.86	25.14	100.18	2.013	1.008	.965	3.987	48.9
J	CPX	G3-2	56.14	18.40	25.54	100.07	2.016	.985	.983	3.984	49.9
J	CPX	G8	56.54	19.22	24.63	100.39	2.018	1.023	.942	3.982	47.9
J	CPX	G9	55.66	19.11	24.42	99.20	2.012	1.030	.946	3.988	47.9
J	CPX	H1	56.08	19.13	24.47	99.69	2.016	1.025	.943	3.984	47.9
J	CPX	H4	56.05	18.49	25.61	100.14	2.013	.990	.985	3.987	49.9
J	CPX	F5	55.99	18.41	25.50	99.90	2.015	.988	.983	3.985	49.9

		SI02	MGO	CAO	TOTAL	SI	MG	CA	TOTAL CATION	WO %
J	CPX H5-2	55.81	18.46	25.37	99.64	2.013	.993	.981	3.987	49.7
J	CPX F10	55.02	18.57	24.49	98.09	2.013	1.013	.960	3.987	48.7
J	CPX F12	56.26	18.77	24.13	99.16	2.029	1.009	.932	3.971	48.0
J	CPX F6	56.26	19.18	24.55	99.99	2.016	1.025	.943	3.984	47.9
J	CPX F7	55.40	19.02	24.74	99.16	2.006	1.027	.960	3.994	48.3
J	CPX G12	55.93	18.94	24.73	99.61	2.014	1.017	.954	3.986	48.4
J	CPX I1	56.26	19.41	24.17	99.84	2.017	1.037	.928	3.983	47.2
J	CPX I2	56.64	19.29	24.29	100.22	2.022	1.027	.929	3.978	47.5
J	CPX I3	56.31	18.98	23.92	99.21	2.029	1.019	.923	3.971	47.5
J	CPX I4	56.43	19.24	24.37	100.04	2.020	1.027	.934	3.980	47.7
J	CPX I5	56.11	19.11	24.65	99.87	2.014	1.023	.948	3.986	48.1
J	CPX I6	56.43	19.11	24.43	99.97	2.021	1.020	.937	3.979	47.9
J	CPX I8	56.43	19.12	23.98	99.53	2.027	1.024	.923	3.973	47.4
J	CPX I9	56.16	19.38	24.36	99.99	2.014	1.036	.936	3.986	47.5
H3	OPX B3	60.96	38.92	1.17	101.04	2.019	1.921	.042	3.981	2.1
H3	OPX B8	59.88	38.46	1.22	99.56	2.014	1.928	.044	3.986	2.2
H3	OPX B9	60.34	37.93	1.72	99.99	2.022	1.895	.062	3.978	3.2
H3	OPX B11	60.15	37.97	1.31	99.43	2.024	1.905	.047	3.976	2.4
H3	OPX B13	60.43	38.30	1.28	100.02	2.022	1.910	.046	3.978	2.3
H3	OPX B15	60.74	38.80	1.17	100.72	2.018	1.922	.042	3.982	2.1
H3	CPX B1	56.59	21.42	21.23	99.25	2.023	1.141	.813	3.977	41.6
H3	CPX B2	56.43	21.12	22.29	99.84	2.013	1.123	.852	3.987	43.1
H3	CPX B4	55.69	20.56	22.38	98.64	2.013	1.108	.867	3.987	43.9
H3	CPX B7	55.65	20.70	21.32	97.66	2.024	1.122	.831	3.976	42.5
H3	CPX B12	55.72	21.17	21.85	98.75	2.009	1.138	.844	3.991	42.6

			SI02	MGO	CAO	TOTAL	SI	MG	CA	TOTAL CATION	WO 8
H3	CPX	B14	55.27	20.94	21.65	97.87	2.010	1.135	.844	3.990	42.6
H3	CPX	E7	57.46	23.06	20.27	100.79	2.016	1.206	.762	3.984	38.7
H3	CPX	E8	57.36	22.41	20.63	100.40	2.022	1.178	.779	3.978	39.8
H3	CPX	E9	57.25	22.72	20.72	100.69	2.014	1.191	.781	3.986	39.6
H3	CPX	E10	57.36	22.98	19.79	100.13	2.022	1.208	.748	3.978	38.2
H3	CPX	E11	56.68	21.17	22.56	100.41	2.011	1.120	.858	3.989	43.4
H3	CPX	E12	57.49	21.18	22.18	100.85	2.025	1.112	.837	3.975	42.9
H3	CPX	E13	57.39	22.64	20.60	100.63	2.018	1.187	.776	3.982	39.5
H3	CPX	E14	57.35	22.03	21.75	101.13	2.014	1.153	.818	3.986	41.5
H3	CPX	E15	56.25	21.47	21.29	99.01	2.017	1.148	.818	3.983	41.6
I	OPX	B1-3	61.42	39.24	.68	101.34	2.024	1.928	.024	3.976	1.2
I	OPX	B1-4	60.89	39.39	.62	100.90	2.017	1.945	.022	3.983	1.1
I	OPX	B1-5	59.55	38.41	.57	98.53	2.019	1.941	.021	3.981	1.1
I	OPX	B2-3	61.14	39.15	.64	100.93	2.023	1.931	.023	3.977	1.2
I	OPX	B3-3	61.47	39.99	.38	101.84	2.016	1.955	.013	3.984	.7
I	OPX	B4-4	61.56	39.14	.75	101.45	2.026	1.921	.026	3.974	1.4
I	OPX	B4-5	60.22	38.60	.70	99.52	2.022	1.932	.025	3.978	1.3
I	OPX	B5-3	60.73	39.33	.51	100.57	2.017	1.948	.018	3.983	.9
I	OPX	B6-2	60.82	39.50	.53	100.86	2.015	1.951	.019	3.985	1.0
I	CPX	B8-1	55.90	18.23	24.77	98.90	2.026	.985	.962	3.974	49.4
I	CPX	B2-2	56.22	19.00	25.35	100.57	2.009	1.012	.970	3.991	49.0
I	CPX	B3-1	55.88	18.38	24.18	98.45	2.031	.996	.942	3.969	48.6
I	CPX	B4-1	55.39	18.81	24.16	98.36	2.018	1.022	.943	3.982	48.0
I	CPX	B4-2	56.06	18.83	25.24	100.13	2.011	1.007	.970	3.989	49.1
I	CPX	B6-1	55.75	18.66	24.33	98.73	2.023	1.009	.946	3.977	48.4

		SI02	MGO	CAO	TOTAL	SI	MG	CA	TOTAL CATION	WO %
I	CPX 88	56.16	19.54	23.77	99.46	2.019	1.047	.915	3.981	46.6
I	CPX 89-1	55.94	19.02	25.18	100.14	2.007	1.017	.968	3.993	48.8
I	CPX 11 1	56.39	19.62	24.00	100.01	2.017	1.046	.920	3.983	46.8
I	CPX 11 2	56.45	19.52	24.21	100.18	2.017	1.040	.927	3.983	47.1
I	CPX 11 4	56.49	18.95	25.48	100.92	2.011	1.006	.972	3.989	49.1

APPENDIX 2

A List of Whole Pyroxene Analyses Used in Chapter 4

Due to the rounding-off conventions adopted, the 'total' column may differ by 0.01 from the sum of SiO_2 , FeO, MgO and CaO.

Total Fe as FeO

		SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS			
Z3	OPX	B9	59.66	4.23	34.88	1.65	100.42	2.027	.120	1.766	.060	3.973	3.1	90.7	6.2
Z3	OPX	B21	59.20	4.58	35.11	1.46	100.35	2.017	.130	1.783	.053	3.983	2.7	90.7	6.6
Z3	OPX	B11	59.16	4.27	35.80	1.52	100.75	2.007	.121	1.810	.055	3.993	2.8	91.1	6.1
Z3	OPX	B2	60.31	1.84	37.40	1.58	101.12	2.015	.051	1.863	.057	3.985	2.9	94.5	2.6
Z3	OPX	B22	59.75	3.66	36.07	1.53	101.01	2.014	.103	1.813	.055	3.986	2.8	92.0	5.2
Z3	OPX	B14	60.12	4.23	35.70	1.49	101.55	2.020	.119	1.788	.054	3.980	2.7	91.2	6.1
Z3	OPX	B20	59.12	4.37	35.42	1.43	100.34	2.013	.124	1.798	.052	3.987	2.6	91.1	6.3
Z3	OPX	B18	59.49	4.31	35.81	1.34	100.95	2.012	.122	1.806	.049	3.988	2.5	91.4	6.2
Z3	OPX	B5	59.50	3.95	35.97	1.10	100.52	2.016	.112	1.817	.040	3.984	2.0	92.3	5.7
Z3	OPX	B7	59.78	2.69	36.71	1.10	100.28	2.018	.076	1.848	.040	3.982	2.0	94.1	3.9
Z3	CPX	B19	55.86	2.23	19.89	20.99	98.97	2.022	.068	1.074	.814	3.978	41.6	54.9	3.5
Z3	CPX	B8	55.98	2.02	20.11	21.17	99.27	2.020	.061	1.082	.818	3.980	41.7	55.2	3.1
Z3	CPX	B17	56.29	2.29	20.38	21.30	100.27	2.014	.069	1.087	.817	3.986	41.4	55.1	3.5
Z3	CPX	B4	56.07	2.37	19.61	21.05	99.11	2.028	.072	1.057	.816	3.972	41.9	54.4	3.7
Z3	CPX	B10	55.68	2.26	20.10	21.23	99.27	2.013	.068	1.083	.822	3.987	41.7	54.9	3.5
Z3	CPX	B1	55.36	2.14	19.48	21.27	98.25	2.021	.065	1.060	.832	3.979	42.5	54.2	3.3
Z3	CPX	B15	56.34	2.20	19.68	21.36	99.58	2.027	.066	1.056	.824	3.973	42.3	54.3	3.4
Z3	CPX	B13	54.55	5.75	16.55	22.66	99.51	2.010	.177	.909	.894	3.990	45.2	45.9	8.9
Z3	CPX	B12	55.08	5.74	16.83	22.68	100.33	2.011	.175	.916	.887	3.989	44.8	46.3	8.9
P1	OPX	B18	56.07	15.85	27.64	1.75	101.31	1.997	.472	1.467	.067	4.003	3.3	73.1	23.5
P1	OPX	B14	56.32	16.09	27.61	1.76	101.78	1.998	.477	1.460	.067	4.002	3.3	72.8	23.8
P1	OPX	B4	55.64	15.51	27.28	1.78	100.21	2.001	.467	1.463	.069	3.999	3.4	73.2	23.4
P1	OPX	B21	56.07	16.00	27.78	1.80	101.65	1.992	.475	1.472	.069	4.008	3.4	73.0	23.6
P1	OPX	B12	56.23	15.92	27.43	1.82	101.39	2.001	.474	1.455	.069	3.999	3.5	72.8	23.7
P1	OPX	B5	55.83	15.72	26.97	1.85	100.37	2.006	.472	1.445	.071	3.994	3.6	72.7	23.8

		SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS	
PI	OPX	B8	55.95	15.80	27.29	1.91	100.95	2.000	.472	1.454	.073	4.000	3.7 72.7 23.6
PI	OPX	B10	55.79	16.02	27.30	1.95	101.07	1.995	.479	1.456	.075	4.005	3.7 72.4 23.8
PI	OPX	B19	53.99	15.57	26.10	1.99	97.66	1.999	.482	1.441	.079	4.001	3.9 72.0 24.1
PI	OPX	B6	56.18	15.59	27.01	2.20	100.99	2.006	.466	1.438	.084	3.994	4.2 72.3 23.4
PI	CPX	B13	54.47	9.08	17.66	18.60	99.81	2.008	.280	.970	.735	3.992	37.0 48.9 14.1
PI	CPX	B17	54.52	9.41	17.83	18.10	99.86	2.008	.290	.979	.714	3.992	36.0 49.4 14.6
PI	CPX	B9	54.42	9.41	17.95	17.86	99.64	2.008	.290	.987	.706	3.992	35.6 49.8 14.6
PI	CPX	B7	54.47	9.81	18.15	17.89	100.32	2.000	.301	.994	.704	4.000	35.2 49.7 15.1
PI	CPX	B16	54.82	9.83	18.27	17.59	100.52	2.006	.301	.997	.690	3.994	34.7 50.2 15.1
PI	CPX	B20	54.36	10.02	18.24	17.07	99.70	2.006	.309	1.004	.675	3.994	34.0 50.5 15.6
PI	CPX	B3	54.14	9.97	18.43	17.08	99.62	2.000	.308	1.015	.676	4.000	33.8 50.8 15.4
PI	CPX	B15	55.02	10.02	18.76	17.00	100.80	2.006	.305	1.019	.664	3.994	33.4 51.3 15.4
PI	CPX	B1	54.28	10.21	18.50	16.91	99.91	2.001	.315	1.016	.668	3.999	33.4 50.9 15.7
PI	CPX	B2	54.53	9.93	18.66	16.90	100.02	2.004	.305	1.022	.665	3.996	33.4 51.3 15.3
2C1	OPX	A15	56.20	14.79	27.16	2.18	100.33	2.012	.443	1.450	.084	3.988	4.2 73.4 22.4
2C1	OPX	A17	55.86	14.68	27.21	2.09	99.83	2.009	.442	1.459	.081	3.991	4.1 73.6 22.3
2C1	OPX	A13	55.93	14.51	27.50	2.05	99.99	2.007	.435	1.471	.079	3.993	4.0 74.1 21.9
2C1	OPX	A2	55.24	14.56	26.97	1.96	98.73	2.009	.443	1.462	.076	3.991	3.9 73.8 22.3
2C1	OPX	A26	54.81	14.63	27.05	1.90	98.40	2.003	.447	1.473	.074	3.997	3.7 73.9 22.4
2C1	OPX	A4	56.46	15.07	27.67	1.80	101.00	2.008	.448	1.467	.069	3.992	3.5 73.9 22.6
2C1	OPX	A11	55.58	15.01	27.92	1.66	100.18	1.996	.451	1.494	.064	4.004	3.2 74.4 22.4
2C1	OPX	A19	55.46	15.97	27.71	.79	99.93	1.999	.481	1.489	.031	4.001	1.5 74.4 24.1
2C1	OPX	A9	55.36	15.26	27.89	.69	99.20	2.003	.462	1.505	.027	3.997	1.3 75.5 23.2
2C1	CPX	A5	54.40	9.10	17.86	18.46	99.82	2.005	.280	.981	.729	3.995	36.6 49.3 14.1
2C1	CPX	A10	53.29	8.41	17.62	18.54	97.86	2.002	.264	.987	.746	3.998	37.4 49.4 13.2

			SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS
2C1	CPX	A3	54.71	9.11	17.82	18.75	100.39	2.005	.279	.974	.736	3.995	37.0 48.9 14.0
2C1	CPX	A20	53.51	8.53	17.58	19.07	98.70	1.997	.266	.978	.762	4.003	38.0 48.7 13.3
2C1	CPX	A24	53.66	8.34	17.65	19.48	98.84	1.997	.250	.979	.777	4.003	38.7 48.8 12.5
2C1	CPX	A18	53.94	7.93	17.26	19.53	98.66	2.008	.247	.958	.779	3.992	39.3 48.3 12.4
2C1	CPX	A14	52.38	7.76	16.44	19.67	96.25	2.004	.248	.938	.806	3.996	40.5 47.1 12.5
2C1	CPX	A12	54.59	7.42	16.92	21.37	100.30	2.003	.228	.926	.840	3.997	42.1 46.4 11.4
2C1	CPX	A7	54.45	7.59	16.62	21.39	100.05	2.005	.234	.912	.844	3.995	42.4 45.8 11.7
2C1	CPX	A23	54.45	7.46	16.20	22.02	100.13	2.006	.230	.890	.869	3.994	43.7 44.7 11.6
2C1	CPX	A16	54.66	6.93	16.12	22.43	100.14	2.010	.213	.884	.884	3.990	44.6 44.6 10.8
T4	CPX	A1	53.27	20.01	18.79	8.11	100.18	1.998	.628	1.051	.326	4.002	16.3 52.4 31.3
T4	CPX	A2	52.99	19.83	19.14	7.68	99.64	1.996	.625	1.075	.310	4.004	15.4 53.5 31.1
T4	CPX	A3	52.76	20.31	18.84	7.12	99.02	2.001	.644	1.065	.289	3.999	14.5 53.3 32.2
T4	CPX	A4	52.68	18.29	16.94	10.95	98.86	2.005	.582	.961	.447	3.995	22.4 48.3 29.3
T4	CPX	A5	52.81	20.25	18.91	7.25	99.22	1.999	.641	1.067	.294	4.001	14.7 53.3 32.0
T4	CPX	A6	53.09	19.86	18.39	8.62	99.96	1.998	.625	1.032	.348	4.002	17.3 51.5 31.2
T4	CPX	A7	53.37	20.85	18.63	7.78	100.63	1.998	.653	1.040	.312	4.002	15.6 51.9 32.6
T4	CPX	B2	52.99	20.34	18.95	6.94	99.22	2.004	.643	1.068	.281	3.996	14.1 53.6 32.3
T5	OPX	A1	53.64	22.48	21.99	2.36	100.47	1.994	.699	1.219	.094	4.006	4.7 60.6 34.7
T5	OPX	A4	53.39	21.81	21.75	2.64	99.59	1.999	.683	1.214	.106	4.001	5.3 60.6 34.1
T5	OPX	A6	53.48	22.26	21.96	2.52	100.22	1.993	.694	1.220	.101	4.007	5.0 60.6 34.4
T5	OPX	A9	53.02	22.63	21.74	2.58	99.96	1.987	.709	1.214	.104	4.013	5.1 59.9 35.0
T5	OPX	A10	53.38	22.10	21.87	2.68	100.02	1.993	.690	1.217	.107	4.007	5.3 60.4 34.3
T5	OPX	A12	52.98	22.86	21.53	2.83	100.20	1.984	.716	1.202	.114	4.016	5.6 59.2 35.2
T5	CPX	A2	53.07	20.45	19.06	7.15	99.72	1.999	.644	1.070	.289	4.001	14.4 53.4 32.2
T5	CPX	A3	53.32	19.24	18.12	9.80	100.48	1.996	.602	1.011	.393	4.004	19.6 50.4 30.0

			SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS
T5	CPX	A5	53.17	20.28	19.09	7.56	100.10	1.996	.637	1.068	.304	4.004	15.1 53.2 31.7
T5	CPX	A7	52.83	19.91	18.66	8.28	99.69	1.994	.628	1.050	.335	4.006	16.6 52.2 31.2
T5	CPX	A8	53.03	19.67	18.66	8.40	99.76	1.997	.619	1.048	.339	4.003	16.9 52.2 30.9
T5	CPX	B1	52.68	18.51	16.90	11.83	99.91	1.992	.585	.952	.479	4.008	23.8 47.2 29.0
O1	OPX	A18	52.84	22.70	21.82	2.13	99.49	1.988	.714	1.224	.086	4.012	4.2 60.5 35.3
O1	OPX	A4	53.23	22.70	21.86	2.23	100.02	1.991	.710	1.219	.089	4.009	4.4 60.4 35.2
O1	OPX	A22	52.86	22.67	21.95	2.30	99.78	1.984	.712	1.228	.092	4.016	4.6 60.4 35.0
O1	OPX	A11	53.18	22.24	21.99	2.33	99.74	1.991	.696	1.228	.093	4.009	4.6 60.8 34.5
O1	OPX	A2	53.44	22.34	22.06	2.39	100.23	1.991	.696	1.226	.095	4.009	4.7 60.8 34.5
O1	OPX	A10	53.21	21.90	22.43	2.41	99.96	1.986	.684	1.248	.096	4.014	4.8 61.5 33.7
O1	OPX	A15	52.87	22.71	21.76	2.51	99.85	1.984	.713	1.218	.101	4.016	5.0 59.9 35.1
O1	OPX	A9	52.98	22.37	21.60	2.53	99.48	1.992	.703	1.211	.102	4.008	5.1 60.1 34.9
O1	OPX	A21	53.12	22.34	21.59	2.55	99.60	1.994	.701	1.208	.103	4.006	5.1 60.0 34.9
O1	OPX	A14	53.31	22.16	21.49	2.84	99.80	1.996	.694	1.200	.114	4.004	5.7 59.8 34.6
O1	OPX	A7	53.33	21.33	21.45	3.85	99.96	1.992	.666	1.195	.154	4.008	7.6 59.3 33.1
O1	CPX	A16	52.63	16.12	16.21	14.35	99.32	1.995	.511	.916	.583	4.005	29.0 45.6 25.4
O1	CPX	A19	52.16	16.25	16.19	13.73	98.33	1.996	.520	.924	.563	4.004	28.1 46.0 25.9
O1	CPX	A13	52.50	16.51	16.45	13.68	99.14	1.994	.524	.931	.557	4.006	27.7 46.3 26.1
O1	CPX	A20	52.29	16.67	16.45	13.65	99.06	1.990	.531	.933	.557	4.010	27.5 46.2 26.3
O1	CPX	A6	52.79	16.61	16.76	13.64	99.80	1.991	.524	.942	.551	4.009	27.3 46.7 26.0
O1	CPX	A5	52.34	16.86	16.28	13.47	98.95	1.994	.537	.925	.550	4.006	27.3 46.0 26.7
O1	CPX	A8	52.56	16.95	16.46	13.25	99.22	1.996	.538	.932	.539	4.004	26.8 46.4 26.8
O1	CPX	A1	52.81	16.92	16.84	13.18	99.75	1.993	.534	.947	.533	4.007	26.5 47.0 26.5
O1	CPX	A17	52.36	16.91	16.36	13.15	98.77	1.997	.539	.930	.537	4.003	26.8 46.3 26.9
O1	CPX	A3	52.95	17.47	16.74	12.24	99.40	2.003	.553	.944	.496	3.997	24.9 47.4 27.7

			SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS
P7	OPX	A4	53.22	23.15	22.58	1.97	100.42	1.985	.722	1.228	.079	4.015	3.9 60.5 35.6
P7	OPX	A8	53.23	22.55	22.15	2.03	99.95	1.999	.705	1.234	.081	4.010	4.0 61.1 34.9
P7	OPX	A16	53.30	23.27	21.87	2.10	100.54	1.987	.726	1.216	.084	4.013	4.1 60.0 35.8
P7	OPX	A2	53.65	22.86	21.99	2.05	100.55	1.994	.711	1.219	.082	4.006	4.1 60.6 35.3
P7	OPX	A22	53.27	23.32	21.98	2.11	100.68	1.984	.726	1.221	.084	4.016	4.1 60.1 35.8
P7	OPX	A10	53.38	23.33	21.81	2.13	100.66	1.988	.727	1.211	.085	4.012	4.2 59.9 35.9
P7	OPX	A6	53.54	23.20	21.81	2.17	100.72	1.991	.722	1.209	.086	4.009	4.3 59.9 35.8
P7	OPX	A18	53.17	23.03	21.56	2.20	99.96	1.993	.722	1.205	.088	4.007	4.4 59.8 35.8
P7	OPX	A20	53.19	22.81	21.94	2.23	100.17	1.988	.713	1.222	.089	4.012	4.4 60.4 35.2
P7	OPX	A12	53.13	23.03	21.83	2.24	100.24	1.987	.720	1.217	.090	4.013	4.4 60.0 35.5
P7	CPX	A1	52.96	17.33	16.48	13.43	100.20	1.994	.546	.925	.542	4.006	26.9 46.0 27.1
P7	CPX	A21	52.44	17.70	16.50	12.93	99.57	1.990	.562	.933	.526	4.010	26.0 46.2 27.8
P7	CPX	A3	52.97	17.32	16.36	12.91	99.57	2.003	.548	.922	.523	3.997	26.2 46.3 27.5
P7	CPX	A5	52.68	17.92	16.48	12.66	99.74	1.994	.567	.930	.514	4.006	25.5 46.3 28.2
P7	CPX	A11	52.75	17.86	16.51	12.53	99.65	1.997	.566	.932	.508	4.003	25.3 46.5 28.2
P7	CPX	A7	52.88	17.78	16.75	12.47	99.87	1.996	.561	.943	.504	4.004	25.1 46.9 27.9
P7	CPX	A17	52.83	17.83	16.69	12.43	99.75	1.996	.564	.941	.503	4.004	25.1 46.8 28.1
P7	CPX	A15	52.61	17.92	16.66	12.41	99.59	1.994	.568	.941	.504	4.006	25.0 46.8 28.2
P7	CPX	A19	52.85	18.28	16.87	12.29	100.30	1.991	.576	.947	.496	4.009	24.6 46.9 28.5
P7	CPX	A9	51.82	17.84	16.65	12.14	98.46	1.988	.572	.952	.499	4.012	24.7 47.1 28.3
2A5	OPX	A23	52.83	24.16	20.51	2.39	99.89	1.994	.762	1.154	.097	4.006	4.8 57.3 37.9
2A5	OPX	A16	53.65	24.19	20.18	2.16	100.18	2.013	.759	1.129	.087	3.987	4.4 57.2 38.4
2A5	OPX	A2	52.24	25.02	20.65	2.15	100.06	1.978	.792	1.165	.087	4.022	4.3 57.0 38.7
2A5	OPX	A10	53.25	25.28	20.75	2.16	101.44	1.986	.788	1.154	.086	4.014	4.3 56.9 38.9
2A5	OPX	A6	52.59	24.78	20.43	2.10	99.90	1.989	.784	1.152	.085	4.011	4.2 57.0 38.8

			S102	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS
2A5	OPX	A18	52.49	24.50	20.33	2.09	99.40	1.993	.778	1.151	.085	4.007	4.2 57.1 38.6
2A5	OPX	A14	52.46	24.79	20.51	1.99	99.75	1.988	.785	1.158	.081	4.012	4.0 57.2 38.8
2A5	OPX	A4	53.14	25.15	20.93	1.73	100.95	1.988	.787	1.167	.069	4.012	3.4 57.7 38.9
2A5	OPX	A8	52.94	25.29	20.83	1.72	100.78	1.986	.793	1.165	.069	4.014	3.4 57.5 39.1
2A5	OPX	A12	53.11	25.11	21.11	1.45	100.78	1.989	.786	1.178	.058	4.011	2.9 58.3 38.9
2A5	CPX	A15	52.11	18.29	15.28	13.57	99.25	1.994	.585	.871	.556	4.006	27.6 43.3 29.1
2A5	CPX	A21	53.35	18.20	15.44	14.58	101.57	1.994	.569	.860	.584	4.006	29.0 42.7 28.3
2A5	CPX	A5	52.87	17.95	15.36	14.68	100.86	1.990	.565	.862	.592	4.010	29.3 42.7 28.0
2A5	CPX	A23	52.58	17.01	14.93	15.45	99.96	1.994	.540	.844	.628	4.006	31.2 42.0 26.8
2A5	CPX	A19	52.24	17.31	15.01	14.71	99.28	1.995	.553	.855	.602	4.005	30.0 42.5 27.5
2A5	CPX	A11	52.57	17.10	14.88	14.73	99.28	2.004	.545	.846	.602	3.996	30.2 42.4 27.4
2A5	CPX	A9	52.19	17.40	14.95	14.75	99.29	1.994	.556	.852	.604	4.006	30.0 42.3 27.6
2A5	CPX	A22	52.58	17.56	15.14	14.87	100.14	1.992	.556	.855	.604	4.008	30.0 42.4 27.6
2A5	CPX	A17	52.69	17.79	15.18	14.92	100.57	1.990	.562	.855	.604	4.010	29.9 42.3 27.8
2A5	CPX	A3	52.12	17.10	14.75	15.20	99.16	1.994	.547	.841	.623	4.006	31.0 41.8 27.2
2A5	CPX	A7	52.46	16.81	14.79	15.57	99.63	1.996	.535	.839	.635	4.004	31.6 41.8 26.6
2A5	CPX	A1	52.57	16.89	14.87	15.61	99.94	1.994	.536	.841	.634	4.006	31.5 41.8 26.6
2A5	CPX	B1	51.92	16.63	14.51	15.87	98.94	1.992	.534	.830	.652	4.008	32.4 41.2 26.5
2A5	CPX	A13	52.57	16.14	14.87	16.29	99.87	1.993	.512	.840	.662	4.007	32.9 41.7 25.4
P5	OPX	A10	52.44	25.73	20.08	2.19	100.44	1.983	.814	1.132	.089	4.017	4.4 55.6 40.0
P5	OPX	A12	52.45	25.29	20.31	2.23	100.28	1.983	.800	1.145	.090	4.017	4.4 56.3 39.3
P5	OPX	A2	51.80	24.84	19.84	2.20	98.68	1.988	.797	1.135	.090	4.012	4.5 56.1 39.4
P5	OPX	A6	53.36	24.95	19.90	2.21	100.41	2.006	.784	1.115	.089	3.994	4.5 56.1 39.4
P5	OPX	A17	52.35	25.22	20.12	2.26	99.94	1.985	.800	1.138	.092	4.015	4.5 56.1 39.4
P5	OPX	A8	52.60	25.51	20.12	2.28	100.51	1.985	.805	1.132	.092	4.015	4.5 55.8 39.7

			SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS
P5	OPX	A23	52.47	25.54	19.94	2.38	100.33	1.985	.808	1.125	.096	4.015	4.8 55.4 39.8
P5	OPX	A4	52.59	25.26	19.68	2.43	99.96	1.994	.801	1.112	.099	4.006	4.9 55.3 39.8
P5	OPX	B4	51.77	24.95	19.95	2.44	99.11	1.981	.799	1.138	.100	4.019	4.9 55.9 39.2
P5	CPX	A15	52.17	19.11	15.17	13.16	99.60	1.993	.611	.864	.539	4.007	26.8 42.9 30.3
P5	CPX	A18	51.93	19.32	14.95	12.99	99.19	1.994	.621	.856	.535	4.006	26.6 42.6 30.9
P5	CPX	A5	52.26	19.45	15.22	12.80	99.74	1.995	.621	.866	.523	4.005	26.0 43.1 30.9
P5	CPX	B3	52.16	19.97	15.14	12.77	100.03	1.993	.637	.861	.522	4.010	25.8 42.6 31.5
P5	CPX	A7	52.17	19.35	15.18	12.53	99.23	1.999	.620	.867	.514	4.001	25.7 43.3 31.0
P5	CPX	A24	52.05	19.68	14.97	12.45	99.14	1.999	.632	.857	.512	4.001	25.6 42.8 31.6
P5	CPX	A27	52.04	19.77	15.44	11.92	99.17	1.996	.634	.883	.490	4.004	24.4 44.0 31.6
P5	CPX	A14	52.22	20.24	15.69	11.57	99.72	1.994	.646	.893	.473	4.006	23.5 44.4 32.1
P5	CPX	A3	52.47	20.41	15.66	11.36	99.90	1.999	.650	.889	.464	4.001	23.1 44.4 32.5
P5	CPX	A1	51.34	20.55	15.20	11.20	98.30	1.993	.667	.880	.466	4.007	23.1 43.7 33.1
P5	CPX	A11	52.18	20.84	15.58	11.17	99.76	1.994	.666	.888	.457	4.006	22.7 44.1 33.1
P5	CPX	A9	51.99	20.61	15.87	10.86	99.33	1.993	.661	.907	.446	4.007	22.2 45.0 32.8
P5	CPX	B5	52.09	22.26	16.08	9.94	100.38	1.985	.710	.914	.406	4.015	20.0 45.0 35.0
P5	CPX	B2	51.55	22.11	16.16	9.49	99.32	1.985	.712	.927	.391	4.015	19.3 45.7 35.1
P5	CPX	A21	52.21	21.60	16.46	9.18	99.45	1.997	.691	.939	.376	4.003	18.8 46.8 34.4
P5	CPX	A20	51.66	21.68	16.29	8.96	98.60	1.995	.700	.938	.371	4.005	18.5 46.7 34.9
P5	CPX	A13	52.20	22.31	16.72	8.50	99.72	1.994	.713	.952	.348	4.006	17.3 47.3 35.4
P5	CPX	A28	51.79	22.38	16.89	8.10	99.16	1.990	.719	.967	.333	4.010	16.5 47.9 35.6
P5	CPX	A19	51.97	22.31	16.91	8.04	99.23	1.993	.716	.967	.330	4.007	16.4 48.0 35.6
P5	CPX	A29	52.43	22.66	16.94	8.01	100.04	1.995	.721	.961	.327	4.005	16.3 47.8 35.9
P5	CPX	A22	51.97	22.87	16.86	8.00	99.69	1.989	.732	.962	.328	4.011	16.2 47.6 36.2
P5	CPX	A26	51.92	22.52	17.16	7.85	99.45	1.988	.721	.980	.322	4.012	15.9 48.4 35.7

		SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS	
P5	CPX	A16	51.99	23.09	17.20	7.69	99.97	1.985	.737	.979	.315	4.015	15.5 48.2 36.3
286	OPX	A19	52.06	26.28	18.95	2.50	99.79	1.989	.840	1.079	.102	4.011	5.1 53.4 41.5
286	OPX	A21	52.49	26.19	19.26	2.47	100.41	1.990	.630	1.089	.100	4.010	5.0 53.9 41.1
286	OPX	A10	51.97	25.60	19.58	2.41	99.55	1.985	.818	1.115	.099	4.015	4.9 54.9 40.3
286	OPX	A16	53.19	26.68	19.61	2.44	101.92	1.988	.834	1.093	.098	4.012	4.8 54.0 41.2
286	OPX	A4	52.42	26.21	19.29	2.22	100.14	1.992	.833	1.093	.090	4.008	4.5 54.2 41.3
286	OPX	A17	52.54	26.49	19.42	2.16	100.62	1.989	.839	1.096	.088	4.011	4.3 54.2 41.5
286	OPX	A8	52.43	26.42	19.43	2.11	100.40	1.989	.838	1.099	.086	4.011	4.2 54.3 41.4
286	OPX	A14	52.28	26.56	19.45	2.11	100.40	1.985	.843	1.101	.086	4.015	4.2 54.2 41.5
286	OPX	A2	52.07	27.07	19.05	2.04	100.23	1.985	.863	1.083	.083	4.015	4.1 53.4 42.5
286	OPX	A23	52.26	26.29	19.26	1.87	99.69	1.994	.839	1.096	.076	4.006	3.8 54.5 41.7
286	OPX	A12	52.70	26.26	20.40	1.16	100.52	1.988	.829	1.148	.047	4.012	2.3 56.7 41.0
286	CPX	A15	51.92	18.88	14.40	13.28	98.48	2.006	.610	.829	.550	3.994	27.6 41.7 30.7
286	CPX	A1	50.67	19.09	13.65	12.79	96.19	2.009	.633	.807	.543	3.991	27.4 40.7 31.9
286	CPX	A22	52.41	19.34	14.85	13.34	99.94	1.998	.616	.844	.545	4.002	27.2 42.1 30.7
286	CPX	A7	51.96	19.68	14.73	12.93	99.30	1.996	.632	.844	.532	4.004	26.5 42.0 31.5
286	CPX	A13	52.30	20.03	14.72	12.61	99.65	2.001	.641	.840	.517	3.999	25.9 42.0 32.1
286	CPX	A11	52.10	20.03	14.47	12.52	99.12	2.005	.645	.830	.516	3.995	25.9 41.7 32.4
286	CPX	A18	52.43	20.14	14.82	12.39	99.79	2.003	.643	.844	.507	3.997	25.4 42.3 32.3
286	CPX	A6	52.04	20.89	15.06	11.53	99.51	1.997	.670	.862	.474	4.003	23.6 42.9 33.4
286	CPX	A9	52.49	21.02	15.03	11.47	100.00	2.003	.671	.855	.469	3.997	23.5 42.9 33.6
286	CPX	A20	53.42	20.95	14.93	11.43	100.73	2.018	.662	.841	.463	3.982	23.5 42.8 33.7
286	CPX	A5	52.26	21.25	15.51	10.77	99.79	1.998	.679	.884	.441	4.002	22.0 44.1 33.9
Q1	CPX	A15	51.62	20.00	14.71	12.31	98.64	1.997	.647	.848	.510	4.003	25.4 42.3 32.3
Q1	CPX	A12	51.98	20.59	15.05	12.17	99.80	1.991	.660	.859	.499	4.009	24.7 42.6 32.7

		SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS	
Q1	CPX	A11	51.97	20.41	14.93	12.34	99.66	1.993	.654	.853	.507	4.007	25.2 42.4 32.5
Q1	CPX	A4	52.20	20.88	15.31	11.88	100.28	1.990	.666	.870	.485	4.010	24.0 43.1 32.9
Q1	CPX	A3	52.05	20.97	15.09	11.83	99.94	1.992	.671	.861	.485	4.008	24.0 42.7 33.3
Q1	CPX	A5	52.55	21.19	15.35	11.72	100.81	1.992	.672	.868	.476	4.008	23.6 43.0 33.3
Q1	CPX	A13	52.14	20.89	15.23	11.70	99.96	1.993	.668	.868	.479	4.007	23.8 43.1 33.1
Q1	CPX	A16	52.09	20.88	15.17	11.59	99.73	1.995	.669	.866	.476	4.005	23.7 43.1 33.3
Q1	CPX	A1	51.74	20.98	15.23	11.51	99.46	1.989	.675	.873	.474	4.011	23.5 43.2 33.4
Q1	CPX	A8	51.95	21.18	15.28	11.41	99.82	1.990	.679	.873	.468	4.010	23.2 43.2 33.6
Q1	CPX	A18	52.05	22.43	15.60	10.28	100.37	1.988	.716	.888	.421	4.012	20.8 43.9 35.4
Q1	CPX	A14	51.88	22.07	15.60	10.28	99.83	1.989	.708	.892	.422	4.011	20.9 44.1 35.0
Q1	CPX	A6	52.01	22.28	15.88	10.24	100.41	1.984	.711	.903	.418	4.016	20.6 44.4 35.0
Q1	CPX	A17	51.88	22.21	15.44	10.12	99.65	1.993	.714	.884	.417	4.007	20.7 43.9 35.4
Q1	CPX	A19	52.54	22.51	15.68	10.06	100.80	1.994	.715	.887	.409	4.006	20.3 44.1 35.5
Q1	CPX	A25	51.57	22.00	15.42	9.98	98.97	1.993	.711	.889	.413	4.007	20.5 44.1 35.3
Q1	CPX	A24	51.62	21.31	15.25	9.94	98.11	2.005	.692	.883	.414	3.995	20.8 44.4 34.8
Q1	CPX	A10	51.86	22.41	15.84	9.94	100.04	1.985	.717	.904	.408	4.015	20.1 44.6 35.4
Q1	CPX	A2	52.12	22.62	15.63	9.94	100.31	1.990	.722	.890	.407	4.010	20.1 44.1 35.8
Q1	CPX	A7	52.71	21.86	15.35	9.77	99.68	2.014	.698	.874	.400	3.986	20.3 44.3 35.4
Q1	CPX	A22	52.10	22.95	16.18	9.39	100.62	1.984	.731	.918	.383	4.016	18.8 45.2 36.0
Q1	CPX	A21	51.83	22.79	15.89	9.11	99.63	1.991	.732	.910	.375	4.009	18.6 45.1 36.3
Q1	CPX	A23	51.52	22.73	15.92	9.09	99.25	1.988	.733	.916	.376	4.012	18.6 45.2 36.2
2D2	OPX	A13	51.60	27.00	19.15	2.19	99.94	1.976	.865	1.093	.090	4.024	4.4 53.4 42.2
2D2	OPX	A4	51.83	25.82	19.60	2.20	99.46	1.983	.826	1.118	.090	4.017	4.4 55.0 40.6
2D2	OPX	A11	51.88	27.52	18.99	2.26	100.64	1.976	.877	1.078	.092	4.024	4.5 52.7 42.8
2D2	OPX	A6	52.02	25.59	20.21	2.30	100.12	1.975	.813	1.144	.094	4.025	4.6 55.8 39.6

		SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS	
2D2	OPX	A17	52.08	27.26	19.18	2.32	100.83	1.977	.866	1.086	.094	4.023	4.6 53.1 42.3
2D2	OPX	A1	51.32	26.49	19.38	2.36	99.55	1.971	.851	1.110	.097	4.029	4.7 53.9 41.4
2D2	OPX	A112	52.08	25.97	19.10	2.44	99.58	1.991	.830	1.088	.100	4.009	5.0 53.9 41.1
2D2	OPX	A15	51.84	27.00	18.92	2.49	100.25	1.979	.862	1.077	.102	4.021	5.0 52.8 42.2
2D2	OPX	A1-2	51.22	27.32	19.13	2.51	100.17	1.964	.876	1.093	.103	4.036	5.0 52.8 42.3
2D2	OPX	A9	52.00	26.46	19.57	2.60	100.63	1.974	.840	1.107	.106	4.026	5.2 53.9 40.9
2D2	CPX	A16	51.66	20.90	14.83	12.35	99.75	1.985	.672	.850	.508	4.015	25.1 41.9 33.1
2D2	CPX	A13	51.47	21.38	14.78	12.04	99.66	1.983	.689	.849	.497	4.017	24.4 41.7 33.9
2D2	CPX	A8	51.43	21.13	14.67	12.00	99.23	1.988	.683	.845	.497	4.012	24.5 41.7 33.7
2D2	CPX	A3	51.20	21.67	14.75	11.65	99.27	1.982	.702	.851	.483	4.018	23.7 41.8 34.5
2D2	CPX	A2	51.32	22.21	15.03	11.62	100.18	1.973	.714	.861	.479	4.027	23.3 41.9 34.8
2D2	CPX	A19	52.13	21.42	15.69	11.54	100.78	1.981	.681	.889	.470	4.019	23.0 43.6 33.4
2D2	CPX	A18	51.54	22.12	14.73	11.45	99.85	1.985	.712	.846	.472	4.015	23.3 41.6 35.1
2D2	CPX	A12	51.78	22.30	14.98	11.32	100.38	1.983	.714	.855	.464	4.017	22.8 42.0 35.1
2D2	CPX	A7	49.84	22.29	14.23	11.29	97.64	1.972	.738	.839	.479	4.028	23.3 40.8 35.9
2D2	CPX	A5	52.69	20.81	14.31	11.27	99.08	2.024	.669	.820	.464	3.976	23.8 42.0 34.3
2D2	CPX	A10	51.42	21.61	14.77	11.16	98.97	1.992	.700	.853	.463	4.008	23.0 42.3 34.7
Q2	OPX	A12	51.94	27.86	18.92	2.15	100.87	1.976	.887	1.073	.088	4.024	4.3 52.4 43.3
Q2	OPX	A18	51.82	27.34	19.00	2.16	100.31	1.979	.873	1.081	.088	4.021	4.3 52.9 42.7
Q2	OPX	A11	52.01	28.07	19.01	2.17	101.25	1.973	.891	1.075	.088	4.027	4.3 52.3 43.4
Q2	OPX	A5	51.57	27.70	18.71	2.20	100.18	1.976	.888	1.069	.090	4.024	4.4 52.2 43.4
Q2	OPX	A8	51.64	26.77	19.01	2.22	99.65	1.981	.859	1.087	.091	4.019	4.5 53.4 42.2
Q2	OPX	A9	51.88	27.69	18.94	2.22	100.73	1.976	.882	1.075	.091	4.024	4.4 52.5 43.1
Q2	OPX	A16	51.90	27.28	19.20	2.22	100.59	1.976	.868	1.090	.091	4.024	4.4 53.2 42.4
Q2	OPX	A20	51.69	27.40	19.11	2.24	100.44	1.973	.875	1.087	.092	4.027	4.5 52.9 42.6

		SIO2	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS
Q2	OPX	A14	52.12	27.55	18.90	2.50	101.07	.874	1.069	.102	4.022	5.0 52.3 42.8
Q2	OPX	A7	51.99	27.27	19.11	2.57	100.94	.866	1.082	.105	4.026	5.1 52.7 42.2
Q2	CPX	A13	51.14	22.65	14.87	11.04	99.69	.732	.857	.457	4.023	22.3 41.9 35.8
Q2	CPX	A17	51.70	22.66	14.97	10.93	100.26	.727	.856	.449	4.016	22.1 42.1 35.8
Q2	CPX	A6	51.82	22.70	14.84	10.84	100.20	.728	.849	.446	4.012	22.0 42.0 36.0
Q2	CPX	B1	51.53	22.77	15.21	10.50	100.01	.732	.872	.433	4.018	21.2 42.8 36.0
Q2	CPX	A3	51.84	22.94	15.05	10.49	100.32	.735	.860	.431	4.013	21.3 42.4 36.3
Q2	CPX	A19	51.58	22.84	15.23	10.33	99.99	.735	.873	.426	4.017	20.9 42.9 36.1
Q2	CPX	A2	51.66	22.98	15.08	10.25	99.96	.739	.865	.422	4.013	20.8 42.7 36.5
Q2	CPX	A15	51.62	22.86	15.13	10.18	99.80	.736	.869	.420	4.012	20.7 42.9 36.4
Q2	CPX	A10	51.65	23.18	15.15	10.03	100.02	.746	.869	.413	4.014	20.4 42.8 36.8
Q2	CPX	A4	51.38	23.26	15.34	9.44	99.42	.752	.884	.391	4.014	19.3 43.6 37.1
Q2	CPX	A1	51.68	24.01	16.09	8.21	99.99	.771	.921	.338	4.015	16.6 45.4 38.0
285	OPX	A18	51.95	26.94	19.07	2.10	100.06	.860	1.086	.086	4.016	4.2 53.4 42.3
285	OPX	A11	52.78	26.65	19.16	2.29	100.88	.842	1.079	.093	4.007	4.6 53.6 41.8
285	OPX	A4	51.88	27.15	18.76	2.35	100.15	.868	1.069	.096	4.017	4.7 52.6 42.7
285	OPX	A20	52.17	26.77	18.85	2.36	100.16	.854	1.071	.096	4.011	4.8 53.0 42.2
285	OPX	A17	52.50	26.87	19.15	2.37	100.89	.850	1.080	.096	4.013	4.7 53.3 42.0
285	OPX	A8	52.48	26.52	18.60	2.40	100.00	.845	1.057	.098	4.000	4.9 52.8 42.3
285	OPX	A10	52.87	27.00	19.03	2.42	101.32	.851	1.069	.098	4.008	4.8 53.0 42.2
285	OPX	A14	52.56	25.90	18.62	2.55	99.63	.826	1.059	.104	3.995	5.2 53.2 41.5
285	OPX	A7	51.53	26.32	18.36	2.60	98.82	.851	1.058	.108	4.008	5.3 52.5 42.2
285	OPX	A2	51.62	26.50	18.07	3.04	99.23	.855	1.039	.126	4.009	6.2 51.5 42.3
285	CPX	A9	51.71	22.72	15.39	10.13	99.96	.730	.881	.417	4.014	20.6 43.5 36.0
285	CPX	A16	51.85	21.30	15.11	11.31	99.57	.684	.866	.466	4.008	23.1 42.9 34.0

		SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS	
285	CPX	A6	51.39	20.92	14.49	12.28	99.08	1.989	.677	.836	.509	4.011	25.2 41.3 33.5
285	CPX	A5	51.59	20.87	14.81	12.38	99.65	1.985	.671	.849	.510	4.015	25.1 41.8 33.1
285	CPX	A3	52.17	20.61	14.47	12.63	99.88	1.998	.660	.826	.518	4.002	25.9 41.2 32.9
285	CPX	A1	52.26	20.38	14.70	12.82	100.17	1.994	.650	.836	.524	4.006	26.1 41.6 32.3
285	CPX	A132	52.38	19.78	14.56	13.30	100.02	1.998	.631	.828	.544	4.002	27.1 41.3 31.5
285	CPX	A13	51.39	19.48	14.33	13.31	98.51	1.993	.632	.829	.553	4.007	27.5 41.2 31.4
285	CPX	A19	51.87	19.79	14.40	13.55	99.61	1.991	.635	.824	.557	4.009	27.6 40.9 31.5
P9	OPX	B20	51.59	28.95	18.24	2.02	100.79	1.975	.927	1.041	.083	4.025	4.0 50.8 45.2
P9	OPX	B2	51.07	28.84	17.68	2.05	99.64	1.979	.935	1.022	.085	4.021	4.2 50.0 45.8
P9	OPX	B3	51.00	28.39	17.89	2.06	99.34	1.979	.921	1.035	.086	4.021	4.2 50.7 45.1
P9	OPX	B5	51.21	28.38	17.87	2.10	99.56	1.982	.918	1.031	.087	4.018	4.3 50.6 45.1
P9	OPX	B9	51.52	29.41	17.93	2.14	101.00	1.973	.942	1.024	.088	4.027	4.3 49.9 45.9
P9	OPX	B14	51.05	29.07	17.81	2.16	100.08	1.973	.939	1.026	.089	4.027	4.4 49.9 45.7
P9	OPX	B12	51.27	28.87	17.83	2.22	100.19	1.976	.931	1.025	.092	4.024	4.5 50.1 45.5
P9	OPX	B17	51.33	28.98	17.72	2.23	100.25	1.978	.934	1.018	.092	4.022	4.5 49.8 45.7
P9	OPX	B19	51.54	28.47	18.01	2.24	100.26	1.981	.915	1.032	.092	4.019	4.5 50.6 44.9
P9	OPX	B10	51.20	28.68	18.14	2.28	100.30	1.971	.923	1.041	.094	4.029	4.6 50.6 44.9
P9	CPX	B13	50.93	26.92	15.30	7.12	100.27	1.974	.873	.884	.296	4.026	14.4 43.1 42.5
P9	CPX	B16	51.34	26.79	15.18	7.06	100.37	1.984	.866	.874	.292	4.016	14.4 43.0 42.6
P9	CPX	B7	50.53	26.69	14.94	7.01	99.16	1.979	.874	.872	.294	4.021	14.4 42.7 42.8
P9	CPX	B6	50.93	25.86	15.15	6.92	98.86	1.991	.845	.883	.290	4.009	14.4 43.7 41.9
P9	CPX	B8	51.16	26.69	15.14	6.78	99.78	1.987	.867	.877	.282	4.013	13.9 43.3 42.8
P9	CPX	B18	50.76	27.01	15.39	6.78	99.93	1.974	.878	.892	.282	4.026	13.8 43.5 42.8
P9	CPX	B21	51.23	27.20	15.24	6.69	100.36	1.982	.880	.879	.277	4.018	13.6 43.2 43.2
P9	CPX	B1	50.43	26.32	14.71	6.64	98.10	1.992	.869	.866	.281	4.008	13.9 43.0 43.1

		SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS	
P9	CPX	B4	50.71	26.22	15.42	6.48	98.82	1.985	.858	.900	.272	4.015	13.4 44.3 42.3
P9	CPX	B11	49.97	27.24	15.14	6.21	98.56	1.973	.900	.891	.263	4.027	12.8 43.4 43.8
P11	OPX	A10	51.34	30.33	18.34	.00	100.01	1.982	.979	1.056	.000	4.018	.0 51.9 48.1
P11	OPX	A3	50.98	30.13	18.25	.00	99.36	1.982	.979	1.058	.000	4.018	.0 51.9 48.1
P11	OPX	A9	51.25	30.50	18.20	.00	99.95	1.982	.986	1.049	.000	4.018	.0 51.5 48.5
P11	OPX	A2	50.62	30.12	18.07	.00	98.81	1.980	.985	1.054	.000	4.020	.0 51.7 48.3
P11	OPX	A13	51.26	30.87	17.86	.00	99.99	1.985	1.000	1.031	.000	4.015	.0 50.8 49.2
P11	OPX	A11	51.67	29.82	17.73	.00	99.22	2.004	.967	1.025	.000	3.996	.0 51.5 48.5
P11	OPX	A4	50.83	30.69	17.72	.00	99.24	1.984	1.002	1.031	.000	4.016	.0 50.7 49.3
P11	OPX	A1	51.43	29.62	17.50	.00	98.55	2.007	.967	1.018	.000	3.993	.0 51.3 48.7
P11	OPX	A12	49.80	30.04	17.65	.00	97.48	1.978	.998	1.045	.000	4.022	.0 51.2 48.8
P11	OPX	A5	51.41	30.16	17.64	.00	99.22	1.999	.981	1.022	.000	4.001	.0 51.0 49.0
Q3	OPX	D6	47.27	42.28	8.44	1.43	99.43	1.969	1.473	.524	.064	4.031	3.1 25.4 71.5
Q3	OPX	A3	47.34	42.12	8.43	1.62	99.51	1.970	1.466	.523	.072	4.030	3.5 25.4 71.1
Q3	OPX	A5	47.49	41.89	8.45	1.67	99.50	1.973	1.456	.523	.074	4.027	3.6 25.5 70.9
Q3	OPX	B1	47.04	42.38	8.42	1.67	99.51	1.962	1.478	.524	.075	4.038	3.6 25.2 71.2
Q3	OPX	A11	47.41	42.28	8.39	1.73	99.81	1.968	1.468	.519	.077	4.032	3.7 25.2 71.1
Q3	OPX	D4	46.95	41.80	8.46	1.76	98.96	1.965	1.463	.528	.079	4.035	3.8 25.5 70.7
Q3	OPX	A1	47.61	40.77	8.97	1.77	99.12	1.976	1.415	.555	.079	4.024	3.8 27.1 69.1
Q3	OPX	A10	47.26	41.14	8.92	1.78	99.10	1.967	1.432	.554	.079	4.033	3.8 26.8 69.4
Q3	OPX	D8	46.94	41.76	8.60	1.79	99.10	1.962	1.460	.536	.080	4.038	3.9 25.8 70.3
Q3	OPX	D2	47.00	41.73	8.92	1.84	99.49	1.956	1.452	.553	.082	4.044	3.9 26.5 69.6
Q3	OPX	D9	47.73	40.95	9.04	1.85	99.57	1.973	1.415	.557	.082	4.027	4.0 27.1 68.9
Q3	CPX	A2	47.50	40.14	7.89	3.95	99.48	1.971	1.393	.488	.176	4.029	8.5 23.7 67.7
Q3	CPX	A6	47.75	40.04	7.98	3.94	99.71	1.974	1.385	.492	.175	4.026	8.5 24.0 67.5

		SI02	FEO	MGO	CAO	TOTAL	SI	FE	HG	CA	TOTAL	WO - EN - FS	
Q3	CPX	D10	47.35	40.03	7.86	3.90	99.14	1.972	1.394	.488	.174	4.028	8.5 23.7 67.8
Q3	CPX	A4	47.40	39.89	8.07	3.95	99.30	1.969	1.386	.500	.176	4.031	8.5 24.2 67.2
Q3	CPX	A9	46.50	40.30	7.46	3.81	98.07	1.966	1.425	.470	.173	4.034	8.3 22.7 68.9
Q3	CPX	D7	47.52	40.20	7.90	3.78	99.41	1.973	1.396	.489	.168	4.027	8.2 23.8 68.0
Q3	CPX	D3	47.23	40.61	7.97	3.77	99.58	1.963	1.412	.494	.168	4.037	8.1 23.8 68.1
Q3	CPX	D5	47.32	40.67	7.77	3.62	99.38	1.970	1.416	.482	.161	4.030	7.8 23.4 68.7
Q3	CPX	A8	47.62	41.20	7.47	3.62	99.90	1.974	1.429	.462	.161	4.026	7.8 22.5 69.6
Q3	CPX	D1	47.55	40.69	8.08	3.57	99.89	1.968	1.408	.498	.158	4.032	7.7 24.1 68.2
Z4	OPX	D5	47.85	42.80	8.33	2.00	100.97	1.966	1.470	.510	.088	4.034	4.3 24.7 71.1
Z4	OPX	D2	47.50	42.62	8.18	1.80	100.10	1.969	1.477	.505	.080	4.031	3.9 24.5 71.6
Z4	OPX	D16	48.92	41.85	8.05	1.66	100.48	2.002	1.432	.491	.073	3.998	3.6 24.6 71.8
Z4	OPX	D12	47.65	42.03	8.40	1.53	99.60	1.977	1.458	.520	.068	4.023	3.3 25.4 71.3
Z4	OPX	D3	46.57	42.34	8.27	1.27	98.45	1.964	1.494	.520	.057	4.036	2.8 25.1 72.1
Z4	OPX	D6	46.94	42.51	8.48	1.22	99.14	1.964	1.488	.529	.055	4.036	2.6 25.5 71.8
Z4	OPX	D15	47.22	41.78	8.74	1.05	98.79	1.974	1.461	.545	.047	4.026	2.3 26.5 71.2
Z4	OPX	D10	47.63	42.20	8.65	.90	99.38	1.979	1.466	.536	.040	4.021	2.0 26.2 71.8
Z4	OPX	D8	49.22	41.10	8.15	.75	99.22	2.026	1.415	.500	.033	3.974	1.7 25.7 72.6
Z4	CPX	D7	47.16	41.18	7.71	3.26	99.30	1.968	1.437	.480	.146	4.032	7.1 23.3 69.7
Z4	CPX	D13	46.92	41.20	7.48	3.33	98.93	1.968	1.446	.468	.150	4.032	7.3 22.7 70.1
Z4	CPX	D14	47.19	41.39	7.62	3.33	99.53	1.967	1.443	.474	.149	4.033	7.2 22.9 69.9
Z4	CPX	D1	47.58	41.05	7.65	3.42	99.70	1.975	1.425	.473	.152	4.025	7.4 23.1 69.5
Z4	CPX	D11	47.57	40.80	7.82	3.46	99.65	1.973	1.416	.484	.154	4.027	7.5 23.6 69.0
Z4	CPX	D4	48.08	41.54	8.02	3.59	101.24	1.966	1.421	.489	.157	4.034	7.6 23.7 68.7
Z4	CPX	D9	47.60	41.28	7.65	3.63	100.15	1.969	1.428	.472	.161	4.031	7.8 22.9 69.3
Z4	CPX	D5	47.99	41.23	7.53	3.70	100.45	1.977	1.420	.462	.163	4.023	8.0 22.6 69.4

			SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS
R1	OPX	A12	51.71	27.93	18.77	1.85	100.26	1.979	.894	1.071	.076	4.021	3.7 52.5 43.8
R1	OPX	A4	51.66	27.61	18.87	1.97	100.11	1.979	.884	1.077	.081	4.021	4.0 52.7 43.3
R1	OPX	A13	51.98	27.72	18.75	1.98	100.43	1.984	.885	1.067	.081	4.016	4.0 52.5 43.5
R1	OPX	A6	51.47	28.40	18.50	2.07	100.44	1.973	.911	1.057	.085	4.027	4.1 51.5 44.4
R1	OPX	A23	51.83	28.22	18.46	2.08	100.59	1.981	.902	1.052	.085	4.019	4.2 51.6 44.2
R1	OPX	A11	52.16	27.39	18.93	2.23	100.72	1.983	.871	1.073	.091	4.017	4.5 52.7 42.8
R1	OPX	A17	51.78	27.90	18.37	2.31	100.36	1.982	.893	1.048	.095	4.018	4.7 51.5 43.9
R1	OPX	A14	51.23	27.76	18.12	2.33	99.44	1.981	.898	1.044	.097	4.019	4.7 51.2 44.0
R1	OPX	A8	51.98	27.22	18.70	2.75	100.64	1.980	.867	1.062	.112	4.020	5.5 52.0 42.5
R1	OPX	A19	52.02	26.78	18.43	2.82	100.04	1.989	.856	1.050	.116	4.011	5.7 51.9 42.3
R1	CPX	A16	52.47	16.98	13.24	17.23	99.92	2.001	.542	.753	.704	3.999	35.2 37.7 27.1
R1	CPX	A15	52.39	17.38	13.56	16.48	99.81	2.000	.555	.772	.674	4.000	33.7 38.6 27.7
R1	CPX	A18	52.56	16.74	13.36	16.22	98.88	2.016	.537	.764	.667	3.984	33.9 38.8 27.3
R1	CPX	A3	51.89	18.51	14.17	14.75	99.31	1.993	.595	.812	.607	4.007	30.2 40.3 29.5
R1	CPX	A2	52.11	18.17	14.26	14.70	99.23	1.999	.583	.815	.604	4.001	30.2 40.7 29.1
R1	CPX	A5	51.67	19.25	13.85	14.63	99.40	1.990	.620	.795	.604	4.010	29.9 39.4 30.7
R1	CPX	A7	52.20	19.43	13.79	14.45	99.86	1.999	.622	.787	.593	4.001	29.6 39.3 31.1
R1	CPX	A21	52.93	17.75	14.20	14.14	99.03	2.022	.567	.809	.579	3.978	29.6 41.4 29.0
R1	CPX	A9	52.38	18.72	14.72	13.99	99.80	1.997	.597	.837	.572	4.003	28.5 41.7 29.8
R1	CPX	A10	52.30	18.53	14.55	13.98	99.37	2.002	.593	.830	.573	3.998	28.7 41.6 29.7
R1	CPX	A1	51.69	19.88	14.78	12.51	98.86	1.995	.642	.850	.517	4.005	25.7 42.3 31.9
2D1	CPX	A1	52.08	17.49	14.00	16.26	99.82	1.989	.559	.797	.665	4.011	32.9 39.4 27.6
2D1	CPX	A5	52.46	20.32	15.17	12.77	100.71	1.989	.644	.858	.519	4.011	25.7 42.4 31.9
2D1	CPX	A12	52.54	21.62	15.38	11.65	101.19	1.988	.684	.868	.472	4.012	23.3 42.9 33.8
2D1	CPX	A4	51.91	22.31	15.47	10.81	100.50	1.982	.712	.881	.442	4.018	21.7 43.3 35.0

			SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS
2D1	CPX	A6	52.62	21.61	15.53	10.80	100.56	1.998	.686	.879	.439	4.002	21.9 43.9 34.2
2D1	CPX	A10	51.91	21.76	15.25	10.72	99.64	1.993	.699	.873	.441	4.007	21.9 43.4 34.7
2D1	CPX	A3	51.70	22.41	15.37	10.34	99.82	1.987	.720	.881	.426	4.013	21.0 43.5 35.5
2D1	CPX	A11	52.54	22.74	15.96	10.08	101.32	1.987	.719	.900	.408	4.013	20.1 44.4 35.5
2D1	CPX	A2	51.92	22.98	15.72	9.73	100.34	1.985	.735	.896	.399	4.015	19.6 44.2 36.2
2D1	CPX	A9	52.12	23.13	16.06	9.29	100.60	1.986	.737	.912	.379	4.014	18.7 45.0 36.3
2D1	CPX	A8	52.16	23.21	16.12	9.10	100.59	1.987	.739	.915	.371	4.013	18.3 45.2 36.5
2D1	CPX	A7	52.23	23.69	16.00	8.46	100.37	1.994	.756	.910	.346	4.006	17.2 45.2 37.6
R2	OPX	A4	52.05	29.37	19.00	.00	100.43	1.989	.939	1.083	.000	4.011	.0 53.6 46.4
R2	OPX	A2	51.18	28.91	18.84	.00	98.93	1.986	.938	1.090	.000	4.014	.0 53.7 46.3
R2	OPX	A7	51.39	28.94	18.69	.00	99.03	1.991	.938	1.080	.000	4.009	.0 53.5 46.5
R2	OPX	A8	51.66	30.27	18.67	.00	100.60	1.981	.971	1.067	.000	4.019	.0 52.4 47.6
R2	OPX	A6	51.65	30.64	18.25	.00	100.55	1.985	.985	1.046	.000	4.015	.0 51.5 48.5
R2	OPX	A3	51.27	29.85	18.20	.00	99.31	1.989	.969	1.053	.000	4.011	.0 52.1 47.9
R2	OPX	A10	51.06	29.77	18.12	.00	98.95	1.989	.970	1.052	.000	4.011	.0 52.0 48.0
R2	OPX	A1	50.99	30.24	17.60	.00	98.83	1.993	.988	1.026	.000	4.007	.0 50.9 49.1
R2	OPX	A9	50.77	31.02	17.35	.00	99.14	1.986	1.015	1.012	.000	4.014	.0 49.9 50.1
R2	OPX	A5	51.14	31.74	17.23	.00	100.10	1.986	1.031	.997	.000	4.014	.0 49.2 50.8
2D1	CPX	A1	49.21	37.34	13.32	.00	99.88	1.975	1.253	.797	.000	4.025	.0 38.9 61.1
2D1	CPX	A3	49.58	36.68	13.61	.00	99.87	1.982	1.226	.811	.000	4.018	.0 39.8 60.2
2D1	CPX	A4	49.45	37.46	13.29	.00	100.19	1.977	1.253	.792	.000	4.023	.0 38.7 61.3
2D1	CPX	A5	48.87	37.67	12.95	.00	99.48	1.974	1.272	.780	.000	4.026	.0 38.0 62.0
2D1	CPX	A6	48.51	37.30	13.09	.00	98.90	1.970	1.267	.793	.000	4.030	.0 38.5 61.5
P2	OPX	A11	55.57	14.94	27.68	2.33	100.53	1.992	.448	1.479	.089	4.008	4.4 73.4 22.2
P2	OPX	A5	55.78	14.59	27.41	2.45	100.23	2.001	.438	1.466	.094	3.999	4.7 73.4 21.9

			SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS
P2	OPX	A2	55.85	15.01	27.55	2.47	100.87	1.995	.448	1.467	.095	4.005	4.7 73.0 22.3
P2	OPX	A15	55.94	15.96	27.55	2.53	101.08	1.995	.449	1.465	.097	4.005	4.8 72.9 22.3
P2	OPX	A20	55.52	14.90	27.26	2.61	100.29	1.995	.448	1.461	.101	4.005	5.0 72.7 22.3
P2	OPX	A14	55.65	14.71	27.25	2.64	100.25	1.999	.442	1.459	.102	4.001	5.1 72.9 22.1
P2	OPX	A17	55.65	14.76	27.47	2.66	100.55	1.994	.442	1.467	.102	4.006	5.1 72.9 22.0
P2	OPX	A8	55.65	14.69	27.30	2.77	100.41	1.996	.441	1.460	.106	4.004	5.3 72.7 22.0
P2	OPX	A19	55.32	14.39	27.14	2.85	99.71	1.997	.434	1.461	.110	4.003	5.5 72.8 21.7
P2	OPX	A18	55.65	14.40	27.21	2.96	100.22	1.998	.432	1.457	.114	4.002	5.7 72.7 21.6
P2	CPX	A16	54.41	10.07	19.01	16.45	99.94	2.000	.310	1.042	.648	4.000	32.4 52.1 15.5
P2	CPX	A9	54.58	10.43	19.14	15.85	100.00	2.004	.320	1.048	.624	3.996	31.3 52.6 16.1
P2	CPX	A10	54.42	10.16	18.91	15.84	99.33	2.009	.314	1.041	.627	3.991	31.6 52.5 15.8
P2	CPX	A6	54.69	10.07	19.31	15.85	99.91	2.006	.309	1.056	.623	3.994	31.3 53.1 15.5
P2	CPX	A12	54.24	10.42	19.05	15.67	99.37	2.004	.322	1.049	.620	3.996	31.1 52.7 16.2
P2	CPX	A7	54.29	10.81	19.62	14.81	99.53	2.002	.333	1.078	.585	3.998	29.3 54.0 16.7
P2	CPX	A4	54.32	10.45	19.64	14.66	99.07	2.007	.323	1.082	.580	3.993	29.2 54.5 16.3
P2	CPX	A3	54.13	10.50	19.50	14.87	99.00	2.004	.325	1.076	.590	3.996	29.6 54.1 16.3
P2	CPX	A13	54.44	10.46	20.02	14.59	99.51	2.003	.322	1.098	.575	3.997	28.8 55.0 16.1
P2	CPX	A1	54.19	11.02	20.01	13.80	99.02	2.004	.341	1.103	.547	3.996	27.5 55.4 17.1
Q4	CPX	B5	53.90	19.85	21.20	5.90	100.84	1.992	.614	1.168	.234	4.008	11.6 58.0 30.4
Q4	CPX	A2	53.40	20.58	20.32	5.66	99.97	1.998	.644	1.133	.227	4.002	11.3 56.6 32.1
Q4	CPX	B1	53.64	19.90	21.23	5.52	100.30	1.993	.618	1.176	.220	4.007	10.9 58.4 30.7
Q4	CPX	B3	53.76	19.84	21.25	5.47	100.32	1.995	.616	1.176	.218	4.005	10.8 58.5 30.7
Q4	CPX	A3	53.96	19.97	21.59	5.33	100.85	1.992	.617	1.188	.211	4.008	10.5 59.0 30.6
Q4	CPX	B2	53.40	20.12	20.99	5.25	99.76	1.996	.629	1.169	.210	4.004	10.5 58.2 31.3
Q4	CPX	B4	54.13	19.83	21.95	4.94	100.84	1.994	.611	1.206	.195	4.006	9.7 59.9 30.4

			SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS
Q4	CPX	A5	53.65	20.79	21.26	4.85	100.55	1.992	.646	1.177	.193	4.008	9.6 58.4 32.0
Q4	CPX	A1	53.49	20.26	21.54	4.70	100.00	1.993	.631	1.196	.188	4.007	9.3 59.4 31.3
Q4	CPX	A4	53.72	19.93	21.84	4.66	100.15	1.994	.619	1.208	.185	4.006	9.2 60.1 30.7
2N2	CPX	A8	52.80	19.26	20.90	5.82	98.78	1.991	.607	1.175	.235	4.009	11.7 58.2 30.1
2N2	CPX	A5	53.33	19.87	21.51	5.51	100.22	1.984	.618	1.193	.220	4.016	10.8 58.7 30.4
2N2	CPX	A3	53.48	19.93	21.46	5.57	100.45	1.986	.619	1.168	.222	4.014	10.9 58.6 30.5
2N2	CPX	A7	53.31	19.62	21.51	5.46	99.91	1.987	.612	1.195	.218	4.013	10.8 59.0 30.2
2N2	CPX	A2	53.34	19.65	21.30	5.42	99.71	1.992	.614	1.186	.217	4.008	10.8 58.8 30.4
2N2	CPX	A4	53.23	20.19	21.12	5.42	99.96	1.988	.631	1.176	.217	4.012	10.7 58.1 31.2
2N2	CPX	A1	53.18	19.44	21.38	5.36	99.36	1.991	.609	1.194	.215	4.009	10.7 59.2 30.2
2N2	CPX	A6	53.40	19.82	21.11	5.24	99.58	1.997	.620	1.177	.210	4.003	10.5 58.6 30.9
2N2	OPX	B6	60.87	13.85	22.31	2.06	99.09	2.164	.412	1.182	.078	3.836	4.7 70.7 24.6
2N2	OPX	B1	54.92	17.35	25.15	2.29	99.71	2.006	.530	1.369	.090	3.994	4.5 68.8 26.6
2N2	OPX	B5	54.39	16.03	26.01	2.86	99.29	1.990	.490	1.418	.112	4.010	5.5 70.2 24.3
2N2	CPX	B4	54.05	11.59	26.31	13.65	99.59	1.993	.357	1.117	.539	4.007	26.8 55.5 17.8
2N2	CPX	B3	53.46	13.41	18.93	13.38	99.18	1.996	.419	1.054	.535	4.004	26.7 52.5 20.9
2N2	CPX	B2	53.44	13.22	19.01	13.34	99.01	1.997	.413	1.059	.534	4.003	26.6 52.8 20.6
02	CPX	A9	53.50	17.85	19.54	8.27	99.16	2.007	.560	1.093	.332	3.993	16.7 55.0 28.2
02	CPX	A3	53.76	18.34	19.49	7.98	99.57	2.010	.574	1.086	.320	3.990	16.1 54.9 29.0
02	CPX	A13	53.79	18.92	19.76	7.70	100.17	2.003	.589	1.097	.307	3.997	15.4 55.0 29.6
02	CPX	A12	53.43	18.44	19.80	7.59	99.25	2.004	.579	1.107	.305	3.996	15.3 55.6 29.1
02	CPX	A7	53.69	18.28	19.84	7.44	99.26	2.011	.573	1.108	.299	3.989	15.1 56.0 28.9
02	CPX	A11	53.45	18.48	19.54	7.42	98.89	2.011	.582	1.096	.299	3.989	15.1 55.4 29.4
02	CPX	A16	53.85	18.49	20.35	7.40	100.10	2.001	.575	1.128	.295	3.999	14.8 56.5 28.8
02	CPX	A15	53.90	18.57	19.97	7.37	99.80	2.009	.579	1.110	.294	3.991	14.8 56.0 29.2

			SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS
02	CPX	A2	53.83	18.74	19.91	7.24	99.72	2.909	.585	1.108	.289	3.991	14.6 55.9 29.5
02	CPX	A14	54.09	18.77	20.37	7.22	100.15	2.909	.583	1.111	.287	3.991	14.5 56.1 29.4
02	CPX	A162	53.73	18.56	20.15	7.00	99.44	2.908	.580	1.123	.280	3.992	14.1 56.6 29.3
02	CPX	A8	53.98	19.19	20.02	6.66	99.85	2.912	.598	1.112	.266	3.988	13.5 56.3 30.3
02	CPX	A17	53.74	19.33	20.34	6.58	99.99	2.903	.602	1.130	.263	3.997	13.2 56.6 30.2
02	CPX	A10	54.05	19.38	20.99	5.77	100.19	2.905	.601	1.161	.229	3.995	11.5 58.3 30.2
P8	OPX	A18	52.91	23.16	22.08	2.06	100.21	1.980	.725	1.232	.083	4.020	4.1 60.4 35.5
P8	OPX	A11	53.20	23.24	21.66	2.10	100.21	1.990	.727	1.208	.084	4.010	4.2 59.8 36.0
P8	OPX	A1	52.87	22.96	22.16	2.16	100.14	1.979	.719	1.237	.087	4.021	4.2 60.6 35.2
P8	OPX	A4	52.71	23.11	21.67	2.16	99.66	1.984	.728	1.216	.087	4.016	4.3 59.9 35.8
P8	OPX	A6	52.82	22.66	22.10	2.22	99.80	1.982	.711	1.236	.089	4.018	4.4 60.7 34.9
P8	OPX	A8	53.00	23.51	21.74	2.23	100.48	1.982	.735	1.212	.089	4.018	4.4 59.5 36.1
P8	OPX	A13	52.90	23.42	21.95	2.24	100.51	1.977	.732	1.223	.090	4.023	4.4 59.8 35.8
P8	OPX	A15	53.08	23.22	21.65	2.26	100.21	1.987	.727	1.208	.091	4.013	4.5 59.6 35.9
P8	OPX	A10	52.88	23.67	21.18	2.29	100.02	1.988	.744	1.187	.092	4.012	4.6 58.7 36.8
P8	OPX	A20	52.87	23.64	21.12	2.31	99.94	1.989	.744	1.185	.093	4.011	4.6 58.6 36.8
P8	CPX	A2	52.89	21.04	17.98	8.86	100.77	1.987	.661	1.007	.357	4.013	17.6 49.7 32.6
P8	CPX	A9	52.71	20.51	18.00	8.78	100.00	1.991	.648	1.014	.355	4.009	17.6 50.3 32.1
P8	CPX	A14	52.34	20.76	17.58	8.54	99.21	1.995	.662	.999	.349	4.005	17.4 49.7 32.9
P8	CPX	A7	52.53	20.97	17.89	8.35	99.74	1.992	.665	1.011	.339	4.008	16.8 50.2 33.0
P8	CPX	A5	52.76	20.97	18.17	7.92	99.82	1.996	.663	1.025	.321	4.004	16.0 51.0 33.0
P8	CPX	A17	52.55	21.10	17.99	7.90	99.54	1.995	.670	1.018	.321	4.005	16.0 50.7 33.3
P8	CPX	A21	52.58	21.64	18.52	7.45	100.19	1.986	.684	1.043	.302	4.014	14.9 51.4 33.7
P8	CPX	A12	52.75	22.00	18.31	7.44	100.50	1.988	.694	1.029	.300	4.012	14.9 50.9 34.3
P8	CPX	A3	52.52	21.45	18.28	7.32	99.58	1.994	.681	1.034	.298	4.006	14.8 51.4 33.8

		SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS	
P8	CPX	A19	52.44	21.87	18.74	7.11	100.16	1.982	.691	1.056	.288	4.018	14.1 51.9 34.0
Q7	CPX	A18	51.95	21.15	17.79	8.52	99.40	1.982	.675	1.012	.348	4.018	17.1 49.7 33.2
Q7	CPX	A19	52.75	20.60	17.33	9.09	99.77	1.999	.653	.979	.369	4.001	18.4 48.9 32.6
Q7	CPX	A16	52.31	21.24	17.52	9.13	100.20	1.983	.673	.990	.371	4.017	18.2 48.7 33.1
Q7	CPX	A10	52.31	20.60	18.14	9.43	100.49	1.974	.650	1.021	.381	4.026	18.6 49.7 31.7
Q7	CPX	A2	52.80	20.61	17.81	9.46	100.68	1.986	.648	.999	.381	4.014	18.8 49.2 32.0
Q7	CPX	A12	52.24	21.15	17.46	9.50	100.35	1.979	.670	.986	.386	4.021	18.9 48.3 32.8
Q7	CPX	A13	51.86	20.52	17.42	9.72	99.52	1.979	.655	.991	.397	4.021	19.4 48.5 32.0
Q7	CPX	A3	52.55	20.21	17.83	9.79	100.39	1.982	.638	1.003	.396	4.018	19.4 49.2 31.3
Q7	CPX	A5	52.67	20.65	17.56	9.87	100.74	1.983	.650	.986	.398	4.017	19.6 48.5 32.0
Q7	CPX	A7	51.96	20.63	17.24	9.95	99.79	1.979	.657	.979	.406	4.021	19.9 47.9 32.2
Q7	CPX	A6	52.63	18.80	16.94	11.67	100.03	1.989	.594	.955	.473	4.011	23.4 47.2 29.4
Q7	CPX	A8	52.04	19.15	16.46	12.11	99.77	1.981	.610	.934	.494	4.019	24.2 45.8 29.9
Q7	CPX	A21	51.96	18.65	16.29	12.49	99.39	1.983	.595	.927	.511	4.017	25.1 45.6 29.3
Q7	CPX	A20	52.57	18.90	16.82	12.49	100.79	1.979	.595	.944	.504	4.021	24.7 46.2 29.1
Q7	CPX	A11	52.58	18.84	16.42	12.57	100.40	1.986	.595	.925	.509	4.014	25.1 45.6 29.3
Q7	CPX	A1	52.50	18.63	16.53	12.59	100.25	1.985	.589	.932	.510	4.015	25.1 45.9 29.0
Q7	CPX	A15	52.15	18.20	16.27	12.93	99.55	1.985	.579	.923	.527	4.015	26.0 45.5 28.5
Q7	CPX	A4	52.62	18.31	16.05	12.95	99.93	1.994	.580	.907	.526	4.006	26.1 45.0 28.8
Q7	CPX	A17	52.29	18.43	16.41	12.99	100.13	1.981	.584	.927	.527	4.019	25.9 45.5 28.7
Q7	CPX	A14	52.50	17.62	16.21	13.90	100.24	1.984	.557	.913	.563	4.016	27.7 44.9 27.4
P6	CPX	A5	51.91	22.36	17.61	7.59	99.46	1.985	.715	1.004	.311	4.015	15.3 49.5 35.2
P6	CPX	A1	52.03	22.25	17.25	7.93	99.45	1.990	.712	.984	.325	4.010	16.1 48.7 35.2
P6	CPX	A4	52.33	22.51	17.37	7.67	99.88	1.992	.717	.986	.313	4.008	15.5 48.9 35.6
P6	CPX	A8	51.61	22.20	17.34	7.51	98.65	1.989	.716	.996	.310	4.011	15.3 49.3 35.4

			SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS
P6	CPX	A6	51.73	22.36	17.33	7.43	98.85	1.990	.719	.994	.336	4.010	15.2 49.2 35.6
P6	CPX	A2	51.99	22.64	17.42	7.28	99.33	1.991	.725	.994	.299	4.009	14.8 49.3 35.9
P6	CPX	A3	51.95	23.10	17.68	7.01	99.74	1.984	.738	1.007	.287	4.016	14.1 49.6 36.3
P6	CPX	A7	52.14	23.09	17.58	6.95	99.75	1.990	.737	1.000	.284	4.010	14.1 49.5 36.5
P6	CPX	A10	52.12	23.28	17.50	6.77	99.67	1.991	.744	.997	.277	4.009	13.7 49.4 36.9
P6	CPX	A9	52.19	22.94	17.94	6.40	99.47	1.992	.732	1.021	.262	4.008	13.0 50.7 36.3
2E2	CPX	A5	52.03	23.38	16.59	8.28	100.28	1.986	.746	.944	.339	4.014	16.7 46.5 36.8
2E2	CPX	A7	51.36	23.60	16.81	7.83	99.60	1.977	.760	.964	.323	4.023	15.8 47.1 37.1
2E2	CPX	A4	51.67	23.60	17.05	7.77	100.09	1.977	.755	.973	.319	4.023	15.6 47.5 36.9
2E2	CPX	A8	52.03	23.63	16.88	7.67	100.21	1.986	.754	.960	.314	4.014	15.5 47.4 37.2
2E2	CPX	A9	51.52	23.88	16.80	7.64	99.84	1.978	.767	.962	.314	4.022	15.4 47.1 37.5
2E2	CPX	B1	51.57	23.23	17.10	7.64	99.54	1.980	.746	.979	.314	4.020	15.4 48.0 36.6
2E2	CPX	A2	52.12	24.05	17.10	7.60	100.88	1.979	.764	.968	.309	4.021	15.1 47.4 37.4
2E2	CPX	A1	52.24	23.46	17.09	7.44	100.23	1.989	.747	.970	.304	4.011	15.0 48.0 37.0
2E2	CPX	B2	51.28	24.15	16.80	7.05	99.29	1.980	.780	.967	.292	4.020	14.3 47.4 38.3
2E2	CPX	A6	51.57	23.78	17.40	6.90	99.64	1.979	.763	.995	.284	4.021	13.9 48.7 37.4
Q5	CPX	A6	51.67	25.46	16.87	5.79	99.80	1.987	.819	.967	.239	4.013	11.8 47.8 40.4
Q5	CPX	A5	51.64	25.10	17.48	5.35	99.57	1.985	.807	1.002	.220	4.015	10.9 49.4 39.8
Q5	CPX	A7	51.84	25.48	17.46	5.30	100.08	1.985	.816	.997	.217	4.015	10.7 49.1 40.2
Q5	CPX	A2	51.85	25.24	17.66	5.27	100.03	1.984	.808	1.008	.216	4.016	10.6 49.6 39.8
Q5	CPX	A10	51.76	25.89	17.33	5.25	100.24	1.983	.829	.990	.215	4.017	10.6 48.6 40.8
Q5	CPX	A1	52.00	25.58	17.31	5.18	100.07	1.990	.819	.988	.212	4.010	10.5 48.9 40.6
Q5	CPX	A9	51.79	25.57	17.31	5.06	99.74	1.989	.821	.991	.208	4.011	10.3 49.0 40.6
Q5	CPX	A4	51.81	25.49	17.41	5.05	99.76	1.989	.818	.996	.208	4.011	10.3 49.3 40.5
Q5	CPX	A3	51.04	25.40	17.51	4.76	98.71	1.982	.825	1.014	.198	4.018	9.7 49.8 40.5

			SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS
Q5	CPX	A8	51.85	25.37	17.69	4.94	99.85	1.987	.813	1.011	.203	4.013	10.0 49.9 40.1
P10	OPX	A2	51.77	28.50	18.42	1.67	100.37	1.983	.913	1.052	.069	4.017	3.4 51.7 44.9
P10	OPX	A1-1	51.64	28.77	18.68	1.78	100.27	1.984	.924	1.035	.073	4.016	3.6 50.9 45.5
P10	OPX	A4	51.69	28.83	18.33	1.78	100.63	1.979	.923	1.046	.073	4.021	3.6 51.2 45.2
P10	OPX	A8	51.45	28.86	18.10	1.82	100.23	1.979	.928	1.038	.075	4.021	3.7 50.8 45.5
P10	OPX	A12	51.58	28.65	17.99	1.96	100.19	1.983	.921	1.031	.081	4.017	4.0 50.7 45.3
P10	OPX	A13	51.63	28.68	17.87	2.01	100.18	1.985	.922	1.024	.083	4.015	4.1 50.5 45.4
P10	OPX	A9	51.25	28.69	17.94	2.08	99.96	1.978	.926	1.032	.086	4.022	4.2 50.5 45.3
P10	OPX	A5	51.33	28.52	17.95	2.12	99.92	1.980	.920	1.032	.088	4.020	4.3 50.6 45.1
P10	OPX	A1-3	51.64	28.82	17.97	2.15	100.58	1.980	.924	1.027	.088	4.020	4.3 50.4 45.3
P10	OPX	A1-2	51.34	28.94	17.70	2.47	100.45	1.976	.931	1.015	.102	4.024	5.0 49.6 45.5
P10	CPX	A15	51.14	28.12	16.55	4.38	100.19	1.978	.909	.954	.181	4.022	8.9 46.7 44.5
P10	CPX	A14	49.40	27.72	15.89	4.02	97.03	1.976	.927	.948	.172	4.024	8.4 46.3 45.3
P10	CPX	A6-2	51.19	28.32	16.45	3.98	99.93	1.983	.918	.950	.165	4.017	8.1 46.7 45.1
P10	CPX	A6	51.06	28.32	16.96	3.68	100.02	1.976	.917	.979	.153	4.024	7.5 47.8 44.8
P10	CPX	A11	50.87	28.28	16.79	3.64	99.57	1.978	.920	.973	.152	4.022	7.4 47.6 45.0
P10	CPX	A19	51.25	28.35	16.96	3.62	100.17	1.979	.916	.976	.150	4.021	7.3 47.8 44.8
P10	CPX	A10	51.19	28.53	16.87	3.57	100.16	1.979	.922	.972	.148	4.021	7.2 47.6 45.2
P10	CPX	A17	51.28	28.48	16.86	3.56	100.18	1.981	.920	.971	.147	4.019	7.2 47.6 45.1
P10	CPX	A7	51.33	28.94	16.96	3.54	100.76	1.975	.931	.973	.146	4.025	7.1 47.5 45.4
P10	CPX	A3	52.04	28.67	16.74	3.10	100.56	1.997	.920	.958	.127	4.003	6.4 47.8 45.9
P12	OPX	A9	50.87	30.67	18.32	.00	99.86	1.973	.995	1.059	.000	4.027	.0 51.6 48.4
P12	OPX	A4	50.93	30.88	18.25	.00	100.06	1.973	1.000	1.054	.000	4.027	.0 51.3 48.7
P12	OPX	A10	51.07	30.53	18.23	.00	99.83	1.979	.989	1.053	.000	4.021	.0 51.6 48.4
P12	OPX	A5	50.83	30.88	18.16	.00	99.88	1.973	1.003	1.051	.000	4.027	.0 51.2 48.8

		SI02	FEO	MGO	CAO	TOTAL	SI	FE	MG	CA	TOTAL	WO - EN - FS			
R3	OPX	A5	51.75	28.87	18.50	1.81	100.93	1.976	.922	1.053	.074	4.024	3.6	51.4	45.0
R3	OPX	A12	51.59	28.89	18.44	1.84	100.76	1.974	.925	1.052	.075	4.026	3.7	51.3	45.1
R3	OPX	A11	52.11	28.96	18.65	1.87	101.60	1.976	.918	1.054	.076	4.024	3.7	51.5	44.8
R3	OPX	A16	51.49	28.64	18.39	1.92	100.44	1.975	.919	1.052	.079	4.025	3.9	51.3	44.8
R3	OPX	A13	50.99	27.76	18.26	1.98	98.99	1.981	.901	1.057	.082	4.020	4.0	51.8	44.2
R3	OPX	A14	51.37	28.19	18.28	2.16	100.00	1.977	.907	1.049	.089	4.023	4.4	51.3	44.4
R3	OPX	A6	51.83	28.08	18.79	2.20	100.89	1.974	.895	1.067	.090	4.026	4.4	52.0	43.6
R3	OPX	A9	51.44	28.36	18.41	2.35	100.57	1.971	.909	1.052	.096	4.029	4.7	51.1	44.2
R3	CPX	A1	51.76	16.96	14.14	16.41	99.27	1.986	.544	.809	.675	4.014	33.3	39.9	26.8
R3	CPX	A4	51.34	16.73	13.95	16.38	98.40	1.987	.542	.805	.679	4.013	33.5	39.7	26.7
R3	CPX	A15	52.18	18.05	14.41	15.48	100.12	1.988	.575	.818	.632	4.012	31.2	40.4	28.4
R3	CPX	A17	52.11	17.88	14.62	15.34	99.95	1.986	.570	.831	.627	4.014	30.9	41.0	28.1
R3	CPX	A2	52.36	17.77	14.95	15.30	100.38	1.985	.563	.845	.621	4.015	30.6	41.6	27.8
R3	CPX	A19	51.74	18.61	14.14	15.07	99.56	1.987	.598	.809	.620	4.013	30.6	39.9	29.5
R3	CPX	A10	51.95	17.79	14.50	15.03	99.27	1.992	.570	.829	.617	4.008	30.6	41.1	28.3
R3	CPX	A3	51.72	17.88	14.71	14.98	99.28	1.984	.574	.841	.616	4.016	30.3	41.4	28.2
R3	CPX	A7	52.26	18.30	15.21	14.59	100.35	1.983	.581	.860	.593	4.017	29.2	42.3	28.5
R3	CPX	A8	52.03	18.87	14.62	14.42	99.94	1.987	.603	.832	.590	4.013	29.1	41.1	29.8
202	CPX	A1	48.60	39.36	11.80	.00	99.76	1.974	1.337	.715	.000	4.026	.0	34.8	65.2
202	CPX	A2	48.18	38.49	12.28	.00	98.95	1.968	1.315	.748	.000	4.032	.0	36.3	63.7
202	CPX	A3	47.99	38.82	12.33	.00	99.13	1.961	1.327	.751	.000	4.039	.0	36.2	63.8
202	CPX	A5	48.17	39.97	11.37	.00	99.51	1.970	1.367	.693	.000	4.030	.0	33.6	66.4
202	CPX	A6	47.86	40.11	11.39	.00	99.35	1.964	1.376	.697	.000	4.036	.0	33.6	66.4
202	CPX	A7	48.34	38.66	11.89	.00	98.89	1.977	1.322	.725	.000	4.023	.0	35.4	64.6

APPENDIX 3

A List of Representative Analyses for Olivine, Orthopyroxene,
Clinopyroxene and Garnet Used in Chapter 6

1. Total Fe as FeO
2. When 0.0 wt% is reported for NiO, it was not detected or not analyzed.

	DD4	DD4	DD4	DD4	DD4	DD3	DD3	DD3	DD3	DD3	DD2	DD2	DD2	DD2	DD2	DD2	DD1
	OLI	OPX	CPX	GAR	OLI	OPX	CPX	GAR	OLI	OPX	CPX	GAR	OLI	OPX	CPX	GAR	OLI
SI02	41.12	56.50	54.66	41.87	41.94	57.42	54.72	40.14	41.15	56.69	53.52	40.31	.20	40.66			
TI02	.00	.25	.54	.92	.00	.23	.64	1.36	.00	.27	.84	1.63	57.96	.00			
AL203	.29	2.43	3.85	22.06	.00	1.35	3.55	23.51	.00	1.82	4.54	21.51	.53	.00			
FE0	8.44	4.82	3.17	7.05	9.89	5.85	3.66	8.35	12.59	7.44	4.39	10.19	26.27	12.50			
MNO	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.25	.16	.00			
MGO	50.08	32.66	19.18	20.91	49.70	33.35	18.71	20.05	46.96	31.50	16.85	18.47	13.46	46.91			
CAO	.13	1.56	15.75	5.24	.00	1.27	15.35	5.10	.16	1.62	15.56	5.58	.24	.08			
NA20	.00	.29	1.89	.00	.00	.00	2.03	.00	.00	.31	2.66	.00	.00	.00			
CR203	.00	.35	.97	2.97	.00	.32	1.17	2.08	.00	.32	.96	1.86	1.77	.00			
NIO	.23	.00	.00	.00	.28	.00	.00	.00	.48	.00	.00	.00	.21	.29			
TOTAL	100.29	98.86	100.01	100.12	101.81	99.79	99.83	100.59	101.34	99.97	99.32	99.80	100.80	100.44			
SI	.998	1.962	1.952	2.968	1.008	1.981	1.961	2.855	1.007	1.971	1.940	2.922	.018	1.004			
TI	.000	.007	.014	.049	.000	.006	.017	.073	.000	.007	.023	.089	3.927	.000			
AL	.008	.099	.162	1.843	.000	.055	.150	1.971	.000	.075	.194	1.838	.056	.000			
FE	.171	.140	.095	.418	.199	.169	.110	.497	.258	.216	.133	.618	1.979	.258			
MN	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.015	.012	.000			
MG	1.812	1.691	1.021	2.210	1.780	1.715	1.000	2.126	1.714	1.632	.911	1.996	1.808	1.726			
CA	.003	.058	.603	.398	.000	.047	.589	.389	.004	.060	.604	.433	.023	.002			
NA	.000	.020	.131	.000	.000	.000	.141	.000	.000	.021	.187	.000	.000	.000			
CR	.000	.010	.027	.116	.000	.009	.033	.117	.000	.009	.028	.107	.126	.000			
NI	.004	.000	.000	.000	.005	.000	.000	.000	.009	.000	.000	.000	.015	.006			
TOTAL	2.998	3.986	4.005	8.003	2.992	3.981	4.001	8.028	2.993	3.991	4.020	8.017	7.964	2.996			

	X11 OPX	X11 CPX	X11 GAR	X11 ILM	FF8 OLI	FF8 OPX	FF8 CPX	FF8 GAR	T10 OLI	T10 OPX	T10 CPX	T10 GAR	T11 OLI	T11 OPX
S102	55.21	53.89	41.31	.32	40.60	54.83	53.29	41.19	40.45	54.90	53.22	41.69	39.53	54.71
T102	.00	.63	.68	55.40	.00	.30	.57	.79	.00	.22	.34	.53	.00	.52
AL203	1.89	3.64	21.95	.29	.31	3.63	4.62	21.63	.54	3.76	3.62	22.18	.87	3.22
FE0	7.92	3.78	10.92	28.59	11.76	7.06	3.93	8.18	11.90	6.84	4.41	8.28	12.20	7.66
MNO	.00	.00	.21	.23	.00	.00	.00	.00	.00	.00	.00	.15	.00	.00
MGO	32.75	16.02	18.30	12.01	46.99	31.00	17.50	18.70	47.10	31.80	18.12	19.48	46.45	31.96
CAO	.78	19.44	5.96	.32	.12	1.48	17.03	6.26	.22	1.60	17.86	5.88	.00	1.11
NA20	.00	1.89	.00	.00	.00	.49	1.60	.00	.00	.18	1.39	.00	.28	.26
CR203	.25	1.26	1.53	1.54	.00	.49	1.12	2.62	.00	.76	1.11	2.56	.00	.48
NIO	.00	.00	.00	.43	.24	.00	.00	.00	.22	.00	.00	.00	.40	.00
TOTAL	98.80	100.55	100.86	99.13	100.02	99.28	99.66	99.37	100.43	100.06	100.07	100.75	99.73	99.92
SI	1.945	1.944	2.964	.030	1.003	1.921	1.925	2.971	.996	1.907	1.925	2.963	.984	1.909
TI	.000	.017	.037	3.875	.000	.008	.015	.043	.000	.006	.009	.028	.000	.014
AL	.078	.155	1.856	.032	.009	.150	.197	1.839	.016	.154	.154	1.858	.026	.132
FE	.233	.114	.655	2.224	.243	.207	.119	.494	.245	.199	.133	.492	.254	.224
MN	.000	.000	.013	.018	.000	.000	.000	.000	.000	.000	.000	.009	.000	.000
MG	1.720	.861	1.958	1.666	1.730	1.619	.942	2.011	1.729	1.647	.977	2.064	1.724	1.662
CA	.029	.751	.458	.032	.003	.056	.659	.484	.006	.060	.692	.448	.000	.041
NA	.000	.132	.000	.000	.000	.033	.112	.000	.000	.012	.097	.000	.014	.018
CR	.007	.036	.087	.113	.000	.014	.032	.149	.000	.021	.032	.144	.000	.013
NI	.000	.000	.000	.032	.005	.000	.000	.000	.004	.000	.000	.000	.008	.000
TOTAL	4.013	4.010	8.028	8.022	2.993	4.006	4.001	7.991	2.996	4.005	4.021	8.007	3.010	4.013

	T11	T11	T11	T12	T12	T12	T12	T12	T12	T12	FF7	FF7	FF7	FF7	FF7	FF6	FF6	FF6
	CPX	GAR	ILM	OLI	OPX	CPX	GAR	ILM	OLI	OPX	CPX	GAR	OLI	OPX	CPX	GAR	OLI	OPX
S102	52.68	40.33	1.73	39.93	55.31	52.37	41.05	1.51	40.50	56.02	53.64	41.24	40.04	56.14				
T102	.40	.87	55.63	.00	.16	.46	.94	55.15	.00	.00	.34	.51	.00	.00		.00	.00	.00
AL203	4.00	21.53	.78	.52	2.92	3.97	20.85	.74	.00	1.19	2.62	21.54	.00	1.44		.00	.00	1.44
FEO	4.40	9.01	27.55	12.98	7.71	4.27	9.97	27.78	11.97	7.70	3.82	10.39	12.73	7.77				
MNO	.00	.00	.19	.00	.00	.00	.20	.26	.00	.00	.00	.23	.00	.00		.00	.00	.00
MGO	17.58	18.57	14.01	46.34	31.88	17.36	17.75	13.60	46.72	32.43	17.15	18.01	46.27	32.47				
CAO	17.77	6.84	.30	.00	1.14	18.32	7.06	.27	.00	.70	19.01	5.93	.00	.66		.00	.00	.66
NA20	1.54	.00	.34	.00	.18	1.27	.00	.00	.00	.00	1.33	.00	.00	.00		.00	.00	.00
CR203	.91	3.07	1.66	.00	.44	1.00	2.55	2.99	.00	.32	1.19	2.40	.00	.39		.00	.00	.39
N10	.00	.00	.42	.40	.00	.00	.00	.48	.21	.00	.00	.00	.31	.00		.00	.00	.00
TOTAL	99.28	100.22	102.61	100.17	99.74	99.02	100.37	102.78	99.40	98.36	99.10	100.25	99.35	98.87				
SI	1.921	2.912	.153	.992	1.930	1.917	2.969	.134	1.007	1.976	1.959	2.977	1.001	1.971				
TI	.011	.047	3.703	.000	.004	.013	.051	3.680	.000	.000	.009	.028	.000	.000		.000	.000	.000
AL	.172	1.832	.081	.015	.120	.171	1.777	.077	.000	.049	.113	1.832	.000	.060		.000	.000	.060
FE	.134	.544	2.040	.270	.225	.131	.603	2.062	.249	.227	.117	.627	.266	.228		.000	.000	.228
MN	.000	.000	.014	.000	.000	.000	.012	.020	.000	.000	.000	.014	.000	.000		.000	.000	.000
MG	.956	1.999	1.849	1.716	1.659	.947	1.914	1.799	1.732	1.706	.934	1.938	1.725	1.699		.000	.000	1.699
CA	.694	.529	.028	.000	.043	.718	.547	.026	.000	.026	.744	.459	.000	.025		.000	.000	.025
NA	.109	.000	.058	.000	.012	.090	.000	.000	.000	.000	.094	.000	.000	.000		.000	.000	.000
CR	.026	.175	.116	.000	.012	.029	.146	.210	.000	.009	.034	.137	.000	.011		.000	.000	.011
NI	.000	.000	.030	.008	.000	.000	.000	.034	.004	.000	.000	.000	.006	.000		.000	.000	.000
TOTAL	4.023	8.038	8.074	3.001	4.005	4.016	8.019	8.042	2.993	3.994	4.005	8.011	2.999	3.994				

	FF6	FF6	FF6	T6	T6	T6	T6	T6	T6	T6	T7	T7	T7	T7	T7	T7	T8
	CPX	GAR	ILM	OLI	OPX	CPX	GAR	SPI	OLI	OPX	CPX	GAR	ILM	OLI			
SI02	54.28	41.00	.47	39.97	56.59	53.17	41.61	1.54	40.87	55.01	52.98	42.03	.42	40.68			
TI02	.29	.48	55.55	.00	.00	.00	1.01	4.37	.00	.17	.27	.58	56.45	.00			
AL203	2.52	22.06	.26	.00	2.06	1.93	22.66	13.22	.00	2.54	2.14	21.85	.41	.00			
FEO	3.31	10.58	28.21	11.20	7.25	3.36	9.35	21.68	12.26	7.69	3.81	10.25	27.65	12.22			
MNO	.00	.26	.25	.00	.00	.00	.20	.00	.00	.00	.00	.20	.18	.00			
MGO	16.71	17.85	12.32	48.60	32.48	17.70	18.06	11.11	45.93	31.64	17.18	17.87	12.46	46.95			
CAO	19.48	5.86	.32	.00	.91	20.73	7.08	.23	.00	.81	20.55	6.91	.22	.00			
NA20	1.47	.00	.00	.00	.23	.64	.19	.40	.00	.00	.60	.00	.00	.00			
CR203	1.27	2.36	2.53	.00	.68	1.00	1.23	48.18	.00	.85	.74	2.38	2.30	.00			
NIO	.00	.00	.41	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00			
TOTAL	99.33	100.45	100.32	99.77	100.20	98.53	101.39	100.73	99.06	98.71	98.27	102.07	100.09	99.85			
SI	1.975	2.955	.043	.988	1.959	1.958	2.956	.049	1.019	1.939	1.957	2.981	.038	1.007			
TI	.008	.026	3.833	.000	.000	.000	.054	.105	.000	.005	.008	.031	3.880	.000			
AL	.108	1.874	.028	.000	.084	.084	1.897	.497	.000	.106	.093	1.827	.044	.000			
FE	.101	.638	2.165	.232	.210	.103	.555	.578	.256	.227	.118	.608	2.114	.253			
MN	.000	.016	.019	.000	.000	.000	.012	.000	.000	.000	.000	.012	.014	.000			
MG	.906	1.918	1.685	1.792	1.676	.972	1.912	.528	1.707	1.662	.946	1.890	1.698	1.733			
CA	.759	.453	.031	.000	.034	.818	.539	.008	.000	.031	.813	.525	.022	.000			
NA	.104	.000	.000	.000	.015	.046	.026	.025	.000	.000	.043	.000	.000	.000			
CR	.037	.134	.184	.000	.019	.029	.069	1.214	.000	.024	.022	.133	.166	.000			
NI	.000	.000	.030	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000			
TOTAL	3.997	8.014	8.018	3.012	3.997	4.009	8.020	3.003	2.981	3.992	4.000	8.008	7.976	2.993			

	T8	T8	T8	T8	T9	T9	T9	T9	T9	A2	A2	A2	A7	A7
	OPX	CPX	GAR	SPI	OLI	OPX	CPX	GAR	ILM	OPX	CPX	GAR	OLI	OPX
SI02	56.22	54.37	41.16	.00	40.71	56.34	53.90	41.27	.68	55.69	53.80	43.35	42.28	56.56
TI02	.00	.28	.73	5.89	.00	.00	.29	.81	56.85	.21	.51	.93	.00	.00
AL203	2.16	2.10	21.65	13.30	.14	1.95	2.56	22.95	.50	5.02	6.03	22.39	.45	3.50
FEO	7.53	3.70	9.98	22.72	12.21	7.53	3.50	10.42	27.78	3.17	2.32	3.42	6.56	3.98
MNO	.00	.00	.23	.00	.00	.00	.00	.21	.16	.00	.00	.00	.00	.00
MGO	32.11	17.35	17.47	11.72	46.71	32.52	16.43	16.95	12.56	32.28	21.87	22.31	49.62	32.48
CAO	.61	20.71	6.98	.23	.00	.66	20.80	6.94	.26	2.43	13.11	6.51	.75	2.20
NA20	.00	.93	.00	.18	.00	.00	1.32	.00	.00	.26	1.17	.00	.48	.00
CR203	.56	.87	1.99	45.80	.00	.41	.94	1.75	2.22	.85	1.26	2.68	.15	.63
NIO	.00	.00	.00	.24	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
TOTAL	99.19	100.31	100.19	100.08	99.77	99.41	99.74	101.30	101.01	99.91	100.07	101.59	100.29	99.35
SI	1.964	1.966	2.973	.000	1.008	1.964	1.962	2.948	.061	1.907	1.896	2.990	1.017	1.949
TI	.000	.008	.040	.143	.000	.000	.008	.044	3.865	.005	.014	.048	.000	.000
AL	.089	.089	1.843	.507	.004	.080	.110	1.932	.053	.203	.250	1.820	.013	.142
FE	.220	.112	.603	.614	.253	.220	.107	.622	2.100	.091	.068	.197	.132	.115
MN	.000	.000	.014	.000	.000	.000	.000	.013	.012	.000	.000	.000	.000	.000
MG	1.672	.935	1.881	.565	1.725	1.690	.891	1.805	1.693	1.648	1.149	2.294	1.780	1.668
CA	.023	.802	.540	.008	.000	.025	.811	.531	.025	.089	.495	.481	.019	.081
NA	.000	.065	.000	.011	.000	.000	.093	.000	.000	.017	.080	.000	.022	.000
CR	.015	.025	.114	1.170	.000	.011	.027	.099	.159	.023	.035	.146	.003	.017
NI	.000	.000	.000	.006	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
TOTAL	3.984	4.002	8.009	3.024	2.990	3.990	4.009	7.993	7.968	3.983	3.988	7.978	2.986	3.972

	A7	A7	A4	A4	A4	A5	A5	A5	A5	A5	C2	C2	C2	C2	C2	C2	C4	C4
	CPX	GAR	OPX	CPX	GAR	OPX	CPX	GAR	CPX	GAR	OLI	OPX	CPX	GAR	OPX	CPX		
SI02	52.45	43.41	55.30	53.72	42.74	54.32	52.86	41.79	41.76	56.36	53.87	42.91	58.60	56.97				
TI02	.91	1.06	.15	.67	.84	.65	.93	1.44	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
AL203	7.14	20.99	4.49	4.88	22.14	5.32	5.30	21.77	.00	2.69	3.04	21.24	.97	1.14				
FEO	3.73	5.62	3.38	3.24	5.22	5.45	3.49	6.04	9.16	5.95	3.20	7.10	2.71	2.42				
MNO	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.14	.00	.00	.00	.00	.00	.00
MGO	21.31	21.39	32.49	20.75	21.77	29.52	18.94	21.33	49.14	32.84	18.64	20.36	34.30	24.23				
CAO	11.70	6.35	2.09	13.71	5.82	2.39	14.20	5.90	.21	1.41	18.47	6.39	2.31	13.56				
NA2O	1.55	.42	.55	1.50	.41	.86	2.00	.39	.24	.22	.92	.35	.00	.63				
CR203	1.23	2.23	.70	1.17	2.19	.61	1.43	2.04	.00	.88	1.40	3.64	.56	1.07				
NIO	.00	.00	.00	.00	.00	.00	.00	.00	.42	.00	.00	.00	.00	.00	.00	.00	.00	.00
TOTAL	100.02	101.47	99.15	99.64	101.13	99.12	99.15	100.70	100.93	100.35	99.54	102.13	99.45	100.02				
SI	1.859	3.029	1.911	1.916	2.983	1.898	1.905	2.946	1.011	1.941	1.948	3.006	2.004	2.005				
TI	.024	.056	.004	.018	.044	.017	.025	.076	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
AL	.298	1.726	.183	.205	1.821	.219	.225	1.809	.000	.109	.130	1.754	.039	.047				
FE	.111	.328	.098	.097	.305	.159	.105	.356	.185	.171	.097	.416	.078	.071				
MN	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.008	.000	.000	.000	.000	.000	.000
MG	1.126	2.225	1.674	1.103	2.265	1.538	1.018	2.242	1.773	1.686	1.005	2.127	1.749	1.271				
CA	.444	.475	.077	.524	.435	.089	.548	.446	.005	.052	.716	.480	.085	.511				
NA	.107	.057	.037	.104	.055	.058	.140	.053	.011	.015	.065	.048	.000	.043				
CR	.034	.123	.019	.033	.121	.017	.041	.114	.000	.024	.040	.202	.015	.030				
NI	.000	.000	.000	.000	.000	.000	.000	.000	.008	.000	.000	.000	.000	.000	.000	.000	.000	.000
TOTAL	4.004	8.019	4.003	3.999	8.030	3.996	4.007	8.043	2.995	3.999	3.999	8.040	3.969	3.978				

APPENDIX 4

GARNET LHERZOLITE AND RELATED NODULES
FROM LESOTHO KIMBERLITES

The petrological study of garnet lherzolite and related nodules in Lesotho kimberlites has been referred to in Chapter 6. This appendix presents microprobe analyses of minerals in the nodules and some brief discussion on the chemistry of garnet.

All the samples were collected and donated by A.J.R. White. Samples K1 to K20 are ultramafic nodules with rock types including garnet lherzolite, garnet harzburgite, harzburgite and dunite. Representative microprobe analyses of minerals are listed in Table 1. Garnets in K4, K10, and K14 have been completely broken down to lower-pressure assemblage. Otherwise, all the minerals were analyzed. Thus, Table 1 also shows mineral assemblage of the nodules.

As has been mentioned in Chapter 6, garnet in the granular lherzolites is more calcic than in the sheared lherzolites. The difference in terms of grossular content has been attributed to the comparatively high pressures in the latter. Fig. 1 shows the difference in chemistry as analyzed by Boyd (in Nixon, 1973). It has been reconfirmed by my probe analyses (Fig. 2).

Another aspect consistently observed in both the figures is that the garnet compositions from the sheared type lherzolites are plotted off the ideal stoichiometry join of garnet towards the pyroxene side, while those from the granular lherzolites are almost on the join. One interpretation is that compositions lie off the join because of the possible presence of ferric iron which should have been incorporated with Al_2O_3 in constructing both the figures. An alternative interpretation is that the low- Al_2O_3 compositions are due to real solubility of pyroxene components in garnet solid solution. Two experimental studies relevant to this topic are available in the literature. Firstly, Ringwood (1967) found a sudden increase of MgSiO_3 solubility in garnet at around 100 kbar. He interprets the results as a formation of a garnet with a composition of $\text{Mg}_{3.5}\text{AlSi}_{3.5}\text{O}_{12}$.

Table 1

Microprobe analyses of minerals of peridotitic inclusions from kimberlite pipes in Lesotho. Analyses presented are of all of the coarse-grained 'primary' constituents of the peridotite inclusions and do not include components of kelyphitic alterations of garnets. Although it is coarse-grained, the petrographic identification of phlogopite as primary or secondary is not obvious.

Correlation between sample numbers in this table and those of La Trobe University, and localities are as follows:

Thesis	La Trobe	Locality	Thesis	La Trobe	Locality
K1	2044	Liqhobong	K11	2081	Mothae
K2	2053	Thaba Putsoa	K12	2082	Mothae
K3	2067	Letseng-la-terae	K13	2023	Kao
K4	2068	Letseng-la-terae	K14	2030	Kao
K5	2072	Mothae	K15	2037	Liqhobong
K6	2040	Liqhobong	K16	2056	Thaba Putsoa
K7	2050	Thaba Putsoa	K17	2069	Mothae
K8	2057	Thaba Putsoa	K18	2075	Mothae
K9	2058	Thaba Putsoa	K19	2086	Mothae
K10	2074	Mothae	K20	2093	Mothae

	K4	K4	K4	K5	K5	K5	K5	K6	K6	K6	K6	K6	K7	K7	K7	K7
	OLI	OPX	CPX	OLI	OPX	CPX	GAR	OLI	OPX	GAR	SP1	OLI	OPX	CPX		
SI02	39.98	57.01	54.55	41.94	58.97	55.26	42.53	42.51	58.33	42.79	.41	40.96	58.45	54.44		
TI02	.00	.00	.00	.00	.00	.00	.10	.00	.00	.00	.00	.00	.00	.00	.00	.00
AL203	.00	.35	1.96	.00	.38	1.14	20.55	.00	1.53	20.35	33.45	.00	.16	.76		
FE0	12.28	7.25	3.83	7.59	4.56	2.00	6.87	4.66	3.04	5.87	9.04	8.95	4.77	2.41		
MNO	.00	.00	.00	.00	.00	.00	.44	.00	.00	.35	.00	.00	.00	.00	.00	.00
MGO	46.77	33.27	16.24	51.28	35.54	17.32	20.81	52.75	36.86	24.83	18.63	48.94	35.59	15.99		
CA0	.00	.46	19.17	.00	.36	20.81	5.77	.00	.06	.42	.07	.00	.27	18.50		
NA20	.00	.00	1.70	.00	.00	1.07	.00	.00	.00	.00	.00	.00	.00	1.84		
K20	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.01		
CR203	.00	.11	1.52	.00	.26	1.40	4.90	.00	.34	6.43	38.62	.00	.21	3.92		
NI0				.39												
TOTAL	99.03	98.45	98.97	101.20	100.07	99.00	101.97	99.92	100.16	101.04	100.22	98.85	99.45	97.87		
SI	1.000	2.001	1.996	1.005	2.009	2.009	2.990	1.015	1.974	2.988	.012	1.009	2.007	2.012		
TI	.000	.000	.000	.000	.000	.000	.005	.000	.000	.000	.000	.000	.000	.000	.000	.000
AL	.000	.014	.085	.000	.015	.049	1.703	.000	.061	1.675	1.117	.000	.006	.033		
FE	.257	.213	.117	.152	.130	.061	.404	.093	.086	.343	.214	.184	.137	.074		
MN	.000	.000	.000	.000	.000	.000	.026	.000	.000	.021	.000	.000	.000	.000	.000	.000
MG	1.744	1.741	.886	1.831	1.805	.939	2.181	1.877	1.859	2.585	.787	1.797	1.822	.881		
CA	.000	.017	.752	.000	.013	.811	.435	.000	.002	.031	.002	.000	.010	.733		
NA	.000	.000	.121	.000	.000	.075	.000	.000	.000	.000	.000	.000	.000	.132		
K	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
CR	.000	.003	.044	.000	.007	.040	.272	.000	.009	.355	.865	.000	.006	.115		
NI				.008												
TOTAL	3.000	3.990	4.000	2.995	3.980	3.984	8.017	2.985	3.991	7.997	2.997	2.991	3.987	3.980		

	K7	K8	K8	K8	K8	K8	K9	K10	K10	K10	K11	K11	K11	K11	K12
	MIC	OLI	OPX	CPX	ILM	OLI	OLI	OLI	CPX	OPX	OLI	OPX	CPX	GAR	OLI
SI02	42.10	39.99	56.11	54.64	.00	40.17	41.02	58.07	54.76	41.82	58.41	55.39	42.68		42.16
TI02	.17	.00	.33	.77	52.67	.00	.00	.13	.38	.00	.00	.00	.56		.00
AL203	11.81	.00	1.62	1.50	.37	.00	.00	.66	2.14	.00	.61	1.76	21.34		.00
FEO	2.83	14.18	8.81	5.51	31.63	12.62	11.09	6.66	4.25	9.43	5.63	3.42	7.86		8.11
MNO	.00	.00	.00	.00	.23	.00	.00	.00	.00	.00	.00	.00	.27		.00
MGO	25.61	45.58	31.56	17.70	12.46	46.48	48.10	33.43	18.47	49.49	34.23	18.92	21.41		50.12
CAO	.00	.00	.79	18.50	.10	.00	.00	1.01	16.02	.00	.98	17.80	4.95		.00
NA20	.00	.00	.00	1.05	.00	.00	.00	.00	1.63	.00	.00	1.18	.00		.00
K20	10.11	.00	.00	.00	.06	.00	.00	.00	.00	.00	.00	.00	.00		.00
CR203	.49	.00	.23	1.07	2.83	.00	.00	.32	1.39	.00	.20	.88	3.12		.00
TOTAL	93.12	99.75	99.45	100.74	100.35	99.27	100.21	100.28	99.04	100.74	100.06	99.35	102.19		100.39
SI	3.304	1.001	1.967	1.973	.000	1.003	1.006	1.998	1.987	1.012	2.003	1.999	2.984		1.017
TI	.010	.000	.009	.021	3.696	.000	.000	.003	.010	.000	.000	.000	.029		.000
AL	1.092	.000	.067	.064	.041	.000	.000	.027	.092	.000	.025	.075	1.758		.000
FE	.186	.297	.258	.166	2.468	.264	.228	.192	.129	.191	.162	.103	.460		.164
MN	.000	.000	.000	.000	.018	.000	.000	.000	.000	.000	.000	.000	.016		.000
MG	2.996	1.701	1.650	.953	1.733	1.730	1.759	1.715	.999	1.785	1.750	1.018	2.231		1.802
CA	.000	.000	.030	.716	.010	.000	.000	.037	.623	.000	.036	.688	.371		.000
NA	.000	.000	.000	.073	.000	.000	.000	.000	.115	.000	.000	.083	.000		.000
K	1.012	.000	.000	.000	.007	.000	.000	.000	.000	.000	.000	.000	.000		.000
CR	.030	.000	.006	.031	.209	.000	.000	.009	.040	.000	.005	.025	.172		.000
TOTAL	8.631	2.999	3.987	3.996	8.183	2.997	2.994	3.981	3.994	2.988	3.981	3.992	8.021		2.983

	K12	K12	K12	K13	K13	K14	K14	K14	K14	K14	K14	K14	K15	K15	K15	K15	K16
	OPX	CPX	GAR	OLI	OPX	OLI	OPX	CPX	SPI	OLI	OPX	CPX	OLI	OPX	CPX	GAR	OLI
S102	58.28	55.74	42.68	41.11	58.68	41.26	58.31	54.50	.00	41.74	58.70	55.12	42.18	41.93			
T102	.14	.30	.23	.00	.00	.00	.00	.00	.23	.00	.00	.00	.00	.00	.00	.00	.00
AL203	.51	1.98	19.65	.00	.26	.00	.36	1.75	9.90	.00	.53	2.65	20.55	.00			
FEO	4.90	3.09	6.94	7.34	4.46	7.28	4.61	2.07	18.75	6.77	4.18	1.82	6.21	7.69			
MNO	.00	.00	.20	.00	.00	.00	.00	.00	.47	.00	.12	.00	.20	.00			
MGO	34.29	18.51	21.11	50.44	35.73	50.59	35.61	16.43	12.52	51.13	35.58	16.19	21.43	51.07			
CAO	.93	17.55	5.07	.00	.37	.00	.36	19.42	.23	.00	.44	18.00	4.77	.00			
NA20	.00	1.56	.00	.00	.00	.00	.00	1.70	.00	.00	.00	2.16	.00	.00			
K20	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00			
CR203	.17	1.31	4.77	.00	.29	.00	.31	2.48	58.07	.00	.34	2.27	4.75	.00			
TOTAL	99.22	100.04	100.65	98.89	99.79	99.13	99.56	98.35	100.17	99.64	99.89	98.21	100.09	100.69			
SI	2.009	1.997	3.031	1.005	2.006	1.006	2.000	1.997	.000	1.010	2.003	2.009	3.000	1.008			
TI	.004	.008	.012	.000	.000	.000	.000	.000	.006	.000	.000	.000	.000	.000			
AL	.021	.084	1.645	.000	.010	.000	.015	.076	.383	.000	.021	.114	1.722	.000			
FE	.141	.093	.412	.150	.127	.148	.132	.063	.515	.137	.119	.055	.369	.155			
MN	.000	.000	.012	.000	.000	.000	.000	.000	.013	.000	.003	.000	.012	.000			
MG	1.762	.989	2.235	1.839	1.820	1.839	1.821	.898	.613	1.844	1.810	.880	2.272	1.830			
CA	.034	.674	.386	.000	.014	.000	.013	.763	.008	.000	.016	.703	.363	.000			
NA	.000	.108	.000	.000	.000	.000	.000	.121	.000	.000	.000	.153	.000	.000			
K	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000			
CR	.005	.037	.268	.000	.008	.000	.008	.072	1.509	.000	.009	.065	.267	.000			
TOTAL	3.975	3.989	8.001	2.995	3.985	2.994	3.989	3.989	3.048	2.990	3.982	3.978	8.006	2.992			

	K16	K16	K16	K16	K17	K17	K17	K17	K17	K17	K18	K18	K18	K18	K18	K18
	OPX	CPX	GAR	MIC	OLI	OPX	GAR	SPI	MIC	OLI	OPX	CPX	GAR	SPI		
S102	58.23	54.26	42.27	39.95	42.45	58.64	42.14	.00	38.56	41.66	58.50	54.79	42.26	.00		
T102	.00	.00	.00	.13	.00	.00	.00	.13	1.97	.00	.00	.00	.00	.34		
AL203	.50	.68	21.27	13.60	.00	1.10	21.23	25.00	17.09	.00	.30	3.83	21.07	13.75		
FEO	4.69	1.64	7.22	2.50	5.95	3.67	6.59	13.44	3.91	6.93	4.24	1.97	6.81	18.35		
MNO	.00	.00	.41	.00	.00	.00	.32	.00	.00	.00	.00	.00	.40	.00		
MGO	35.58	16.69	20.44	25.09	52.79	36.36	23.11	16.18	22.18	51.34	36.07	13.73	21.38	13.35		
CAO	.25	23.30	5.56	.22	.00	.16	2.66	.12	.14	.00	.22	17.22	4.28	.30		
NA2O	.00	.37	.00	.00	.00	.00	.00	.00	.00	.00	.00	3.35	.00	.00		
K2O	.00	.00	.00	8.71	.00	.00	.00	.00	9.60	.00	.00	.00	.00	.00		
CR203	.32	1.84	4.11	1.03	.00	.33	4.64	48.70	1.02	.00	.20	3.97	4.33	57.25		
TOTAL	99.57	98.78	101.28	91.23	101.19	100.26	100.69	103.57	94.47	99.93	99.53	98.86	100.53	103.34		
SI	1.997	1.991	2.987	3.182	1.007	1.987	2.968	.000	3.002	1.006	2.002	1.994	2.994	.000		
TI	.000	.000	.000	.008	.000	.000	.000	.003	.115	.000	.000	.000	.000	.008		
AL	.020	.029	1.771	1.277	.000	.044	1.762	.856	1.568	.000	.012	.164	1.759	.505		
FE	.135	.050	.427	.167	.118	.104	.388	.327	.255	.140	.121	.060	.403	.478		
MN	.000	.000	.025	.000	.000	.000	.019	.000	.000	.000	.000	.000	.024	.000		
MG	1.819	.913	2.153	2.979	1.867	1.837	2.426	.701	2.575	1.848	1.840	.745	2.258	.621		
CA	.009	.916	.421	.019	.000	.006	.201	.004	.012	.000	.008	.671	.325	.010		
NA	.000	.026	.000	.000	.000	.000	.000	.000	.000	.000	.000	.236	.000	.000		
K	.000	.000	.000	.885	.000	.000	.000	.000	.954	.000	.000	.000	.000	.000		
CR	.009	.053	.230	.065	.000	.009	.258	1.119	.063	.000	.005	.114	.243	1.411		
TOTAL	3.989	3.980	8.013	8.582	2.993	3.987	8.022	3.010	8.543	2.994	3.989	3.985	8.006	3.034		

	K19	K19	K19	K19	K20	K20	K20
	OLI	OPX	GAR	SPI	OLI	OPX	SPI
S102	41.90	57.97	42.01	1.41	41.64	57.82	.16
T102	.00	.00	.00	.21	.00	.00	.23
AL203	.00	.81	21.26	21.57	.00	.50	13.73
FEO	6.75	4.45	7.29	14.08	6.88	4.34	16.47
MNO	.00	.00	.50	.00	.00	.00	.34
MGO	50.33	35.94	19.82	16.07	50.85	35.61	12.77
CAO	.00	.17	5.85	.19	.00	.18	.14
NA20	.00	.00	.00	.00	.00	.00	.00
K20	.00	.00	.00	.00	.00	.00	.00
CR203	.21	.27	3.38	47.03	.00	.25	56.47
TOTAL	99.19	99.61	100.11	100.56	99.37	98.70	100.31
SI	1.017	1.986	3.002	.042	1.010	1.997	.005
TI	.000	.000	.000	.005	.000	.000	.006
AL	.000	.033	1.790	.765	.000	.020	.517
FE	.137	.127	.436	.354	.140	.125	.440
MN	.000	.000	.030	.000	.000	.000	.009
MG	1.822	1.835	2.111	.721	1.840	1.833	.608
CA	.000	.006	.448	.006	.000	.007	.005
NA	.000	.000	.000	.000	.000	.000	.000
K	.000	.000	.000	.000	.000	.000	.000
CR	.004	.007	.191	1.118	.000	.007	1.427
TOTAL	2.981	3.994	8.008	3.011	2.990	3.990	3.017

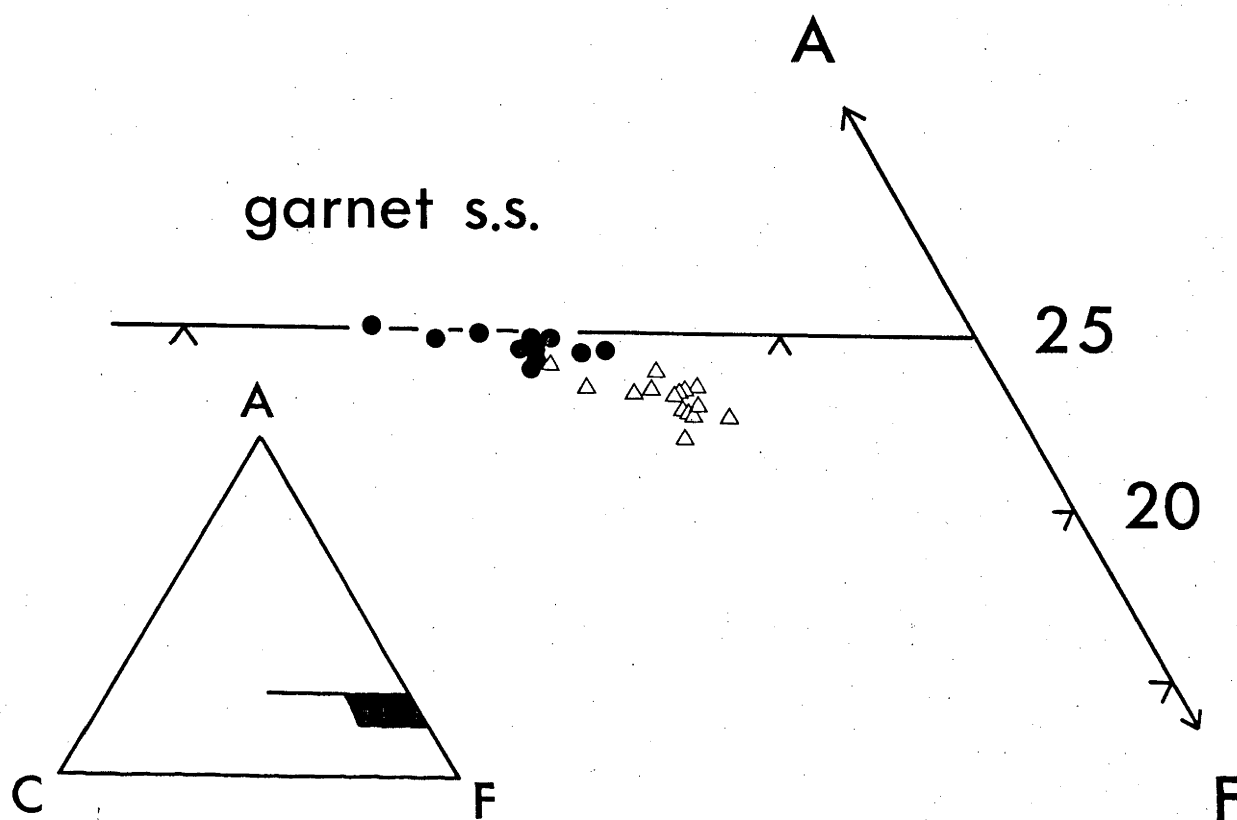


Fig. 1 ACF-plot of garnets in Lesotho lherzolites. All the data are of Boyd (in Nixon, 1973). Circle : garnet in granular type lherzolite. Triangle : garnet in sheared type lherzolite.

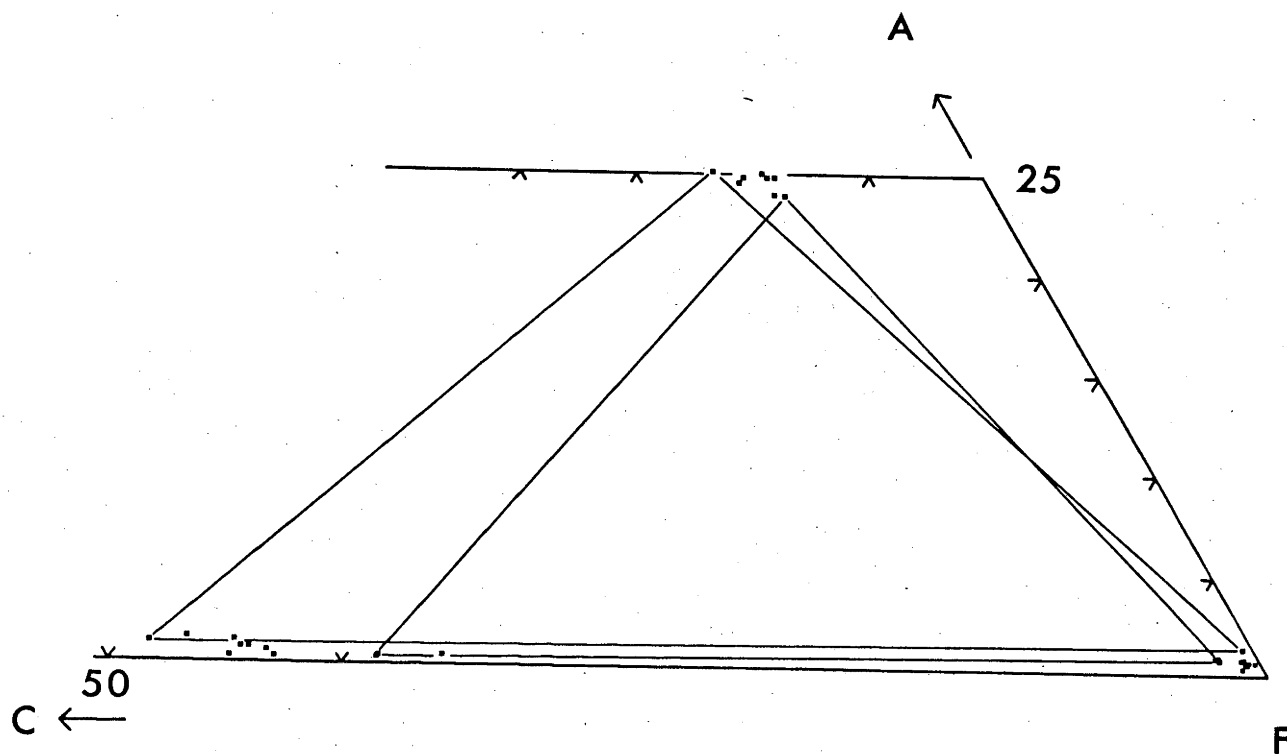


Fig. 2 ACF-plot of garnet, orthopyroxene and clinopyroxene. Data are from Table 1. The two garnet compositions off the garnet solid solution join and rich in F-component are of sheared type lherzolites.

The second experimental study is on the join $\text{FeSiO}_3\text{-Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (Akimoto and Akaogi, 1975, Akaogi, personal communication, 1975). They found steady increase of FeSiO_3 solubility in garnet with increasing pressure above 60 kbar. These two lines of observation are somewhat inconsistent, but at least show that high pressure is necessary for the solubility of pyroxene components in garnet. Therefore, the systematic deviation of the garnet composition from the stoichiometry join may possibly attributed to the higher pressure for the sheared lherzolites and relatively lower pressure for the granular ones.

It should be noted, however, that the experiments may not be directly comparable to the Lesotho garnet lherzolites since it is Ca-free clinopyroxene which coexists with garnet in the experiments instead of orthopyroxene as is the case in the lherzolites. The inference of higher solubility of pyroxene components in garnet at relatively high pressures would probably be still valid because of little difference in thermodynamic properties between orthopyroxene and Ca-free clinopyroxene. In addition, the occurrence of orthopyroxene in the sheared garnet lherzolites implies that the Ca-free clinopyroxene consistently found in laboratories at around 60 kbar and above are formed under relatively high stress (Coe and Kirby, 1975) which is inevitably associated with the high pressure devices to produce such high pressures. Stable phase under hydrostatic condition may be orthopyroxene instead of Ca-free clinopyroxene.

REFERENCES

- Akimoto, S., and Akaogi, M., 1975. Mg-Fe partition between silicate spinel and garnet in the transition zone of the Earth's mantle. Abstracts, The interdisciplinary symposia, IUGG, XVI general assembly, 7-8.
- Coe, R.S., and Kirby, S.H., 1975. The orthoenstatite to clinoenstatite transformation by shearing and reversion by annealing: mechanism and potential applications. Contrib. Mineral. Petrol. 52, 29-55.
- Nixon, P.H., ed., 1973. Lesotho kimberlites. Maseru, Lesotho, Lesotho National Development Corp. 350 p.
- Ringwood, A.E., 1967. The pyroxene-garnet transformation in the Earth's mantle. Earth Planet. Sci. Lett. 2, 255-263.

APPENDIX 5

The Iron-Magnesium Partitioning between Naturally Occurring
Coexisting Olivine and Ca-rich Clinopyroxene : An Application
of the Simple Mixture Model to Olivine Solid Solution

M. Obata, S. Banno and T. Mori

The iron-magnesium partitioning between naturally occurring coexisting olivine and Ca-rich clinopyroxene : an application of the simple mixture model to olivine solid solution

by MASAOKI OBATA,

Dept. Earth and Planetary Sciences, M. I. T. Cambridge, Mass. 02139 U. S. A.

SHOHEI BANNO,

Dept. Earth Sciences, Kanazawa University, Kanazawa 920 Japan.

and TAKESHI MORI,

Research School of Earth Sciences, The Australian National University, Canberra, A. C. T. Australia 2600.

Abstract. — The partitioning of Fe and Mg between olivine and Ca-rich clinopyroxene was treated applying simple mixture and ideal solution models to olivine and clinopyroxene, respectively. The relation between partition coefficient, K and apparent partition coefficient, K' is written :

$$\ln K = \ln K' + \frac{W^{ol}}{RT} (1 - 2X)$$

where W^{ol} is a thermodynamic parameter which depends on temperature and pressure, and X is Fe/(Fe + Mg) ratio of olivine. Using published experimental data on W^{ol} at different physical conditions, the temperature dependence of W^{ol} was examined. Although the physical meaning of temperature dependence of W^{ol} term is not well understood, the apparent partition coefficient between olivine and clinopyroxene is sensitive to temperature through a big temperature dependence of W^{ol} , and hence this partitioning is an useful geothermometer especially at low temperature.

Partage de Fe-Mg entre olivine et clinopyroxène calcique coexistants dans la nature : une application du modèle de simple mélange à la solution solide de l'olivine.

Résumé. — Le partage de Fe et Mg entre olivine et clinopyroxène calcique a été interprété en appliquant des modèles de simple mélange pour l'olivine et de solution idéale pour le clinopyroxène. La relation entre le coefficient de partage, K et le coefficient de partage apparent, K' s'écrit :

$$\ln K = \ln K' + \frac{W^{ol}}{RT} (1 - 2X)$$

où W^{ol} est un paramètre thermodynamique dépendant de la température et de la pression, et X est le rapport Fe/(Fe + Mg) dans l'olivine. En utilisant les données expérimentales publiées sur W^{ol} avec la température a été examinée. Bien que la signification physique du terme W^{ol} ne soit pas bien comprise, le coefficient de partage apparent entre olivine et clinopyroxène est sensible à la température à cause d'une grande dépendance de W^{ol} de la température, et donc, ce coefficient de partage est un géothermomètre utile, spécialement à basse température.

INTRODUCTION.

Fe-Mg partitioning between coexisting olivine and Ca-rich clinopyroxene (herein called simply clinopyroxene) has received little attention, although this parameter has been proposed as an empirical geothermometer (James, 1971; Mori and Banno, 1973).

If the thermodynamics of the Fe-Mg partitioning between olivine and orthopyroxene, and between

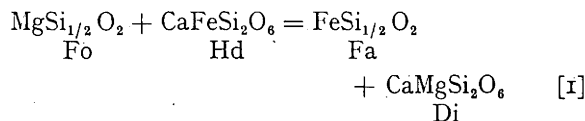
clino- and orthopyroxenes could be understood, the partitioning between olivine and clinopyroxene would be uniquely determined. However, in spite of extensive studies on the thermodynamics of olivine and pyroxenes, we are still far from quantitative understanding of those properties. In this context, the partitioning of Fe and Mg between olivine and clinopyroxene may be used to examine the internal consistency of the available thermodynamic data. In the following, brief review of the

available thermodynamic data of olivine and pyroxenes relevant to the present problem will be followed by an attempt to explain the Fe-Mg partitioning between naturally occurring coexisting olivine and clinopyroxene.

THERMODYNAMIC CONSIDERATIONS.

Partition coefficient.

The Fe-Mg partition between olivine and clinopyroxene is expressed :



Thermodynamic partition coefficient $K_{\text{Fe-Mg}}^{\text{ol-cpx}}$ for this exchange reaction is defined :

$$\begin{aligned} K_{\text{Fe-Mg}}^{\text{ol-cpx}} &= \left(\frac{a_{\text{Fe}}}{a_{\text{Mg}}} \right)^{\text{ol}} / \left(\frac{a_{\text{Fe}}}{a_{\text{Mg}}} \right)^{\text{cpx}} \\ &= K'_{\text{Fe-Mg}}^{\text{ol-cpx}} \left(\frac{\gamma_{\text{Fe}}}{\gamma_{\text{Mg}}} \right)^{\text{ol}} / \left(\frac{\gamma_{\text{Fe}}}{\gamma_{\text{Mg}}} \right)^{\text{cpx}} \end{aligned} \quad [2]$$

where a and γ denote activity and activity coefficient, $K'_{\text{Fe-Mg}}^{\text{ol-cpx}}$ called apparent partition coefficient in this paper, is defined in terms of the overall atomic fraction of minerals, X :

$$K'_{\text{Fe-Mg}}^{\text{ol-cpx}} = \left(\frac{X_{\text{Fe}}}{X_{\text{Mg}}} \right)^{\text{ol}} / \left(\frac{X_{\text{Fe}}}{X_{\text{Mg}}} \right)^{\text{cpx}} \quad [3]$$

The super- and subscripts to K and K' may be dropped wherever no confusion occurs. The partition coefficient K is related to ΔG , the free energy change of the reaction [1], as follows :

$$\ln K = -\Delta G/RT \quad [4]$$

Available thermodynamic properties of the relevant solid solutions are insufficient to apply sophisticated expressions of the non-ideal terms that appear in eq. [2], and hence, we use a crude approach of expressing the solid solutions in terms of the simple mixture in the sense of Guggenheim (1967). The eq. [2] may be rewritten as follows :

$$\begin{aligned} \ln K &= \ln K' + \frac{W^{\text{ol}}}{RT} (1 - 2X_{\text{Fe}}^{\text{ol}}) \\ &\quad - \frac{W^{\text{cpx}}}{RT} (1 - 2X_{\text{Fe}}^{\text{cpx}}) \end{aligned} \quad [5]$$

where W may be a function of temperature. Application of the Fe-Mg partitioning to geology as a geothermometer requires the expression of $\ln K'$ (the parameter obtained by chemical analysis of minerals) to be a function of temperature, pressure and overall compositions of minerals, and hence we need the expressions of $\ln K$, W^{ol} , and W^{cpx} .

Available thermodynamic data of olivine and pyroxenes : The experimental data relevant to the thermodynamics of Fe-Mg olivine has been published by Nafziger and Muan (1967), Larimer (1968), Medaris (1968), Kitayama and Katsura (1968), Matsui and Nishizawa (1972) and Nafziger (1973). Non-ideality of olivine at high temperatures has been suggested by these authors except Medaris. Most of the available experimental data are based on the Fe-Mg partitioning between olivine and orthopyroxene, and hence the estimation of the non-ideality of olivine is based on that of orthopyroxene.

Nafziger and Muan (1967) considered that orthopyroxene is nearly ideal, or slightly positively deviated from Raoult's law. Kitayama and Katsura (1968) and Williams (1971), however, considered that orthopyroxene is distinctively positively non-ideal, and more positive than olivine. As will be shown later, the data on coexisting olivine and orthopyroxene preclude the possibility that orthopyroxene is more positively non-ideal than olivine. Virgo and Hafner (1969) showed that, except for Fe-rich portion of the series, the site preference of Fe and Mg over the M1 and M2 structural sites of orthopyroxene can be explained by the intracrystalline partitioning of ideally double sited minerals. Saxena and Ghose (1971) obtained the similar temperature dependence of the site preference to that obtained by Virgo and Hafner below 800°C. They derived activity-composition relations in orthopyroxene from what they believe partial activities of Fe and Mg at the two sites, which were approximated to be simple mixtures, and showed that orthopyroxene is nearly ideal at 900°C although it is still a little asymmetric. This suggest that positive excess mixing free energy for each site and negative excess mixing free energy due to site preference are of same order and cancel with one another near 900°C. Navrotsky (1971) calculated the excess mixing free energy due to cation ordering for ideally-double sited orthopyroxene. Matsui and Nishizawa (1972) favor the model of orthopyroxene being less non-ideal than expected from the ideally double sited model. Recently, Nafziger (1973) considered that olivine is more positively non-ideal than orthopyroxene and that orthopyroxene is nearly ideal.

The Fe-Mg partitioning between clino- and orthopyroxenes from granulite facies terrains has been demonstrated by Binns (1962) and Davidson (1969), and this has been interpreted in terms of the partitioning between ideal clinopyroxene and ideally-double sited orthopyroxene by Banno and Matsui (1966).

Thermodynamic properties of clinopyroxene are not well known. The Fe-Mg partitioning between garnet and clinopyroxene has been considered to be nearly ideal by many authors (Saxena, 1968; Banno, 1970; Mysen and Heier, 1972). In the crystal structure of clinopyroxene, M2 site is mostly occupied by calcium ion. Therefore, the non-ideality due to Fe-Mg site preference is not expected

TABLE I.

In $K^{\text{ol-opx}}$ and W^{ol} values calculated on two alternative models of orthopyroxene.

No correction for pressure is made except at 1 000° C.

T (° C)	ln $K^{\text{ol-opx}}$ W^{ol}/RT W^{ol} (kcal)			ln $K^{\text{ol-opx}}$ W^{ol}/RT W^{ol} (kcal)			REFERENCES
800	0.40	0.66	1.4	0.46	0.38	0.82	Medaris (1969)
900	0.32	0.21	0.49	0.37	— 0.01	— 0.02	—
1 000 (*)	0.32	0.24	0.6				Matsui and Nishizawa (1972)
1 100	0.28	0.19	0.52	0.35	0.55	0.14	Larimer (1969)
1 200	0.25	0.17	0.50	0.27	0.01	0.03	—
1 200 (**)	0.13		0.27	0.19		0.05	Nafziger and Muan (1967)
1 300	0.27	0.18	0.57	0.29	0.02	0.06	Larimer (1969)

(*) Quoted from Matsui and Nishizawa (1972), corrected for pressure.

(**) Calculated using the data determined by X-ray only.

to be as large as that of orthopyroxene. It is also possible that positive mixing enthalpy for clinopyroxene is comparable to that for orthopyroxene and that in the Fe-Mg partitioning for this pairs, the positive non-ideal terms of both pyroxenes cancel each other leaving the residual non-ideal term to the site preference in orthopyroxene. Considering the above arguments, the thermodynamic properties of orthopyroxene probably lie between those of the ideal and ideally double-sited models.

Estimates of W^{ol} from experimental data: The W^{ol} value of olivine may be calculated from available experimental data on the Fe-Mg partitioning between olivine and orthopyroxene using the following equation :

$$\ln K_{\text{Fe-Mg}}^{\text{ol-opx}} = \ln K_{\text{Fe-Mg}}^{\text{ol-opx}} + \frac{W^{\text{ol}}}{RT} (1 - 2 X_{\text{Fe}}^{\text{ol}}) - \ln \left(\frac{\gamma_{\text{Fe}}}{\gamma_{\text{Mg}}} \right)^{\text{opx}} \quad [6]$$

For an ideal orthopyroxene model, the last term of equation [6] is zero. For the ideally double-sited model, this term may be calculated using the following activity-composition relationship :

$$a_{\text{Fe}}^2 = X_{\text{Fe}} - \frac{\rho^2}{2} + \rho \sqrt{X_{\text{Fe}}^2 - X_{\text{Fe}} - \frac{\rho^2}{4}} \quad [7]$$

where

$$\rho = \frac{1 + Ki}{1 - Ki} \quad [8]$$

Ki is called the internal partition coefficient, which is defined by denoting the atomic fractions of Fe and Mg in M_1 and M_2 sites by $X_{\text{Fe}}^{M_1}$ etc. :

$$Ki = \left(\frac{X_{\text{Fe}}}{X_{\text{Mg}}} \right)^{M_1} / \left(\frac{X_{\text{Fe}}}{X_{\text{Mg}}} \right)^{M_2} \quad [9]$$

and X_{Fe} in the equation is the average atomic fraction of Fe :

$$X_{\text{Fe}} = \frac{X_{\text{Fe}}^{M_1} + X_{\text{Fe}}^{M_2}}{2} \quad [10]$$

The temperature dependence of the internal partition coefficient, Ki was obtained from the data of Virgo and Hafner (1969), excluding the 500° C data :

$$\ln Ki = 1.35 \times 10^3/T + 0.345 \quad [11]$$

The W^{ol} values were calculated by least square method using equation [6] based on the two limiting models for orthopyroxene (Table I). The standard deviations of $\ln K$ and W^{ol} do not differ much between two alternative models of orthopyroxene, suggesting that these experimental data are not sufficient enough to determine the non-ideal parameters of olivine and orthopyroxene simultaneously. In Table I, the data by Medaris (1969) at 800° C are also included. Although Medaris considered his 800° C data indicated disequilibrium, there is no sound reason to think so if we abandon his assumption that olivine is ideal and orthopyroxene is ideally double sited. In Table I, it is seen that the W^{ol} values estimated on ideally double sited model of orthopyroxene are about 0.4 to 0.6 kcal smaller than those on ideal model of orthopyroxene.

In contrast to high temperature Fe-Mg partitioning experiments, Schullien *et al.* (1970) examined the Fe-Mg partitioning between olivine and chloride solution, which indicates a distinct nonideal behavior of olivine solid solution at low temperature and a probable unmixing of olivine below 450° C. Saxena (1972) calculated W^{ol} values from these data assuming that both olivine and chloride solutions are simple mixtures. The W^{ol} value thus obtained has strong temperature dependence and olivine is almost ideal as low as 650° C. This un-

likely result may be due to the application of the simple mixture model to an electrolyte aqueous solution. The W^{ol} value near 450° C, however, does not depend much upon the model used for chloride solution as long as the simple mixture model for olivine is accepted since W^{ol} is equal to $2RT$ at critical temperature.

Summarizing these data (Fig. 1), a strong temperature dependence of W^{ol} has to be accepted, i. e., the W^{ol} value decreases rapidly with increasing temperature, but above 1000° C, W^{ol} is almost constant and olivine is nearly ideal. The tempera-

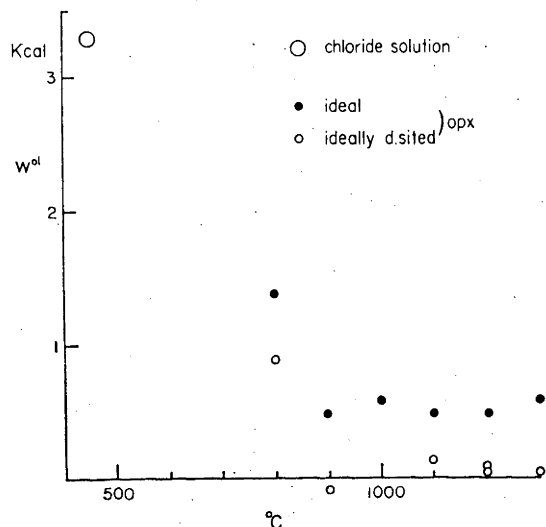


FIG. 1. — The relation between W^{ol} , calculated on the assumptions given in the text, and temperature.

ture dependence of the W term with negative slope has been observed in a few solid solutions such as NaCl-KCl and alkali feldspar (Thompson and Waldbaum, 1969 *a*, 1969 *b*), for which more elaborate theoretical treatments have been applied by introducing asymmetric excess free energy. It is generally expected that non-ideality of solid solution decreases with increasing temperature, but temperature dependence of $\partial W / \partial T$ cannot be easily explained. If the physical meaning of the W term can be interpreted by analogy to the strict regular solution, this term corresponds to the free energy difference between like and unlike pairs of substituting cations, but this analogy cannot explain the strong temperature dependence of $\partial W / \partial T$ unless some kind of second order transition is involved. Fe-Mg cation ordering between M1 and M2 sites in olivine were examined by several authors using X-ray diffraction method (Birle *et al.*, 1968; Finger, 1970; Finger and Virgo, 1971), electronic absorption spectroscopy (Bush *et al.*, 1970; Virgo and Hafner, 1972). Virgo and Hafner reported cation disordering in olivine after heating ordered natural olivine at 1155° C. However, Smyth and Hanzon (1973) demonstrated by high temperature X-ray crystal structure refinements that the

degree of cation ordering increases with increasing temperature. At this stage, the mechanism of Fe-Mg ordering in olivine is not clear yet, but its contribution to non-ideality cannot be expected to be as large as that in orthopyroxene.

Apparently, the symmetric simple mixture model is too crude, and the excess exchange entropy term for like and unlike pairs of substituting cations may have to be taken into account to discuss the physical meaning of the apparent temperature dependence of W^{ol} term obtained here.

GEOLOGIC APPLICATIONS.

Natural olivine-clinopyroxene pairs: Among the available data of natural olivine-clinopyroxene pairs, those from Norwegian garnet lherzolites and associated rocks (O'Hara and Mercy, 1963; Carswell, 1968) cover a wide compositional range and show a systematic variation of K^{ol-cpx} with the chemistry of the rocks (Fig. 2). It is assumed here that nearly all iron in clinopyroxene is divalent, based on the Mössbauer spectroscopy of a diopside from the Mt. Higasi-Akai peridotite, Japan, by Matsui (oral communication), who consider that less than 10% of the total iron is trivalent. The compositional gap of the coexisting pyroxenes and the Fe-Mg partitioning between garnet and clinopyroxene of the Norwegian garnet-clinopyroxene pairs from peridotite association are fairly constant and suggests that these rocks were equilibrated

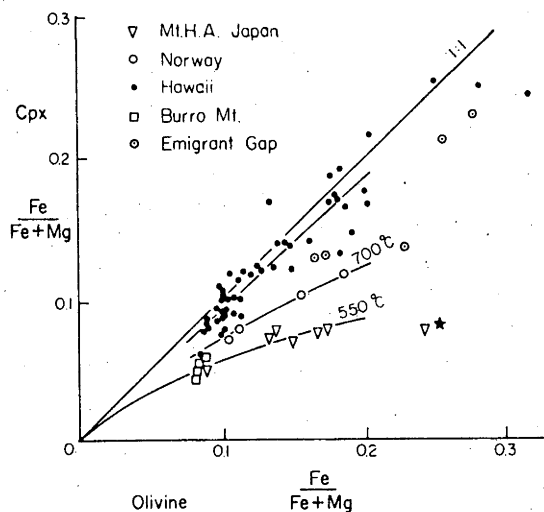


FIG. 2. — The partitioning of Fe and Mg between clinopyroxene and olivine. The temperatures for natural assemblages were based in the same assumptions as Mori and Banno (1973).

ed under narrow range of physical conditions, say 650 ~ 700° C (O'Hara and Mercy, 1963; O'Hara, 1967; Mori and Banno, 1973). The values of $\ln K^{ol-cpx}$ and W^{ol}/RT were calculated from the data on the olivine-clinopyroxene and [olivine-orthopyroxene pairs of the Norwegian rocks using equa-

tion [5] (Table II). For the olivine-clinopyroxene pairs, it is assumed that clinopyroxene is ideal based on the discussion given earlier. The value of W^{ol}/RT calculated from different pairs do not agree well. Although we do not understand the temperature dependence of W^{ol} , $W^{ol}/RT-1/T$ diagram is modified from the $W^{ol}-T$ diagram in Fig. 1, assuming the smooth change of the W^{ol} value with temperature (Fig. 3). The W^{ol}/RT value obtained from the olivine-clinopyroxene pairs gives temperature 550-650° C, and that from olivine-orthopyroxene gives 700-900° C. Estimated temperatures from compositional gaps between clino- and orthopyroxenes and from the Fe-Mg partitioning do not necessarily have to be identical since there is no reason to believe that the diffusion rate of calcium ion is similar to those of iron or magnesium ion in silicate minerals and that these two different geothermometers indicate the same temperature. The diffusion rate of the same cation may even vary in different minerals. The Fe-Mg intracrystalline exchange reaction in olivine is considerably more sluggish than in orthopyroxene (Virgo and Hafner, 1969, 1972). This is likely because oxygens are more closely packed in the olivine structure than in the pyroxene structure. Therefore, if a rock which consists of, say, olivine, clinopyroxene and orthopyroxene cools down slowly, olivine will first become a closed system with respect to Fe and Mg. Even if these three phases are in equilibrium at this moment, the partitioning of Fe and Mg between clino- and orthopyroxenes will keep changing for a while during further cooling until one of the two pyroxenes becomes closed system, and hence olivine and clino- or orthopyroxene are not really in equilibrium any more. On the other hand, if a rock quenched before olivine becomes a closed system, the calculated partitioning pattern will be consistent between these three phases and the same temperature should be obtained from different mineral pairs.

At present, there are too few data available on diffusion rates of cations in silicate minerals to discuss the significance of this process. The geothermometer of the Fe-Mg partitioning may have to be carefully applied to natural rocks considering the effects by other coexisting major ferro-magne-

sian minerals which have large diffusivity of iron and magnesium cations.

Another series of natural olivine-clinopyroxene pairs are available from peridotites and associated garnet clinopyroxenites from Mt. Higasi-Akai mass, Sikoku, Japan (Mori and Banno, 1973). The physical conditions of the equilibrium of garnet-bearing rocks of this mass are also very limited and

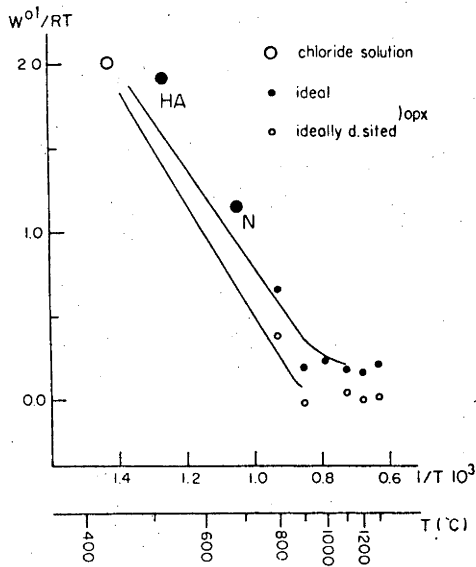


FIG. 3. — Comparison of W^{ol} of Norwegian and Japanese pairs with those calculated from experimental data. $1/T$ scale for temperature.

their temperature is about 150° C lower than those of Norwegian garnet lherzolites, and hence about 550° C. The partitioning of the Japanese pairs is also shown in Fig. 2. Among the seven data points, two are associated with garnets, and one marked «*» contains heterogeneous clinopyroxene with Fe/(Fe + Mg) ratios ranging from 0.062 to 0.086 and varying K^{ol-cpx} , 3.4 to 5.0. For the Japanese pairs excluding «*», we obtained $\ln K = 2.2$ and $W^{ol}/RT = 1.9$ again assuming ideal clinopyroxene. With this value of W^{ol}/RT , olivine should be near the critical temperature of unmixing on the crude model we have adopted. The scatter of plots in Fig. 2 does not allow us to speculate if olivine is

TABLE II.
In K^{ol-cpx} , In K^{ol-opx} and $W^{ol}-RT$ from natural pairs.

AREA	PAIR	In K^{ol-cpx}	In K^{ol-opx}	W^{ol}/RT	DATA
Norway	ol-cpx (ideal)	1.22	0.53*	1.08	O'Hara and Marcy (1963) and Carswell (1968)
	ol-opx (ideal)		0.60	0.67	
	ol-opx (i. d. sited)		0.71	0.42	
Japan	ol-cpx (ideal)	2.2	1.5*	1.96	Mori and Banno (1973)

really near the critical temperature or not. The scatter may partly be due to the fact that not all the olivine-clinopyroxene pairs of this mass are exactly isophysical. Although the majority of the rock types from this mass represent rather limited physical conditions of equilibrium, Yokoyama and Mori (to appear) described a spinel-garnet clinopyroxenite, in which equilibration of more than one temperature is recorded. However, the compositional dependence of the apparent partition coefficient as seen in Fig. 2 is too systematic to be fortuitous.

Geothermometer : The Fe-Mg partitioning between olivine and clinopyroxene depends on temperature and composition of minerals through the temperature dependence of $\ln K^{\text{ol-cpx}}$ and W^{ol} terms that appear in eq. [5]. The temperature dependences of these two terms are not yet clearly separated, but the overall temperature dependence of the partitioning is clear in Fig. 2. Hence we may use this partitioning as an empirical geothermometer. The merit of this geothermometer is that this is more sensitive to temperature through the large temperature dependence of W^{ol} than that of clino- and orthopyroxene partitioning, and this can be more appropriately used at low temperatures as exemplified by the Norwegian and Japanese peridotites. In Fig. 2, the partition data of a few more occurrences are plotted and compared with the Norwegian and Japanese pairs. Probable temperatures are read from the W^{ol}/RT diagram (Fig. 3).

The Burro Mt. peridotite described by Loney *et al.* (1971) plots at about 600°C, which contradicts the interpretation by the original authors. The

Fe-Mg partition coefficient between coexisting pyroxenes, $K^{\text{opx-cpx}}$, in this mass is about 1.45. On the basis that the Norwegian and Japanese peridotites have $K^{\text{opx-cpx}}$ values of 1.35 and 1.87, respectively on a total Fe basis (Mori and Banno, 1973), it appears that the Burro Mt. peridotite was metamorphosed at about 600°C. Although the classic paper by Kretz (1961) and Bartholomé (1962) each gave a value of 1.4 as an average of $K^{\text{opx-cpx}}$ for igneous rocks, Nakamura and Kushiro (1970) gave 1.1 for the pyroxene pairs from a tholeiitic andesite. At least empirically, we may use the apparent partition coefficient on the total Fe basis. Therefore, the consistent variation of $K^{\text{ol-cpx}}$ and $K^{\text{opx-cpx}}$ among Norwegian, Burro Mt. and Japanese peridotite appear to suggest that the temperature of equilibration decreases in this order and that the Burro Mt. peridotite suffered medium temperature metamorphism on its way from the oceanic lithosphere to the Franciscan terrain, if the idea of Loney *et al.* (1971) is defended. Though there is scatter in the olivine-clinopyroxene pairs from the Emigrant Gap mass on Fig. 2, they appear to be in harmony with the statement by James (1971) that this peridotite suffered metamorphism at fairly high temperatures. The data from the peridotite nodules in Hawaiian basalts (White, 1966) are also plotted, and a trial curve with $\ln K = 1.13$ and $W^{\text{ol}}/RT = 0.08$ is drawn.

By applying the Fe-Mg partitioning between olivine and clinopyroxene, the average apparent partition coefficient is not appropriate because of strong compositional dependence. For effective use of this geothermometer, we need pairs covering a reasonable compositional range.

REFERENCES

- BANNO, S. (1970). — Classification of eclogites in terms of physical conditions of their origin. *Phys. Earth Planet. Inter.*, 3, 405-421.
- BANNO, S. and MATSUI, Y. (1965). — Intracrystalline exchange equilibrium in orthopyroxene. *Proc. Japan Academy*, 42, 629-633.
- BARTHOLOMÉ, P. (1962). — Iron-Magnesium ratio in associated pyroxenes and olivines. Petrologic studies: A volume in honor of A. F. Buddington, 1-20. *Geol. Soc. Amer.*
- BINNS, R. A. (1962). — Metamorphic pyroxenes from the Broken Hill district, New South Wales. *Mineral. Mag.*, 33, 320-338.
- BIRLE, J. D., GIBBS, G. V. and SMITH, J. V. (1968). — Crystal structures of natural olivines. *Am. Mineral.*, 53, 807-823.
- BURNS, R. G. (1970). — Crystal field spectra and evidence of cation ordering in olivine minerals. *Am. Mineral.*, 55, 1608-1632.
- BURNS, R. G. and HUGGINS, F. E. (1972). — Cation determinative curves for Mg-Fe-Mn olivines from vibrational spectra. *Am. Mineral.*, 57, 967-985.
- BUSH, W. R., HAFNER, S. S. and VIRGO, D. (1970). — Some ordering of iron and magnesium at the octahedrally coordinated sites in a magnesium rich olivine. *Nature*, 227, 1339-1341.
- CARSWELL, D. A. (1968). — Picritic magma-residual dunite relationships in garnet peridotite at Kalskaret near Tafjord, South Norway. *Contr. Mineral. Petrol.*, 19, 97-124.
- DAVIDSON, L. R. (1968). — Variation in ferrous iron-magnesium distribution coefficient of metamorphic pyroxenes from Quairading, Western Australia. *Contr. Mineral. Petrol.*, 19, 239-259.
- FINGER, L. W. (1969). — Fe/Mg ordering in olivines. *Carnegie Inst. Year Book*, 69, 302-305.
- FINGER, L. W. and VIRGO, D. (1971). — Confirmation of Fe-Mg ordering in olivines. *Carnegie Inst. Year Book*, 70, 221-225.
- GROVER, E. and ORVILLE, P. M. (1969). — The partitioning of cations between single and multi-site phases with application to the assemblage: orthopyroxene-clinopyroxene and orthopyroxene-olivine. *Geoch. Cosmoch. Acta*, 33, 205-266.
- GUGGENHEIM, E. A. (1967). — Thermodynamics. North Holland.
- JAMES, O. B. (1971). — Origin and emplacement of the ultramafic rocks of the Emigrant Gap area, California. *Jour. Petrol.*, 12, 523-560.
- KITAYAMA, K. and KATSURA, T. (1968). — Activity measurements in orthosilicate and metasilicate solid solutions. I. Mg_2SiO_4 - Fe_2SiO_4 and MgSiO_3 - FeSiO_3 at 1204°C. *Chem. Soc. Japan, Jour.*, 41, 1146-1151.
- KRETZ, R. (1961). — Some applications of thermodynamics to coexisting minerals of variable com-

- position. Examples : orthopyroxene-clinopyroxene and orthopyroxene-garnet. *Jour. Geol.* 69, 361-402.
- LONEY, R. A., Himmelberg, G. R. and Coleman, R. G. (1971). — Structure and petrology of the alpine-type peridotite at Burro Mt. California, U. S. A. *Jour. Petrol.*, 12, 245-309.
- LARIMER, J. W. (a 1968). — Experimental studies on the system Fe-MgO-SiO₂-O₂ and their bearing in the petrology of chondritic meteorite. *Geoch. Cosmoch. Acta*, 32, 1187-1207.
- MATSUI, Y. and BANNO, S. (1965). — Intracrystalline exchange equilibria in silicate solid solution. *Proc. Japan Academy*, 41, 461-466.
- MATSUI, Y. and NISIZAWA, A. (1972). — Fe-Mg partitioning between olivine and orthopyroxene (abstract). *Annual Meeting Geochemical Society, Japan*.
- NAKAMURA, Y. and KUSHIRO, I. (1970). — Composition relations of coexisting orthopyroxene, pigeonite and augite in a tholeiitic andesite from Hakone volcano. *Contr. Mineral. Petrol.*, 26, 265-275.
- NAVROTSKY, A. (1971). — The intracrystalline cation distribution and the thermodynamics of solid solution formation in the system FeSiO₃-MgSiO₃. *Am. Mineral.*, 56, 201-211.
- MEDARIS, L. G. Jr. (1969). — Partitioning of Fe⁺⁺ and Mg⁺⁺ Between coexisting synthetic olivine and orthopyroxene, *Amer. Jour. Sci.*, 267, 945-68.
- MORI, T. and BANNO, S. (1973). — Petrology of peridotite and garnet clinopyroxenite of the Mt. Higashi-Akai mass, central Sikoku, Japan-sub-solidus relation of anhydrous phases. *Contr. Mineral. Petrol.*, 41, 301-323.
- MYSÉN, B. O. and HEIER, K. S. (1972). — Petrogenesis of eclogite in high-grade metamorphic gneisses, exemplified by the Hareidland eclogites, Western Norway, *Contr. Mineral. Petrol.*, 36, 73-79.
- NAFZIGER, R. H. and MUAN, A. (1967). — Equilibrium phase compositions and thermodynamic properties of olivine and pyroxenes in the system MgO-FeO-SiO₂. *Am. Mineral.*, 52, 1364-1385.
- O'HARA, M. J. (1967). — Mineral paragenesis in ultrabasic rocks, in : Ultramafic and related rocks. New-York, Wiley, 1967.
- O'Hara, M. J. and MERCY, E. L. P. (1963). — Petrology and petrogenesis of some garnetiferous peridotites. *Trans. Roy. Soc. Edin.*, 65, 251-310.
- SAXENA, S. K. (1968). — Distribution of iron and magnesium between coexisting garnet and clinopyroxene in rocks of varying metamorphic grades. *Am. Mineral.*, 53, 2018-2024.
- SAXENA, S. K. (1969). — Silicate solid solutions and geochemistry 2. Distribution of Fe⁺⁺ and Mg⁺⁺ between coexisting olivine and orthopyroxene. *Contr. Mineral. Petrol.*, 22, 147-156.
- SAXENA, S. K. (1972). — Retrieval of thermodynamic data from a study of intercrystalline and intracrystalline equilibrium. *Am. Mineral.*, 57, 1782-1800.
- SAXENA, S. K. and GHOSE, S. (1971). — Mg²⁺-Fe²⁺ order-disorder and thermodynamics of the orthopyroxene crystalline solution. *Am. Mineral.*, 56, 532-59.
- SCHULIEN, S., FREIEDRICHSEN, H. and HELLNER, E. (1970). — Das Mischkristallverhalten des Olivins zwischen 450° and 650° bei 1Kb Druck. *Neues Jr. Miner. Mh.*, 141-147.
- THOMPSON, J. B. and WALDBAUM, D. R. (1969 a). — Mixing properties of sanidine crystalline solutions : III. Calculations based on two phase data. *Am. Mineral.*, 54, 811-838.
- THOMPSON, J. B. and WALDBAUM, D. R. (1969 b). — Analysis of the two phase regions halite-sylvite in the system NaCl-KCl. *Geoch. Cosmoch. Acta*, 33, 671-690.
- VIRGO, D. and HAFNER, S. (1969). — Fe²⁺-Mg order-disorder in heated orthopyroxene. *Mineral. Soc. Am. Spec. Pap. No. 2*, 67-82.
- VIRGO, D. and HAFNER, S. (1972). — Temperature dependent Mg-Fe distribution in a lunar olivine. *Earth and Planet. Sci. Letters*, 14, 305-312.
- WHITE, R. W. (1966). — Ultramafic inclusions in basaltic rocks from Hawaii. *Contr. Mineral. Petrol.*, 12, 245-314.
- WILLIAMS, R. J. (1971). — Reaction constants in the system Fe-MgO-SiO₂-O₂ at 1 atm between 900° C and 1300° C : Experimental result. *Amer. Jour. Sci.*, 270, 334-360.

APPENDIX 6

Spinel - Garnet - Two Pyroxene Rock from the Iratsu Epidote
Amphibolite Mass, Central Shikoku

K. Yokoyama and T. Mori

SPINEL-GARNET-TWO PYROXENE ROCK FROM THE IRATSU EPIDOTE AMPHIBOLITE MASS, CENTRAL SHIKOKU

KAZUMI YOKOYAMA* and TAKESHI MORI**

(Received June 17, 1974)

Introduction

Garnet-clinopyroxene rocks enclosed in the Mt. Higashi-Akaishi peridotite mass located in the eastern area of the Ehime Prefecture have been studied by HORIKOSHI (1937), YOSHINO (1961, 1964), BANNO (1970), ERNST *et al.* (1970), MORI (1972) and MORI and BANNO (1973). On the basis of the low Al_2O_3 content in clinopyroxene and Fe-Mg partition relationship between garnet and clinopyroxene, BANNO (1970), ERNST *et al.* (1970) and MORI and BANNO (1973) have considered that the garnet-clinopyroxenite were equilibrated at relatively low temperature corresponding to the epidote amphibolite facies. MORI and BANNO (1973) considered that latest equilibration of the garnet-clinopyroxenite took place at 500–600°C and 7–13 Kb.

Recently, a block of spinel-garnet-pyroxene rock was found by IWATA (1970) in the area of the Iratsu epidote amphibolite mass which is in contact with the Mt. Higashi-Akaishi peridotite mass. Subsequently, we confirmed the outcrops of this rock-type in a peridotite mass located in the Iratsu epidote amphibolite mass. Texture of this spinel-garnet-pyroxene rock shows at least two stages of equilibration. An earlier stage is characterized by a spinel-aluminous pyroxene-plagioclase assemblage. Reactions among the minerals

of the earlier stage formed garnet and Al-poor pyroxenes which are minerals of a later stage.

In this paper, we will describe the texture and chemical relations among the minerals in the spinel-garnet-pyroxene rock to estimate a thermal history of this rock.

Geological Outline

Geology of the Iratsu area has been studied by HIDE *et al.* (1956), YOSHINO (1961, 1964) and BANNO (1964). The Iratsu epidote amphibolite mass represents the highest metamorphic grade in the Sanbagawa metamorphic belt in Shikoku (BANNO, 1964). The Iratsu epidote amphibolite mass measures 6 km × 3 km and contacts with the Mt. Higashi-Akaishi peridotite mass to the west, and pelitic and green schists to the others. The mass consists mainly of albite-epidote amphibolite, hornblende eclogite and quartz eclogite and is associated with peridotite. Albite-epidote amphibolite has conspicuous alternation of amphibole-rich part and clinozoisite-rich part, which varies 1 mm to 2 m in thickness.

We have found a few types of spinel-bearing

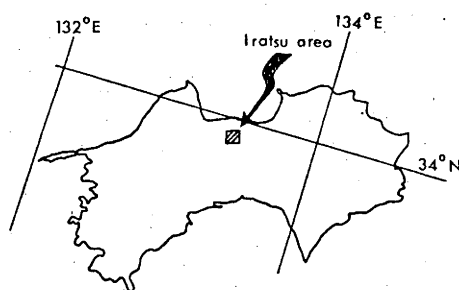


Fig. 1. Location of the Iratsu area.

* Department of Earth Sciences, Kanazawa University, Kanazawa.

Present address: Geological Institute, Faculty of Science, University of Tokyo, Tokyo.

** Research School of Earth Sciences, The Australian National University, Australia.

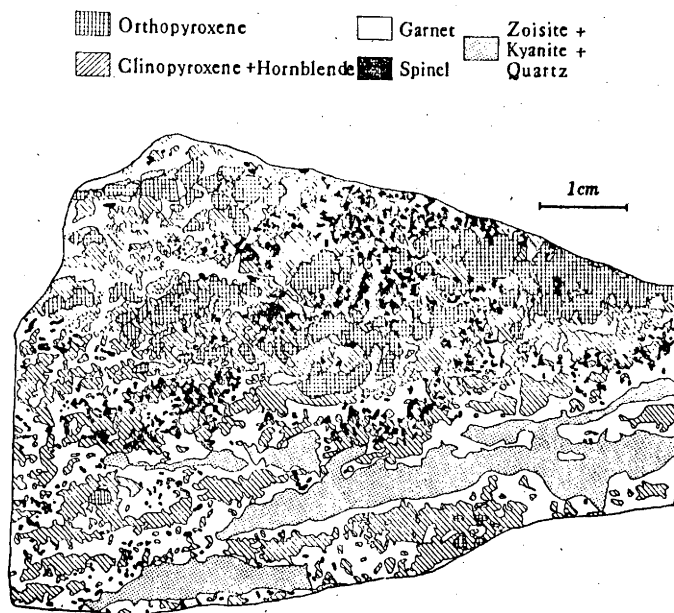


Fig. 2. The texture of the spinel-garnet-pyroxene rock (sample, No. OI 7050802).

rocks in this area. Most of the spinel-bearing rocks were found as blocks on river beds in a western tributary of the Nikubuchi valley which is located within the Iratsu mass, but the spinel-bearing rocks also occur as layers in a peridotite mass at an eastern tributary of the Nikubuchi valley. The peridotite mass measures approximately 200 m × 500 m and mainly consists of dunite and wehrlite. The layers of spinel-bearing rock in the peridotite mass are 10 to 200 cm thick.

Petrography

Spinel-bearing rocks usually consists of the alternation of mafic layers of spinel, garnet, pyroxenes and hornblende, and felsic layers of zoisite, kyanite and quartz. The modes of garnet and hornblende of mafic layer are variable within 1–20 volume percent and 1–30 volume percent, respectively. The samples collected from the peridotite are usually rich in hornblende, while those from the river beds as blocks are poor in it. In some specimens, the mafic layers consist mostly of spinel and pyroxenes, and garnet is present only at the boundary between mafic and felsic layers, and is rare in the mafic

layers.

Our petrographic and chemical studies have been carried out mainly on a garnet-rich type (sample No. OI 7050802), which shows noticeable reaction texture between spinel and pyroxenes to form garnet as shown in Plates I-I and 2.

Distribution of constituent minerals in the spinel-bearing rock (sample No. OI 7050802) is shown in Fig. 2. The constituent minerals of the spinel-bearing rock are spinel, garnet, clinopyroxene, orthopyroxene, pargasite, zoisite, kyanite, quartz, corundum, chlorite and magnetite. The mafic layers are divided into three parts: garnet-rich, spinel-rich and orthopyroxene-rich parts, boundaries of which are transitional. The felsic layer consists of fine-grained zoisite with small amount of kyanite and quartz, and contacts with the garnet-rich parts where garnet is dominant and accompanied by subordinate clinopyroxene, pargasite and fine-grained breakdown products of spinel. The spinel-rich part stretches parallel to the felsic layer. The orthopyroxene-rich part contains some clinopyroxene, spinel, garnet and pargasite. In every part, reaction texture is present.

All the garnet grains in the spinel-bearing rock are reaction products. In the spinel-rich parts, garnet is a reaction product among spinel and pyroxenes as shown in Plates I-1 and 2. Spinel is surrounded by garnet, until it is wholly consumed to form large garnet grains. In one large spinel grain, garnet coexisting with hornblende and chlorite is included. It is probably derived from original pyroxene inclusions. In the orthopyroxene-rich part, garnet occurs at the grain boundaries between pyroxenes as shown in Plate I-3, and the size of garnet increases toward the triple junctions among reactant minerals. Hornblende usually occurs in the interstices of spinel and pyroxenes and is subhedral, implying it also postdated the others.

Spinel grain in the spinel-rich parts is green coloured, embayed in form, and when large, it contains a lot of subhedral magnetite inclusions (0.5 microns in diameter). They are evenly distributed only at the cores of spinel grains, causing an apparent zonation in colour, i. e. deep green at the core to light green at the rim. Sometimes, tiny grains of magnetite are formed along fracture planes of spinel. When the spinel grain is small, no magnetite is found in it.

In the garnet-rich parts, there is a lot of aggregates of very fine-grained corundum and chlorites. Shapes of these aggregates are exactly the same as those of spinel in the spinel parts. Rims of spinel grains show a breakdown to corundum and chlorite in the transitional zone between the spinel-rich and garnet-rich parts. They imply that corundum-chlorite aggregates were originally spinel. Corundum grains are 5 to 25 microns in diameter and contact with each other by sharp boundaries. Chlorite scatters interstitially among corundum grains. The corundum-chlorite aggregates are usually surrounded by garnets and rarely contact with amphiboles. Even if the aggregates locate within only 0.3 mm to the felsic layer where quartz is present, no reaction to form kyanite is visible.

In the orthopyroxene-rich parts, tiny grains of clinopyroxene and hornblende are found

at the boundaries between garnet and orthopyroxene and between orthopyroxenes, suggesting that they were expelled from orthopyroxenes, presumably at the time of the garnet formation.

The felsic layer, now consisting of zoisite, kyanite and quartz, was originally a plagioclase layer. This is affirmed by its bulk chemical composition as will be discussed later.

Based on the petrography described above, we consider that the original rock was a coarse-grained spinel-orthopyroxene-clinopyroxene-plagioclase rock. The mafic layer of a spinel-bearing rock in sample KY No. 5, as shown in Plate I-4, preserves the original mineral assemblage and texture almost completely, although the felsic layer has already broken down into zoisite, kyanite and quartz.

Analyses of Minerals

Chemical analyses of the minerals in the spinel-bearing rock were done using a Hitachi XMA 5 electron microprobe analyser, with 3 channel detecting system and 38° take off angle. Accelerating voltage and specimen current were 15.0 kV and 0.03 μ A, respectively. Synthetic periclase, corundum, quartz, diopside, wollastonite, rutile and rhodonite and natural albite, chromite and hematite were used as standards as well as kaersutite that was used as a working standard. The observed X-ray intensity ratios were corrected by the alpha factor by ALBEE and RAY (1970). The results of the chemical analyses are shown in Table 1 with their atomic ratios.

Pyroxenes: Both ortho- and clinopyroxenes show compositional zonations, especially where garnet is formed around them (Fig. 3). Al_2O_3 content of pyroxenes decreases toward their rims at the contact of garnet. For orthopyroxenes, Al_2O_3 content decreases from 6.7 weight percent at the core to about 1 weight percent at the rim. For clinopyroxenes, Al_2O_3 content decreases from 7.3 to about 2 weight percent. The composition at the core varies slightly from grain to grain. The Fe/Mg ratio decreases toward rims. The tiny clinopyroxene crystals occurring at the boundaries

Table 1. Chemical compositions of the minerals in the spinel-garnet-pyroxene rock (sample, No. OI 7050802).

	1 Opx	2 Cpx	3 Cpx	4 Garnet	5 Garnet	6 Garnet	7 Spinel	8 Spinel	9 Hb	10 Zoisite	11 Felsic
SiO ₂	52.0	50.3	53.2	41.1	39.4	40.3	0.00	0.03	42.7	38.5	44.3
TiO ₂	0.05	0.12	0.14	0.07	0.05	0.03	0.03	0.06	0.14	0.04	n. d
Al ₂ O ₃	6.66	7.26	1.25	22.7	22.4	22.7	61.1	66.0	16.4	31.6	34.8
Fe ₂ O ₃							5.72**	1.28**		1.75**	
FeO	12.9*	3.86*	2.01*	14.1*	17.9*	19.6*	15.6	13.5	4.93*		n. d
MnO	0.09	0.08	0.04	0.31	0.27	0.30	0.01	0.00	0.00	0.00	n. d
MgO	28.1	14.2	17.0	15.8	8.55	14.6	18.3	19.1	16.9	0.15	1.2
CaO	0.80	23.1	25.3	5.93	11.7	2.16	0.00	0.00	13.1	24.0	19.1
Na ₂ O	0.02	0.85	0.29	0.00	0.06	0.03	0.03	0.03	2.80	0.00	n. d
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.24	0.00	n. d
Total	100.62	99.77	99.23	100.01	100.33	99.72	100.79	100.00	97.21	96.04	99.4
Si	0.921	1.845	1.958	3.000	2.976	2.996	0.000	0.001	6.116	3.000	2.115
Al ₃	0.139	0.314	0.054	1.951	1.990	1.986	1.886	1.975	2.757	2.900	1.901
Fe							0.114	0.025		0.114	
Ti	0.000	0.006	0.004	0.004	0.004	0.002	0.001	0.000	0.015	0.002	
Mg ₂	0.741	0.774	0.929	1.717	0.962	1.620	0.715	0.723	3.596	0.017	0.083
Fe	0.190	0.117	0.062	0.861	1.132	1.214	0.343	0.287	0.590		
Mn	0.000	0.003	0.001	0.019	0.018	0.018	0.000	0.000	0.000	0.000	
Ca	0.015	0.907	0.995	0.464	0.944	0.172	0.001	0.000	2.006	2.000	0.950
Na	0.000	0.060	0.021	0.000	0.008	0.004	0.000	0.002	0.777	0.000	
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.044	0.000	
O	3.000	6.000	6.000	12.000	12.000	12.000	4.000	4.000	23.000	12.500	8.000

1 : Core of the large orthopyroxene grain, 2 : Core of the large clinopyroxene grain, 3 : Minute clinopyroxene grain between garnet and clinopyroxene, 4 : Garnet in the mafic layer, 5 : Garnet in the vicinity of the felsic layer, 6 : Garnet in the large spinel grain, 7 : Core of the large spinel grain, 8 : Rim of the large spinel grain, 9 : Pargasite, 10 : Zoisite, 11 : Felsic layer (partial analysis).

* Fe as total FeO.

** Calculated from the structural formula (spinel : $Al + Fe^3 = 2$, Zoisite : Fe as total Fe₂O₃).

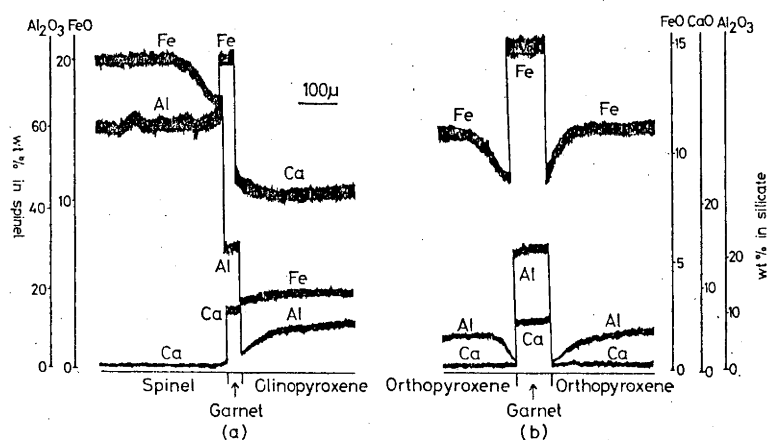


Fig. 3. Scanning profiles by Fe K α , Ca K α and Al K α emissions of the garnet and surrounding minerals in the mafic layer.

(a) garnet at the grain-boundary between spinel and clinopyroxene. (b) garnet between two orthopyroxenes. CaO, FeO and Al₂O₃ contents on the ordinate are approximate value, because correction factor is different for each mineral.

between orthopyroxene and garnet contain far less Al_2O_3 (1.3 weight percent) than the cores of coarse-grained pyroxenes.

Spinel: Magnetite inclusions are contained in spinel grains, but, as they are 0.5 microns in diameter, its contribution to Fe analysis is negligibly small. MgO and Al_2O_3 contents increase toward rims and total iron decreases. Fe_2O_3 content presented in Table 1 was estimated from structural formula. Cr_2O_3 content of spinel was below the detection limit.

Garnet: Chemical composition of garnet varies remarkably depending on the textural situation. In most parts, garnet is homogeneous and pyrope-rich ($\text{Mg} : \text{Fe} : \text{Ca} = 58 : 26 : 16$), but, in the vicinity (2–3 mm wide) of the felsic layer, garnet is grossular-rich ($\text{Mg} : \text{Fe} : \text{Ca} = 32 : 37 : 31$). In addition, the garnet enclosed in the large spinel grain is very poor in the grossular component ($\text{Mg} : \text{Fe} : \text{Ca} = 54 : 40 : 6$).

Hornblende: Hornblende is homogeneous, and as shown in column 9 of Table 1, it is pargasite.

Felsic layer: A bulk chemical composition of the felsic layer was measured using broad electron beam (100 microns in diameter). The bulk chemical composition is similar to anorthite as shown in column 11 of Table 1, suggesting that this layer was originally plagioclase.

In addition, pyroxenes in the spinel-bearing rock that preserves the original textures (Plate I-4) are also aluminous, as do the pyroxene cores of the sample described above in detail, but they are not zoned.

Discussion

Chemical reactions among minerals in the spinel-bearing rock

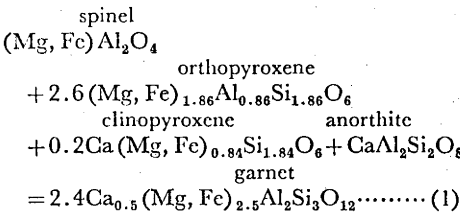
Among the chemical reactions stated above, an important feature is the formation of Mg-rich garnet (pyrope 58 mole percent) in the mafic layer except in the vicinity (2–3 mm wide) of the felsic layers. It is clear that garnet was formed from spinel, orthopyroxene and clinopyroxene in the mafic layer. If the compositions of spinel and pyroxenes exist-

Table 2. Comparison between observed and calculated garnet compositions.

	1	1'	2	2'
SiO_2	41.1	42.1	39.4	41.7
Al_2O_3	22.7	23.9	22.4	23.6
FeO	14.1	9.1	17.9	6.9
MgO	15.8	18.4	8.6	15.0
CaO	5.9	6.5	1.7	13.0

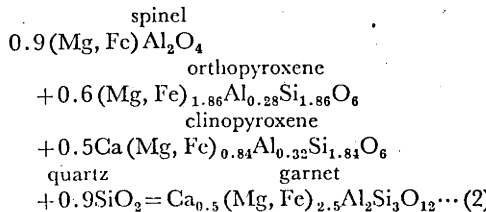
1: Garnet in the mafic layer (Table 1, column 4), 1': Garnet calculated on the basis of equation (1), 2: Garnet in the vicinity of the felsic layer (Table 1, column 5), 2': Garnet calculated on the basis of equation (4).

ed before the formation of the garnet are preserved in the core of each mineral, the following reaction would be an interpretation:



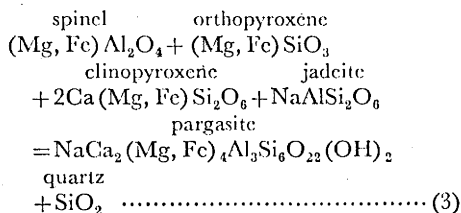
The combination of spinel, orthopyroxene, clinopyroxene and anorthite in the ratios in equation (1) gives a chemical composition of garnet as shown in Table 2. The observed composition of the garnet and that being calculated on the basis of equation (1) coincide with each other except that Fe/Mg ratio. The observed composition is higher in Fe/Mg ratio than the calculated one. The reason for the difference between the observed and calculated Fe/Mg ratios may be due to the selective migration of FeO from spinel and to the Fe-Mg partition among garnet and relic clinopyroxenes.

Another interpretation for the formation of the garnet is considered by introduction of silica in the reaction:



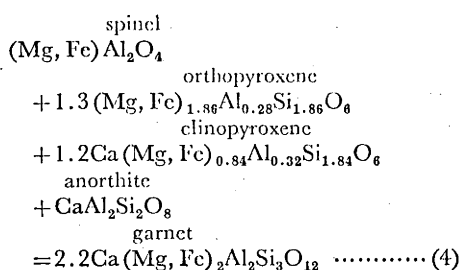
This reaction requires excess silica which

has not been found in the spinel-bearing rocks. However, the following reaction expels the excess silica in equation (2):



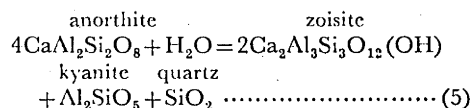
This reaction requires a jadeite molecule. The jadeite content of the aluminous clinopyroxene is about 6 mole percent, and the content is too low to explain the jadeite content in equation (3), but it is possible that jadeite molecule was supplied from the felsic layers which was plagioclase. Usually, plagioclase in a spinel-bearing peridotites contains at least 10 mole percent of albite (MACKENZIE, 1960; LENSCH, 1971), and hence the felsic layer could be the source of jadeite component of equation (3).

The same reaction occurs in the vicinity (2–3 mm wide) of the felsic layers. The garnet composition in its vicinity is grossular-rich and different from the garnet formed by the equation (1) or (2), so the garnet in the vicinity of the felsic layer was formed by the following reaction, incorporating an anorthite component:



Garnet inclusion in large spinel grain is interpreted by a reaction between pre-existing orthopyroxene inclusions and surrounding spinel. In this case, the difficulty of attaining a chemical balance is most remarkable. The problem can not be settled clearly as shown in the case of aluminous pyroxene with spinel lamellae in peridotite nodules.

The breakdown reaction of plagioclase into zoisite, kyanite and quartz is represented by a well-known reaction:



The right sides of these equations represent the mineral assemblages formed by reactions among the pre-existing minerals. All the assemblages on the right sides of the equations are stable at lower temperatures or higher pressures than those on the left sides of the equations, and are consistent with the textural interpretation. Actually, the formation of garnet and pargasite requires metamorphic transfer of materials between mafic and felsic layers.

Thermal History of the Rock

As mentioned in the previous section, garnet, pargasite, zoisite, kyanite, quartz and tiny Al-poor clinopyroxene crystal postdated spinel, aluminous pyroxenes and plagioclase, so paragenesis in the spinel-bearing rock recalls the equilibrium of at least two stages: spinel pyroxenite and garnet pyroxenite stages. The mineral assemblage in the rock taken together is far from chemical equilibrium, so that the estimation of the physical conditions of its formation has to be based on some assumptions. The physical conditions, especially temperature, are roughly estimated by means of the CaO and Al_2O_3 contents of clinopyroxene coexisting with orthopyroxene and an aluminous phase. In an A–C–F diagram (Fig. 4), Al_2O_3 -rich pyroxenes of the spinel pyroxenite stage and garnet and tiny Al_2O_3 -poor clinopyroxene of the garnet pyroxenite stage are plotted.

The tiny clinopyroxene crystal, presumably produced at the time of the formation of the garnet, can give us some informations. The clinopyroxene is poorer in Al_2O_3 and richer in CaO than the pre-existing aluminous clinopyroxene. The Al-poor clinopyroxenes occurs around garnet as shown in Fig. 3. The tiny clinopyroxene crystal is nearly saturated with orthopyroxene component, as

of at least two stages: spinel pyroxenite stage (earlier stage) and garnet pyroxenite stage (later stage). The minerals of the garnet pyroxenite stage were garnet, Al-poor pyroxenes, pargasite, zoisite, kyanite and quartz. These minerals are formed at the same (P, T) conditions as the garnet websterite from the Mt. Higashi-Akaishi peridotite mass, i.e. 500–600°C and 7–13 Kb. The minerals of the spinel pyroxenite stage were spinel, aluminous pyroxenes and plagioclase. Its formative temperature was higher than that of the garnet pyroxenite stage, and probably at below 1000°C.

Such a transition of the physical condition of garnet-bearing rock has been described by many authors, for example, GREEN (1966), LOVERING and WHITE (1969), MATHE (1969), MILLER (1970) and LASNIER (1971). MORI and BANNO (1973) briefly referred to the original rock of garnet clinopyroxenite (eclogite) from the Mt. Higashi-Akaishi peridotite mass in this area.

We concluded that the (P,T) conditions of the garnet pyroxenite stage were the same as that of the garnet websterite and clinopyroxenite. This conclusion will greatly contribute to deciphering the origin of the garnet clinopyroxenite in this area.

Acknowledgements

The authors would like to express their sincere thanks to Dr. S. BANNO for his continuous encouragements and the critical reading of this manuscript and to Mr. O. IWATA for providing the specimen. Suggestions by Mr. K. L. HARRIS improved the manuscript. They also thank Mr. K. NAKAMURA and Mr. H. KASAJIMA for preparing photographs, drafting figures and preparing thin sections.

References

- ALBEE, A. L. and RAY, L. (1970), Correction factors for electron probe microanalysis of silicates, oxides, carbonates, phosphates and sulfates. *Anal. Chem.*, vol. 42, p. 1408–1414.
- BANNO, S. (1964), Petrologic studies on Sanbagawa crystalline schists in the Bessi-Ino district, Central Shikoku, Japan. *Jour. Fac. Sci. Univ. Tokyo Sec.*, vol. 2, 15, p. 203–319.
- (1970), Classifications of eclogite in terms of physical conditions of their origin. *Phys. Earth Planet. Interior*, vol. 3, p. 405–421.
- and YOSHINO, G. (1965), Eclogite-bearing peridotite mass at Higashiakaishi-yama in the Bessi area, Central Shikoku, Japan. Upper Mantle symposium. *New Delhi*, p. 150–160.
- BOETTCHER, A. L. (1970), The system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at high pressures and temperatures. *J. Petrol.*, vol. 11, p. 337–379.
- BOYD, F. R. and SCHAIER, J. F. (1964), The system $\text{MgSiO}_3\text{-CaMgSi}_2\text{O}_6$. *J. Petrol.*, vol. 5, p. 275–309.
- (1970), Garnet peridotites and the system $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$. *Mineral. Soc. Amer. Spec. Pap.*, vol. 3, p. 63–67.
- DAVIDSON, L. R. (1968), Variation in ferrous Iron-Magnesium distribution coefficients of metamorphic pyroxenes from Quairading, Western Australia. *Contr. Mineral. and Petrol.*, vol. 19, p. 239–259.
- DAVIS, B. T. C. and BOYD, F. R. (1966), The join $\text{Mg}_2\text{Si}_2\text{O}_6\text{-CaMgSi}_2\text{O}_6$ at 30 kilobars pressure and its application to pyroxenes from Kimberlites. *J. Geophys. Res.*, vol. 71, p. 3567–3576.
- ERNST, W. G., SEKI, Y., ONUKI, H. and GILBERT, M. C. (1970), Comparative study of low-grade metamorphism in the California Coast Ranges and other metamorphic belt of Japan. *Geol. Soc. Amer. Memoir*, p. 124.
- GREEN, D. H. (1966), The origin of the Eclogites from Salt lake Crater, Hawaii. *Earth Planet. Sci. Lett.*, vol. 1, p. 414–420.
- and RINGWOOD, A. E. (1967), An experimental investigation of the gabbro to eclogite transformation and its petrologic application. *Geochim. Cosmochim. Acta*, vol. 3, p. 767–833.
- GRIFFIN, W. L. and RÄHEIM, A. (1973), Convergent metamorphism of eclogites and dolerites, Kristiansund area, Norway. *Lithos*, vol. 6, p. 21–40.
- HIDE, K., YOSHINO, G. and KOJIMA, G. (1956), Preliminary report on the geologic structure of the Bessi spotted schist zone. *Jour. Geol. Soc. Japan*, vol. 62, p. 574–584. (in Japanese)
- HORIKOSHI, G. (1937), On the eclogite in the vicinity of Mt. Higashi-Akaishi in the province of Iyo. *Jour. Geol. Soc. Japan*, vol. 44, p. 141–144. (in Japanese)

- IWATA, O. (1970), Geology and Petrology of the Iratsu epidote amphibolite mass, Central Shikoku, Japan. Gradation thesis, Kanazawa Univ. (in Japanese)
- KUSHIRO, I. and YODER, H. S. Jr. (1966), Anorthite-forsterite and anorthite-enstatite reactions and their bearing on the basalt-eclogite transformation. *J. Petrol.*, vol. 34, p. 29—42.
- LASNIER, B. (1971), Les péridotites et pyroxénolites à grenat du Bois des Feuilles (Monts du Lyonnais) (France). *Contr. Mineral. and Petrol.*, vol. 34, p. 29—42.
- LENSCH, G. (1971), Das Vorkommen von Saphirin im Peridotitkörper von Finero. *Contr. Mineral. and Petrol.*, vol. 31, p. 145—153.
- LOVERING, J. F. and WHITE, A. J. R. (1969), Granulitic and eclogitic inclusions from basic pipes at Delegate, Australia. *Contr. Mineral. and Petrol.*, vol. 21, p. 9—52.
- MACKENZIE, D. B. (1960), High temperature Alpine-type peridotite from Venezuela. *Geol. Soc. America Bull.*, vol. 71, p. 303.
- MATHÉ, G. (1969), Zur bildung des Granates in Serpentiniten und Eklogiten des sachsichen Granulitgebirge. *Freib. Forsch.* c241, p. 57—70.
- MILLER, C. (1970), Petrology of some eclogites and metagabbros of the Oetztal, Alps, Tirol, Austraria. *Contr. Mineral. and Petrol.*, vol. 28, p. 42—56.
- MIYASHIRO, A. and SEKI, Y. (1958), Mineral assemblage and subfacies of the glaucophane schist facies. *Japan. Jour. Geol. Geogr.*, vol. 29, p. 199—208.
- MORI, T. (1972), Petrology of the Mt. Higashi-Akaishi peridotite and garnet clinopyroxenite. Master thesis of Kanazawa University.
- and BANNO, S. (1973), Petrology of peridotite and garnet clinopyroxenite of the Mt. Higashi-Akaishi mass, Central Shikoku, Japan—Subsolidus relation of Anhydrous phases. *Contr. Mineral. and Petrol.*, vol. 41, p. 301—323.
- YOSHINO, G. (1961), Structural petrological studies of peridotite and associated rocks of the Higashi-akaishi-yama district, Shikoku, South west Japan. *Jour. Sci. Hiroshima Univ. Ser. C*, vol. 3, p. 343—402.
- (1964), Ultrabasic mass in the Higashi-akaishi-yama district Shikoku, Southwest Japan. *Jour. Sci. Hiroshima. Univ. Ser. c*, vol. 4, p. 333—364.

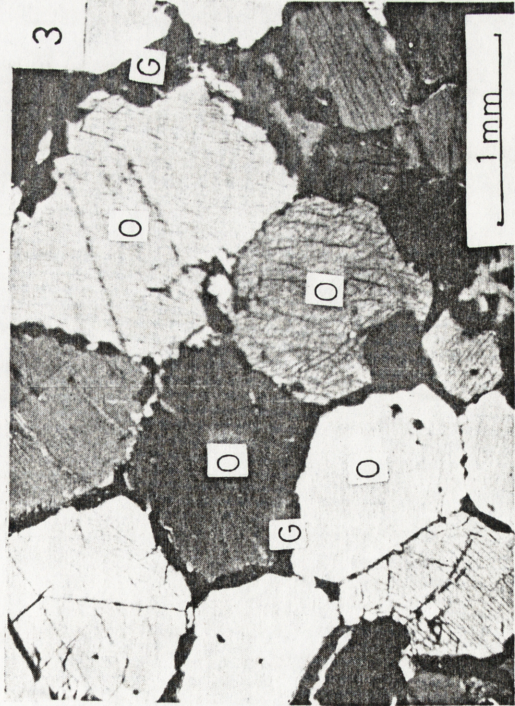
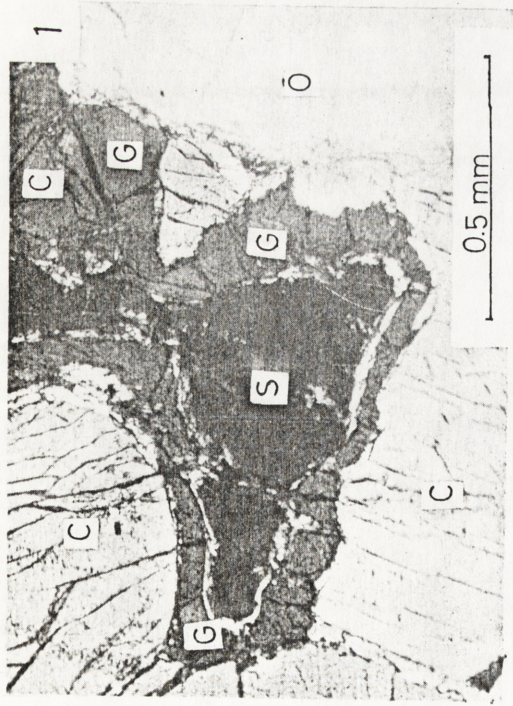
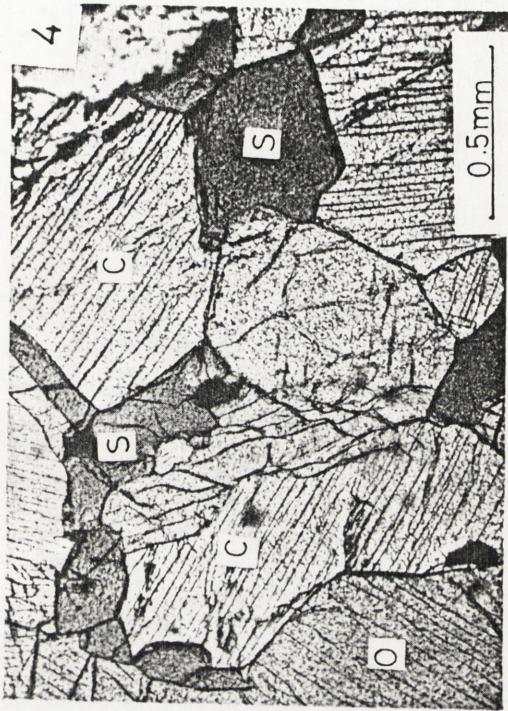
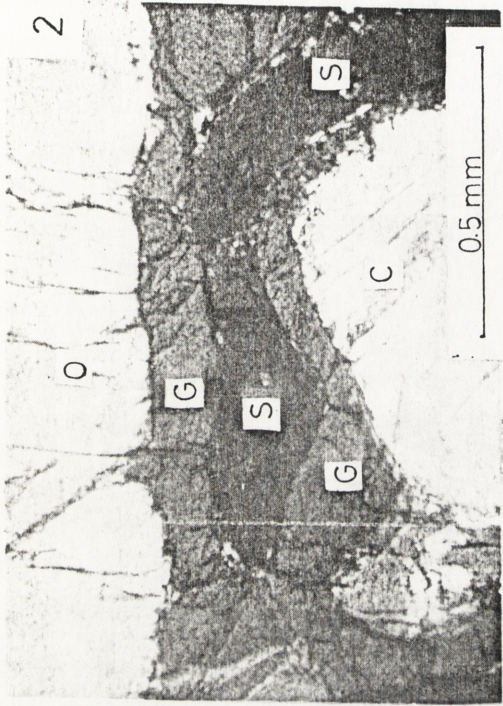
Explanation of Plate

Plates I—1 and 2. Reaction texture of garnet in the spinel-rich part. Garnet is present only at the grain-boundaries among spinel and pyroxenes. (Vibrational direction of the analyser was set faintly oblique to the polarizer to emphasize the contrast.) S: spinel, G: garnet, O: orthopyroxene, C: clinopyroxene.

Plate I-3. Garnet in the orthopyroxene-rich part. Black minerals are garnet. (crossed nicols).

Plate I-4. Mafic layer of the sample KY No. 2. Garnet is not present in this mafic layer. (plane light)

Plate I



APPENDIX 7

Correlation Table for Run Numbers

Run numbers used in this thesis are either probe-mount numbers or consecutive numbers within a chapter. High-pressure laboratory at A.N.U. has, however, a sequential numbering system of piston-cylinder experiments. The following table collates the reported numbers with the A.N.U. numbers.

Table 1. CORRELATION TABLE FOR RUN NUMBERS

THESIS	ANU	THESIS	ANU	THESIS	ANU	THESIS	ANU
1	4722	Y2	5679	R2	5213	DD1	3989
2	5503	Y3	5680	201	6368	DD7	3982
3	5506	2A4	5745	P2	5190	X6	3818
4	4718			Q4	5251	X7	3805
5	4823	2H2	6111	2N2	6361	X8	3905
6	4726	Z3	5689	O2	5174	X9	3843
7	4719	P1	5182	P8	5198	X11	3890
8	4780	2C1	5790	Q7	5262	FF8	4088
9	4782	T4	5522	P6	5195	T10	3833
10	4736	T5	5510	2E2	5840	T11	3804
11	4831	O1	5171	Q5	5256	T12	3831
12	4829	P7	5199	P10	5203	FF7	4076
13	4832	2A5	5752	P12	5188	FF6	4100
14	4957	P5	5194	Q6	5261	T6	3673
15	4827	2B6	5781	204	6378	T7	3679
16	4956	Q1	5254	R3	5267	T8	3659
		2D2	5818	202	6369	T9	3665
2B1	5771	Q2	5257			A2	4539
2B2	5772	2B5	5766	2J	6223	A7	4531
2B3	5777	P9	5204	2L	6246	A4	4560
2B4	5778	P11	5192	2M	6268	A5	4545
2F	5863	Q3	5260			C2	4577
2G	5890	Z4	5702	DD4	3993	C4	4584
Y1	5671	R1	5268	DD3	3999		
2A3	5743	2D1	5810	DD2	3990		