

Garnet pyroxene equilibria in the system $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ and in a natural mineral mixture

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Abstract

Compositions on the pyrope-diopside join in the ternary system $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ have been investigated in the range 26–44 kbar and 1000°–1500°C. Two bulk compositions were utilized in this study, pyrope₇₅diopside₂₅ and pyrope₇₀diopside₃₀, to which 5 weight percent $\text{CaTiAl}_2\text{O}_6$ was added, to test the effect of Ti on the solubility of alumina in the orthopyroxene. The subsolidus phase assemblage for these compositions is garnet + clinopyroxene + orthopyroxene.

Boyd and Nixon (1973) have suggested that the $\text{Ca}/(\text{Ca}+\text{Mg})$ ratio of enstatite in equilibrium with diopside is a useful geothermometer. However, a comparison of the present experimental data obtained at pressures above 30 kbar with the data obtained by Mysen and Boettcher (1975) at 7.5–1.5 kbar suggests that the $\text{Ca}/(\text{Ca}+\text{Mg})$ ratio decreases as pressure increases.

The solubility of Al_2O_3 in the orthopyroxene coexisting with a garnet + clinopyroxene decreases as pressure increases and as temperature decreases. The form of isopleths obtained for the present ternary system is very similar to that obtained for the binary join $\text{MgSiO}_3\text{-Al}_2\text{O}_3$. The presence of small amounts of TiO_2 in the bulk composition does not have a marked effect on the solubility of alumina in pyroxenes.

Natural mineral mixtures of garnet + enstatite + diopside were equilibrated under controlled pressure and temperature conditions. Equilibration pressures estimated for these natural mineral mixtures, using the phase data for the $\text{MgSiO}_3\text{-Al}_2\text{O}_3$ and $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ systems, are higher than the measured pressures. Pressures estimated using Wood and Banno's thermodynamic model agree well with the experimental equilibration pressures for runs at 31 kbar, but for runs at 38 and 44 kbar the estimated pressures are lower by 4–5 kbar.

Introduction

A wide variety of garnet-bearing ultramafic xenoliths has been discovered in kimberlites, alkali olivine basalts, basanites, and nephelinites; and it is an accepted view that these ultramafic xenoliths were brought up from the upper mantle. These xenoliths include lherzolites, pyroxenites, eclogites, and dunites, and this wide variety testifies to the complexity of the mantle.

Experimental phase equilibrium studies can be used in estimating the *P* and *T* conditions of equilibration of these nodules, provided the original equilibria that were established in the upper mantle were not disturbed during eruption. Certain compositional

variables among the minerals in the ultramafic nodules are sensitive functions of pressure and temperature. The *P* and *T* conditions of formation can be estimated, therefore, by equilibrating natural rock samples or mineral mixtures under known conditions, and by studying the compositional variables in the minerals of simple synthetic systems that approximately model those in the natural rocks. The experimental results presented in this paper form a step toward quantifying the interpretation of natural equilibria.

Previous work

The solid solution of enstatite in diopside is temperature-sensitive and is relatively insensitive to pressure (Davis and Boyd, 1966; Warner and Luth, 1974) and can thus be used as a geothermometer. The diop-

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side solvus in the pure system $Mg_2Si_2O_6$ - $CaMgSi_2O_6$ has been determined at atmospheric pressure by Boyd and Schairer (1964), at 30 kbar by Davis and Boyd (1966), and more recently Nehru and Wyllie (1974), Howells and O'Hara (1975) and Mori and Green (1975) have reinvestigated the diopside-enstatite solvus at high pressures. However, diopsidic pyroxenes in the ultramafic xenoliths from kimberlites commonly contain up to 10 mole percent $FeSiO_3$, and Boyd (1973) pointed out that a crude allowance for the effect of $FeSiO_3$ on the solvus can be made, provided the $Ca/(Ca+Mg)$ ratios of the diopsidic pyroxenes are used in estimating their equilibration temperature. However, Wood and Banno (1973) have shown on theoretical grounds that the $Ca/(Ca+Mg+Fe)$ ratio of diopside should be used for the estimation of temperature.

As the pressure is increased at constant temperature on a garnet-pyroxene assemblage, the pyroxene becomes less aluminous and more garnet is formed. The effect of pressure on the solubility of Al_2O_3 in enstatite has been demonstrated by Boyd and England (1964) and MacGregor (1974) in the system $MgSiO_3$ - Al_2O_3 , and Green and Ringwood (1967) for the pyrolite composition.

Nevertheless, in systems that contain Ca, Fe, and Cr, garnet is stable with enstatites that are less aluminous than those in the $MgSiO_3$ - Al_2O_3 system. The ternary system $CaSiO_3$ - $MgSiO_3$ - Al_2O_3 encompasses the garnet join $Ca_3Al_2Si_3O_{12}$ - $Mg_3Al_2Si_3O_{12}$ and the pyroxene join $CaMgSi_2O_6$ - $MgSiO_3$ and also illustrates the solid solutions between them. At high pressures this system contains a three-phase field, enstatite-diopside-garnet, which is invariant at constant pressure and temperature (Boyd, 1970). The compositional coordinates of this three-phase field as a function of pressure and temperature form an important basis for estimation of the equilibration pressures and temperatures of natural garnet peridotites. Boyd

(1970) made preliminary investigations in this system at 1200°C and 30 kbar.

A direct application to a natural system of the data on the solubility of Al_2O_3 in enstatite from a simple synthetic system will result in pressure estimates that are too high, because the presence of other elements such as Fe, Ca, Cr, Na, and Ti in the natural minerals can affect these equilibria, thus complicating the prediction of equilibration conditions. Wood and Banno (1973) and Wood (1974) have derived a thermodynamic model for the solution of Al_2O_3 in enstatite coexisting with garnet from which the effect of contaminating elements such as Fe, Ca, Cr, Na, and Ti can be calculated. They show that application of their model improves the agreement between data for $MgSiO_3$ - Al_2O_3 and for more complex systems.

Present work

The goals of this study were (1) to determine the solubility of Al_2O_3 in the orthopyroxene coexisting with garnet and clinopyroxene as a function of pressure and temperature in the system $CaSiO_3$ - $MgSiO_3$ - Al_2O_3 , (2) to determine the influence of Ti and Fe on the solubility of Al_2O_3 in the orthopyroxene, (3) to check the usefulness of the $Ca/(Ca+Mg)$ ratio of orthopyroxene coexisting with clinopyroxene and

TABLE 2. Electron microprobe analyses of the natural minerals used for starting materials

	1	2	3	4†
SiO ₂	56.51	55.20	42.22	40.85
Al ₂ O ₃	0.84	2.54	20.88	0.13
TiO ₂	0.02	0.33	1.28	...
CaO	0.32	13.62	4.74	...
MgO	34.02	20.78	19.45	51.63
FeO*	7.00	5.34	11.58	7.17
Na ₂ O	...	1.52	0.11	0.02
Cr ₂ O ₃	0.24	0.30	0.45	...
MnO	0.24	0.14	0.34	0.07
Totals	99.18	99.77	101.05	99.87

Number of Cations (x1000)

Si	1975	1979	3016	990
Al	34	107	1758	4
Ti	...	9	69	...
Ca	11	523	363	...
Mg	1270	1111	2072	1866
Fe	204	160	692	145
Na	...	106	15	...
Cr	6	9	25	...
Mn	6	4	21	2
Mg/(Mg+Fe)	0.862	0.874	0.750	0.928

*Total Fe as FeO.

1. Enstatite, Webster, North Carolina.

2. Diopside, PHN 1600E/4, Thaba Putsoa, Lesotho.

3. Garnet, PHN 1503C, Sekameng, Lesotho.

4†. Forsterite, P-140, Balsam Gap, North Carolina.

Gravimetric analysis by H. B. Wiik.

TABLE 1. Primary bulk compositions

	Mix PD 75 Py + 25 Di, wt %		Mix PDT 95(Py ₇ Di ₃) + 5CaTiAl ₂ O ₆ , wt %	
	Intended*	Probe Analysis	Intended**	Probe Analysis
SiO ₂	47.40	47.68	45.54	45.35
Al ₂ O ₃	18.97	17.30	18.96	18.93
TiO ₂	1.68	1.64
CaO	6.47	6.56	8.56	8.05
MgO	27.16	28.20	25.26	25.73

*Composition prepared and used by O'Hara (1963).

**Composition prepared by J. Akella.

garnet as a geothermometer, and (4) to compute and compare the equilibration pressures estimated for experimentally equilibrated natural mineral mixtures, using the phase data for $\text{MgSiO}_3\text{-Al}_2\text{O}_3$, $\text{MgSiO}_3\text{-CaSiO}_3\text{-Al}_2\text{O}_3$, and the thermodynamic approach of Wood.

Some of the results presented in this study have

been briefly reviewed by Akella (1974a, 1974b) and Akella and Boyd (1973, 1974).

Starting materials and experimental procedure

For the present study in the $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ system, two glasses on the pyrope-diopside join were used: pyrope₇₅diopside₂₅ (mix PD) and pyrope₇₀-

TABLE 3. Composition of the coexisting phases for the pyrope₇₅diopside₂₅ bulk composition

T, °C	P, kbar	Σ Time*, hours	Phase	Composition, wt %			Ca
				CaSiO ₃	MgSiO ₃	Al ₂ O ₃	Ca + Mg
1100	26	14	Orthopyroxene	2.0	93.5	4.6	0.019
			Clinopyroxene**				
			Garnet	14.1	62.5	23.4	0.164
1300	26	5	Orthopyroxene	3.8	89.7	6.5	0.034
			Clinopyroxene	35.0	55.3	9.7	0.353
			Garnet	13.3	62.5	24.2	0.155
1000	31	26	Orthopyroxene	1.6	96.0	2.7	0.014
			Clinopyroxene	49.1	50.0	2.1	0.459
			Garnet	13.3	61.2	23.2	0.158
1100	31	20	Orthopyroxene	1.8	94.9	3.2	0.016
			Clinopyroxene**				
			Garnet	11.4	64.2	25.1	0.133
1200	31	10	Orthopyroxene	2.5	93.5	4.0	0.023
			Clinopyroxene	43.3	53.5	3.8	0.412
			Garnet	12.3	65.3	22.4	0.140
1300	31	12	Orthopyroxene	3.3	91.3	5.4	0.029
			Clinopyroxene	40.6	54.3	5.1	0.392
			Garnet	11.8	64.3	23.8	0.136
1500	31	3	Orthopyroxene	4.8	88.1	7.1	0.045
			Clinopyroxene	31.2	56.3	12.2	0.324
			Garnet	11.2	65.0	23.8	0.130
1000	38	29	Orthopyroxene	1.3	97.4	1.8	0.011
			Clinopyroxene**				
			Garnet	12.6	62.4	24.3	0.148
1100	38	15	Orthopyroxene	1.8	97.5	2.4	0.016
			Clinopyroxene	44.6	52.2	2.1	0.425
			Garnet	12.8	62.9	24.8	0.149
1300	38	8	Orthopyroxene	3.2	93.3	3.5	0.028
			Clinopyroxene**				
			Garnet	12.6	63.3	24.1	0.145
1500	38	5	Orthopyroxene	5.5	89.3	5.1	0.050
			Clinopyroxene**				
			Garnet	12.1	63.4	24.5	0.140
1000	44	30	Orthopyroxene	1.1	97.6	1.4	0.010
			Clinopyroxene	49.2	49.5	1.3	0.460
			Garnet	12.8	63.8	24.4	0.148
1100	44	10	Orthopyroxene	1.4	96.5	1.6	0.012
			Clinopyroxene**				
			Garnet	12.1	65.2	23.5	0.139
1300	44	7	Orthopyroxene	2.9	94.6	2.6	0.025
			Clinopyroxene	44.1	53.8	2.1	0.414
			Garnet	12.1	64.5	24.1	0.139
1500	44	8	Orthopyroxene	5.5	90.2	4.3	0.050
			Clinopyroxene	30.4	63.5	4.7	0.290
			Garnet	11.1	64.8	24.1	0.129

*The runs were recycled until a consistent Al₂O₃ value was obtained in the orthopyroxene analysis.

**Clinopyroxene present, but good analyses could not be obtained owing to inclusions.

TABLE 4. Composition of the orthopyroxenes in the reversal runs compared with those crystallized from the pyrope₇₅diopside₂₅ original bulk composition

P, kbar	T, °C	Starting Composition*	Chemical Composition, wt %			
			SiO ₂	Al ₂ O ₃	CaO	MgO
44	1300	Low	57.43 (39)**	2.91 (20)	1.10 (30)	38.01 (40)
		Original	57.54 (80)	2.62 (30)	1.38 (5)	38.45 (40)
		High	57.80 (30)	2.75 (10)	1.08 (10)	37.53 (30)
44	1100	Low†	58.40	1.74	0.86	37.39
		Original	58.16 (54)	1.63 (14)	0.68 (4)	38.76 (35)
		High†	58.20	1.91	0.86	37.79
44	1000	Low†	58.20	1.10	0.57	38.54
		Original	57.84 (52)	1.44 (23)	0.60 (8)	38.85 (50)
		High	58.70 (144)	1.62 (19)	0.55 (6)	38.79 (120)
38	1100	Original	58.73 (35)	2.43 (30)	0.86 (7)	39.16 (28)
		High	57.61 (46)	2.53 (30)	0.67 (5)	37.95 (22)
31	1100	Original	57.11 (30)	3.19 (20)	0.86 (10)	38.09 (30)
		Low	57.70 (27)	3.22 (40)	1.01 (11)	37.60 (23)

*Low: runs from low-alumina side. Original: runs made with Py₇₅Di₂₅ original bulk composition. High: runs from high-alumina side. See text for details.

**Values in parentheses represent the standard deviation in terms of least units cited for the value to their immediate left.

†Chemical analyses made on an ARL-EMX-SM electron microprobe. Analyzed garnet was used as an internal standard.

diopside₃₀ to which 5 weight percent titanium pyroxene component, CaTiAl₂O₆, was added (mix PDT) to test the effect of Ti on these equilibria. Electron microprobe analyses for the glasses per-

formed on an automated MAC probe are given in Table 1.

Starting materials for the natural mineral mixtures included an enstatite with low Al₂O₃ from Webster,

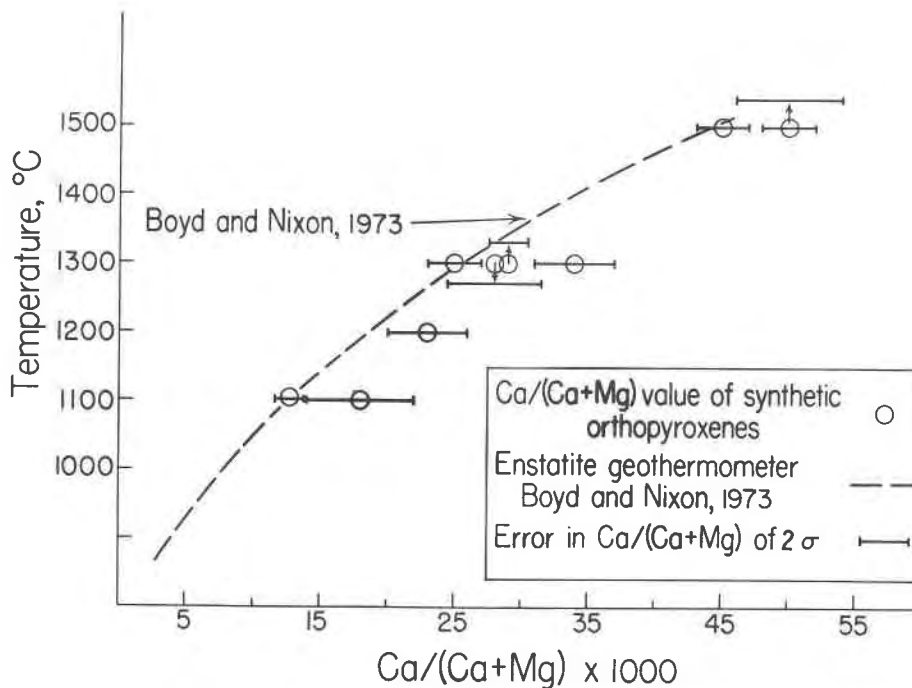


FIG. 1. The Ca/(Ca + Mg) ratios of orthopyroxene coexisting with clinopyroxene and garnet at different pressures as a function of temperature. Dashed line is an "empirical curve" for enstatite in ultramafic nodules given by Boyd and Nixon (1973).

North Carolina; forsterite from Balsam Gap, North Carolina; and discrete garnet (PHN 1503C) and diopside (PHN 1600E4) nodules, respectively from Sekameng and Thaba Putsoa kimberlite pipes in Lesotho (Table 2). The garnet and pyroxenes were combined in a 1:1:1 weight percent mixture to which was added 5 weight percent forsterite, to keep the phases similar to garnet peridotites. The starting mixtures were ground under alcohol for several hours, reducing the grain size to approximately 5–10 μm .

Experimental charges were equilibrated in solid-media, high-pressure apparatus (Boyd and England, 1960). A friction correction of ± 1 kbar was applied to the measured load pressure, depending on the direction of the piston motion (Akella, 1974c). Temperatures were measured using Pt-Pt10Rh and W3%Re-W25%Re thermocouples. No correction for the effect of pressure on thermal emf has been applied to the temperatures reported in this investigation. Williams and Kennedy (1969) have estimated the corrections to be $+5^\circ$ to $+10^\circ\text{C}$ in the pressure-temperature range used in this investigation.

Platinum capsules were used initially as containers for all mixes, but it was found that Fe from the runs

with the natural mineral mixtures dissolved in platinum even under subsolidus conditions. The leaching of Fe caused the silicates to have widely variable FeO contents. This problem was solved by using graphite capsules with tight-fitting lids. The experimental charges were slightly moistened with water to facilitate grain growth and to enhance the reaction rate. Nevertheless, in some runs where natural mineral mixtures were used, 16 hours was not sufficient to produce homogeneous phases. Recycling runs two or three times helped in attaining equilibrium. Surprisingly, grain growth appeared more sluggish in the experiments where natural mineral mixtures were used than for similar experiments with the Fe-free synthetic glasses.

Only the coarsest grains ($>10 \mu\text{m}$) in each run could be analyzed with the electron microprobe. In analyzing grains of this size there is a particular danger of overlooking unobserved intergrowths. This problem was severe during analysis of clinopyroxenes (Table 3) that lacked any shape or form for easy identification under microprobe optics. Attempts were made to obtain at least six analyses for each phase in each run. Standard deviations given for the

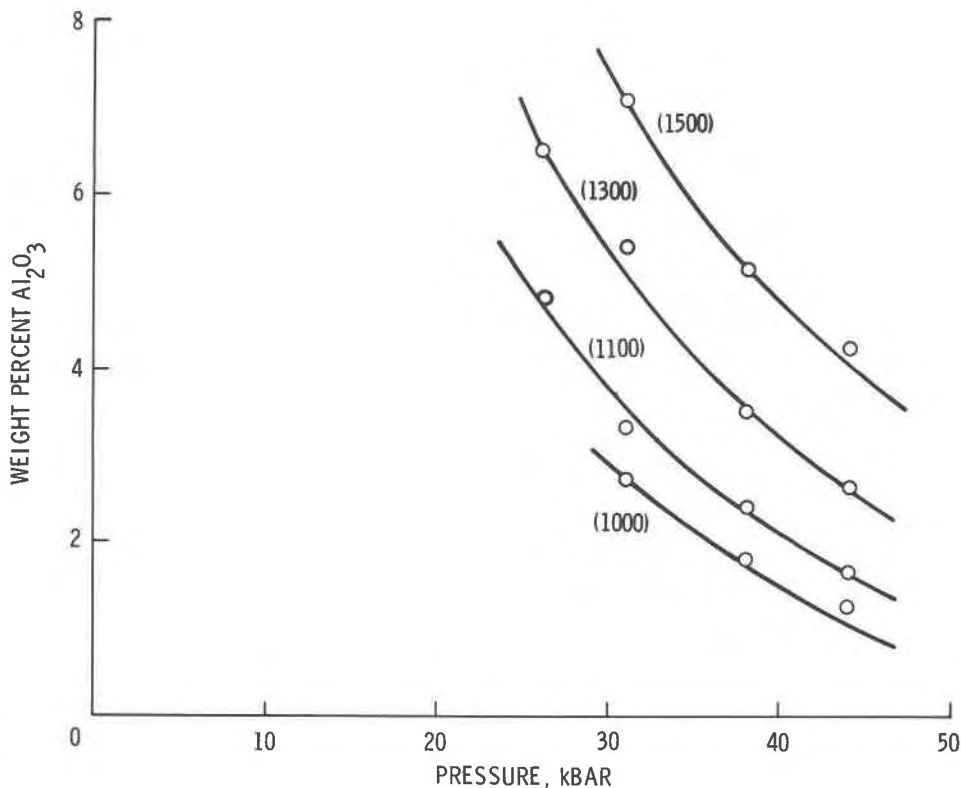


FIG. 2. Weight percentage of Al_2O_3 in orthopyroxene coexisting with clinopyroxene and garnet as a function of pressure. Values in parentheses are temperature in degrees centigrade.

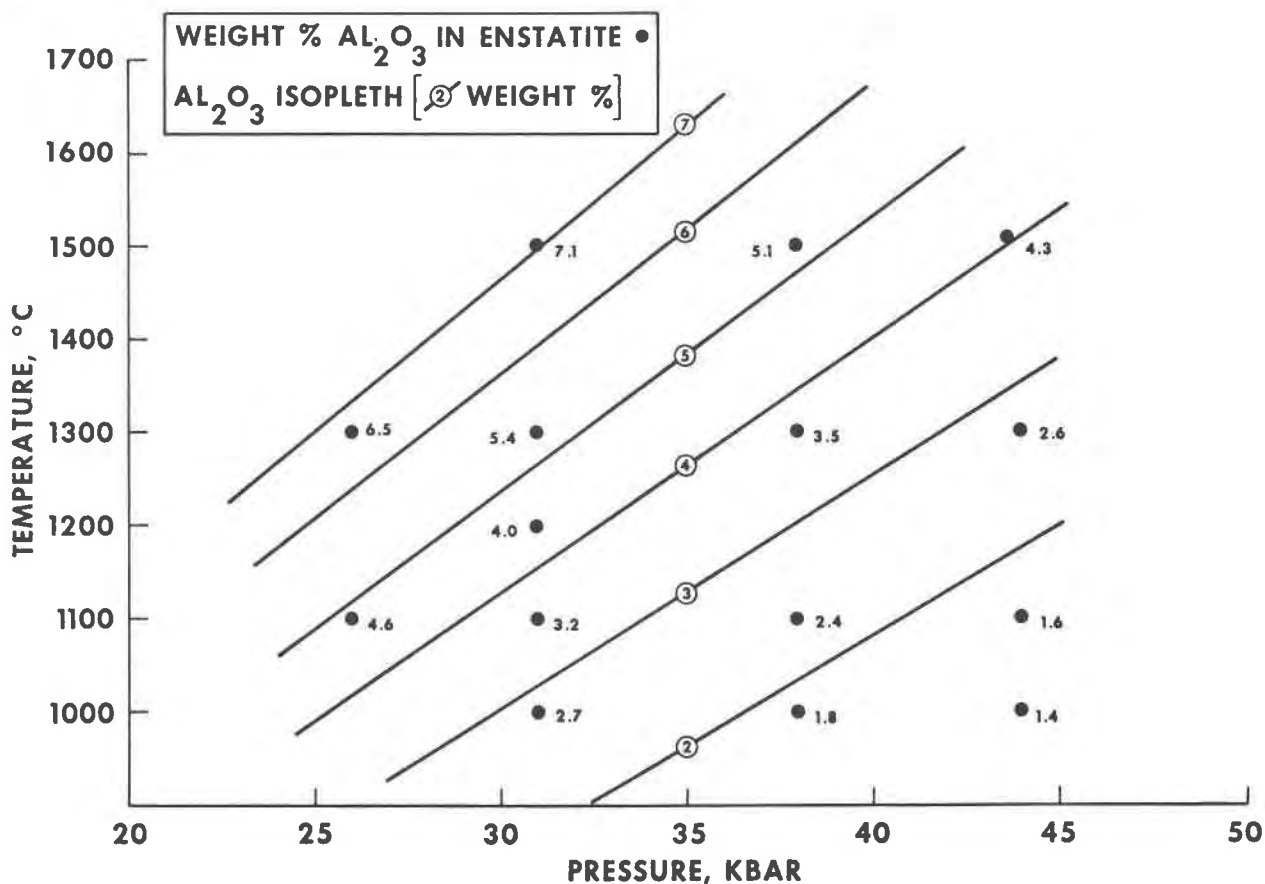


FIG. 3. Al_2O_3 content of enstatite in equilibrium with garnet and clinopyroxene as a function of pressure and temperature. Solid lines represent Al_2O_3 isopleths. Solid circles represent experimentally determined data points.

pyroxene and garnet analyses (Table 4) provide a measure of the degree of homogeneity that has been obtained.

Establishing equilibrium

Reversing a ternary solid solution field is a considerably more complex problem than reversing a binary solvus and requires study of the phase relations at a variety of pressure-temperature conditions over which the solid solution field changes (Boyd, 1970).

In order to establish equilibrium in the present study, two sets of reversal runs were performed under critical pressure and temperature conditions. In the first set, orthopyroxene + clinopyroxene were crystallized by using $\text{Di}_{53}\text{En}_{47}$ (MD-53) glass prepared by J. F. Schairer to which was added synthetic pyrope; this mixture was equilibrated under given pressure and temperature conditions (runs from low-alumina side). In the second set, using original PD glass composition, orthopyroxene + clinopyroxene + garnet

TABLE 5. Composition of orthopyroxene coexisting with clinopyroxene and garnet for both PD and PDT starting compositions

	31 Kbar/1100°C		38 Kbar/1100°C		44 Kbar/1100°C		44 Kbar/1500°C	
	PD	PDT	PD	PDT	PD	PDT	PD	PDT
SiO_2	57.1	56.9	58.7	57.9	58.2	58.6	57.0	56.6
Al_2O_3	3.19	3.1	2.4	2.4	1.65	1.6	4.4	4.3
TiO_2	...	0.25	...	0.25	...	0.19	...	0.4
CaO	0.9	0.9	0.9	1.0	0.7	0.8	2.6	2.3
MgO	38.1	37.7	39.2	39.4	38.8	39.8	35.4	36.3
Totals	99.3	98.85	101.2	100.95	99.3	100.99	99.4	99.9

were crystallized first, and the run product was recharged under different pressure and temperature conditions (runs from high-alumina side). The compositions of the orthopyroxenes in these runs, coexisting with garnet + clinopyroxene, are compared with the composition of the orthopyroxene crystallized from $\text{Py}_{75}\text{Di}_{25}$ original glass (Table 3). Orthopyroxenes crystallized in runs from the low-alumina side and the high-alumina side have compositions similar to those crystallized from the original $\text{Py}_{75}\text{Di}_{25}$ bulk compositions (Table 4) within the limits of analytical accuracy. The standard deviations presented in Table 4 signify the analytical uncertainties. Hence it is believed that the analyses in Table 3 are indeed equilibrium compositions.

Experimental results and discussion

The subsolidus phase assemblage for the synthetic compositions on the pyrope-diopside join (mixes PD and PDT, Table 1) are garnet + clinopyroxene + orthopyroxene at 26–44 kbar pressure and 1000°–1500°C. Electron microprobe analyses of the coexisting phases for runs made with Ti-free composition mix PD are presented in Table 3. The beginning of melting was observed at 31 kbar and 1600° ± 10°C, and the first phase to melt was clinopyroxene. M. J. O'Hara (personal communication) reported 1615°C for this point. The garnet that coexists with orthopyroxene and clinopyroxene contains 10–14 mole percent of the grossular molecule. This amount is in general agreement with the compositions of the garnets from natural garnet + enstatite + diopside assemblages, described by Boyd and Nixon (1973) and Akella and Boyd (1974).

Enstatite geothermometer

The $\text{Ca}/(\text{Ca}+\text{Mg})$ ratio of enstatite in equilibrium with diopside is a potentially useful geothermometer (e.g., Boyd and Nixon, 1973), but there appear to be some difficulties in obtaining a satisfactory laboratory calibration for this curve. Hensen (1973), using natural samples, found that the $\text{Ca}/(\text{Ca}+\text{Mg})$ ratio of enstatite increased with temperature and decreased with pressure. Mysen and Boettcher (1975), in their experiments on natural samples, also reported a systematic increase in the $\text{Ca}/(\text{Ca}+\text{Mg})$ ratio with temperature in enstatite coexisting with diopside.

The $\text{Ca}/(\text{Ca}+\text{Mg})$ ratios of enstatites from the present experiments are plotted as a function of temperature in Figure 1, along with the empirical "enstatite thermometer" obtained by Boyd and Nixon (1973) for pyroxene compositions from lherzolite nodules

from Lesotho. The present experimental data plot close to the empirical curve but are displaced to slightly higher values of $\text{Ca}/(\text{Ca}+\text{Mg})$. The standard deviation for calcium provided by analyses on different orthopyroxene grains in a given sample ranges from 0.1 to 0.4 weight percent. The uncertainties in the $\text{Ca}/(\text{Ca}+\text{Mg})$ ratio for $\pm 2\sigma$ are larger than would be expected from analytical errors and may reflect slight variations in the CaO content of the orthopyroxene or errors induced in the analysis owing to the small grain size of the phases in the run products. These runs were made in the pressure range 31–44 kbar, and there is a suggestion that pressure decreases $\text{Ca}/(\text{Ca}+\text{Mg})$. It is not possible to be certain that the effect is present within the uncertainties established by the σ values. Nevertheless, a comparison of these data obtained at pressures above 30 kbar with the data obtained by Mysen and Boettcher (1975) in the range 7.5–15 kbar supports the concept of a pressure effect in the direction suggested by Hensen (1973).

It is interesting to note in Figure 1 that at any given temperature none of the experimental data points fall at a lower $\text{Ca}/(\text{Ca}+\text{Mg})$ ratio than that given by Boyd and Nixon's empirical curve. If allowance is made for the probability that many of the Lesotho lherzolites have equilibrated at pressures higher than the range 31–44 kbar, then the present results lend qualitative support to the empirical "enstatite thermometer" proposed by Boyd and Nixon (1973).

Solubility of Al_2O_3 in enstatite: CaSiO_3 - MgSiO_3 - Al_2O_3 system

The Al_2O_3 content of orthopyroxene coexisting with garnet and clinopyroxene in the system CaSiO_3 -

TABLE 6. Solubility of Al_2O_3 (wt %) in orthopyroxene coexisting with garnet and clinopyroxene at 31 and 44 kbar pressure and 1100°C in different systems

	Al_2O_3	
	31 kbar/1100°C	44 kbar/1100°C
MgSiO_3 - Al_2O_3 *	3.3	[1.5]††
CaSiO_3 - MgSiO_3 - Al_2O_3	3.2	1.6
CaSiO_3 - MgSiO_3 - $\text{CaTiAl}_2\text{O}_6$	3.1	1.6
CaSiO_3 - MgSiO_3 **	2.6	1.4
FeSiO_3 - $\text{CaTiAl}_2\text{O}_6$		
Natural mixture†	2.5	1.39

*MacGregor, 1974

**Akella and Boyd, 1973

†Akella and Boyd, 1974

††Extrapolated value in brackets

MgSiO₃-Al₂O₃ is presented in Table 3 and is plotted as a function of pressure in Figure 2. In the present investigation the Al₂O₃ content of orthopyroxene at 31 kbar and 1200°C is 4.1 weight percent, whereas under the same conditions Boyd (1970) reported 3.7 to 4.5 weight percent, and for the Ca-free system

MacGregor (1974) reported 4.9 weight percent Al₂O₃ in the orthopyroxene. The form of the isopleths obtained for the ternary system CaSiO₃-MgSiO₃-Al₂O₃ (Figure 3) is very similar to that obtained for the binary join MgSiO₃-Al₂O₃ (Boyd and England, 1964; MacGregor, 1974). Green and Ringwood (1967) and

TABLE 7. Compositions of equilibrated garnets and pyroxenes

	En		Di		Ga		En		Di		Ga	
	31 kbar/1100°C, N-8						31 kbar/1300°C, N-7 (A)					
SiO ₂	55.77	<u>0.5*</u>	53.14	<u>0.6</u>	43.03	<u>0.8</u>	55.06	<u>0.6</u>	53.27	<u>0.2</u>	42.75	<u>0.7</u>
Al ₂ O ₃	2.48	<u>0.3</u>	2.83	<u>0.3</u>	20.45	<u>0.4</u>	3.54	<u>0.2</u>	4.20	<u>0.2</u>	21.88	<u>0.5</u>
TiO ₂	0.13	<u>0.02</u>	0.25	<u>0.02</u>	0.86	<u>0.1</u>	0.14	<u>0.01</u>	0.26	<u>0.02</u>	0.73	<u>0.3</u>
CaO	1.11	<u>0.2</u>	19.40	<u>0.7</u>	5.07	<u>0.2</u>	1.80	<u>0.1</u>	16.30	<u>0.2</u>	5.55	<u>0.5</u>
MgO	33.28	<u>0.8</u>	19.53	<u>1.1</u>	20.27	<u>0.9</u>	32.21	<u>0.4</u>	20.23	<u>0.3</u>	19.99	<u>0.2</u>
FeO†	6.25	<u>0.7</u>	2.80	<u>0.6</u>	9.57	<u>0.5</u>	7.32	<u>0.4</u>	5.18	<u>0.2</u>	9.73	<u>0.9</u>
Na ₂ O	0.02	...	0.59	<u>0.1</u>	0.03	<u>0.02</u>	0.13	<u>0.03</u>	0.89	<u>0.1</u>	0.09	<u>0.03</u>
Cr ₂ O ₃	0.28	<u>0.03</u>	0.43	<u>0.04</u>	0.60	<u>0.1</u>	0.29	<u>0.02</u>	0.46	<u>0.04</u>	0.85	<u>0.2</u>
MnO	0.22	<u>0.03</u>	0.16	<u>0.02</u>	0.42	<u>0.04</u>	0.18	<u>0.02</u>	0.20	<u>0.02</u>	0.37	<u>0.02</u>
Totals	99.54		99.13		100.30		100.67		100.99		101.94	
Number of Cations (x1000)												
Si	1938		1931		3069		1907		1904		3008	
Al	102		121		1719		144		177		1814	
Ti	3		7		46		4		7		39	
Ca	41		755		387		67		624		418	
Mg	1724		1058		2155		1663		1078		2097	
Fe	182		85		571		212		155		572	
Na	1		42		4		9		62		12	
Cr	8		12		34		8		13		47	
Mn	6		5		25		5		6		22	
Mg/(Mg+Fe)	0.905		0.926		0.791		0.887		0.874		0.786	
44 kbar/1300°C, N-10												
SiO ₂	55.59	<u>0.7</u>	52.79	<u>0.4</u>	43.80	<u>1.5</u>	56.50	<u>0.4</u>	52.66	<u>1.0</u>	43.16	<u>0.5</u>
Al ₂ O ₃	2.43	<u>0.4</u>	5.45	<u>0.7</u>	20.00	<u>1.1</u>	1.69	<u>0.2</u>	3.88	<u>1.1</u>	20.71	<u>0.6</u>
TiO ₂	0.08	<u>0.01</u>	0.20	<u>0.02</u>	0.97	<u>0.2</u>	0.11	<u>0.03</u>	0.46	<u>0.1</u>	0.83	<u>0.1</u>
CaO	1.23	<u>0.3</u>	14.36	<u>0.6</u>	5.08	<u>0.5</u>	1.01	<u>0.2</u>	20.37	<u>1.5</u>	5.46	<u>0.2</u>
MgO	32.66	<u>0.8</u>	19.41	<u>0.4</u>	20.62	<u>0.6</u>	33.91	<u>0.7</u>	17.81	<u>1.1</u>	20.52	<u>0.5</u>
FeO†	6.77	<u>0.4</u>	4.84	<u>0.1</u>	9.77	<u>1.0</u>	7.07	<u>0.4</u>	3.27	<u>0.7</u>	10.09	<u>0.4</u>
Na ₂ O	0.29	<u>0.1</u>	1.57	<u>0.3</u>	0.08	<u>0.02</u>	0.10	<u>0.03</u>	1.13	<u>0.3</u>	0.10	<u>0.02</u>
Cr ₂ O ₃	0.22	<u>0.02</u>	0.41	<u>0.03</u>	0.51	<u>0.05</u>	0.20	<u>0.02</u>	0.35	<u>0.04</u>	0.69	<u>0.1</u>
MnO	0.20	<u>0.02</u>	0.19	<u>0.02</u>	0.35	<u>0.04</u>	0.18	<u>0.03</u>	0.11	<u>0.03</u>	0.36	<u>0.04</u>
Totals	99.47		99.22		101.18		100.17		100.04		101.92	
Number of Cations (x1000)												
Si	1939		1907		3096		1946		1908		3042	
Al	100		232		1666		69		166		1720	
Ti	2		5		52		3		13		44	
Ca	46		556		385		37		791		412	
Mg	1699		1046		2173		1741		962		2156	
Fe	198		146		578		204		99		595	
Na	20		110		11		7		79		14	
Cr	6		12		29		5		10		38	
Mn	6		6		21		5		3		21	
Mg/(Mg+Fe)	0.896		0.877		0.790		0.895		0.907		0.784	
38 kbar/1100°C, N-13												
SiO ₂	55.59	<u>0.7</u>	52.79	<u>0.4</u>	43.80	<u>1.5</u>	56.50	<u>0.4</u>	52.66	<u>1.0</u>	43.16	<u>0.5</u>
Al ₂ O ₃	2.43	<u>0.4</u>	5.45	<u>0.7</u>	20.00	<u>1.1</u>	1.69	<u>0.2</u>	3.88	<u>1.1</u>	20.71	<u>0.6</u>
TiO ₂	0.08	<u>0.01</u>	0.20	<u>0.02</u>	0.97	<u>0.2</u>	0.11	<u>0.03</u>	0.46	<u>0.1</u>	0.83	<u>0.1</u>
CaO	1.23	<u>0.3</u>	14.36	<u>0.6</u>	5.08	<u>0.5</u>	1.01	<u>0.2</u>	20.37	<u>1.5</u>	5.46	<u>0.2</u>
MgO	32.66	<u>0.8</u>	19.41	<u>0.4</u>	20.62	<u>0.6</u>	33.91	<u>0.7</u>	17.81	<u>1.1</u>	20.52	<u>0.5</u>
FeO†	6.77	<u>0.4</u>	4.84	<u>0.1</u>	9.77	<u>1.0</u>	7.07	<u>0.4</u>	3.27	<u>0.7</u>	10.09	<u>0.4</u>
Na ₂ O	0.29	<u>0.1</u>	1.57	<u>0.3</u>	0.08	<u>0.02</u>	0.10	<u>0.03</u>	1.13	<u>0.3</u>	0.10	<u>0.02</u>
Cr ₂ O ₃	0.22	<u>0.02</u>	0.41	<u>0.03</u>	0.51	<u>0.05</u>	0.20	<u>0.02</u>	0.35	<u>0.04</u>	0.69	<u>0.1</u>
MnO	0.20	<u>0.02</u>	0.19	<u>0.02</u>	0.35	<u>0.04</u>	0.18	<u>0.03</u>	0.11	<u>0.03</u>	0.36	<u>0.04</u>
Totals	99.47		99.22		101.18		100.17		100.04		101.92	
Number of Cations (x1000)												
Si	1939		1907		3096		1946		1908		3042	
Al	100		232		1666		69		166		1720	
Ti	2		5		52		3		13		44	
Ca	46		556		385		37		791		412	
Mg	1699		1046		2173		1741		962		2156	
Fe	198		146		578		204		99		595	
Na	20		110		11		7		79		14	
Cr	6		12		29		5		10		38	
Mn	6		6		21		5		3		21	
Mg/(Mg+Fe)	0.896		0.877		0.790		0.895		0.907		0.784	

*Values underlined are standard deviations; each analysis is an average for six or more grains.

†Total Fe as FeO.

Abbreviations: En, enstatite; Di, diopside; Ga, garnet.

Boyd (1970) reported a decrease in the Al_2O_3 solubility in orthopyroxene from a Ca-undersaturated to a Ca-saturated system. The Al_2O_3 solubility data for enstatite in the garnet stability field reported by MacGregor (1974) are higher than the present data at and above 1200°C ; however, the values reported by him for the $1100^\circ\text{--}950^\circ\text{C}$ temperature range are lower than those obtained in the present study.

Effect of TiO_2 and FeO on the solubility of Al_2O_3 in orthopyroxene

Natural enstatites in ultramafic nodules commonly contain as much as 0.1–0.3 weight percent TiO_2 , and hence it is interesting to explore the effect of Ti on Al solubility in enstatite. Exploratory runs were made at 31–44 kbar and 1100° and 1500°C , using a starting composition of pyrope₇₀diopside₃₀ to which was added 5 weight percent $\text{CaTiAl}_2\text{O}_6$ (Table 1).

The compositions of orthopyroxenes coexisting with clinopyroxene and garnet from runs made at 31–44 kbar pressure and at 1100°C and 1500°C , using Ti-free (mix PD) and Ti-bearing (mix PDT) mixtures (Table 5), show no significant difference in their Al_2O_3 content. The present results suggest that small amounts of TiO_2 in the original bulk composition do not seem to have a marked effect on the solubility of Al_2O_3 in the pyroxenes. Hensen (1973) arrived at the same conclusion based on his studies on natural mixtures.

The Al_2O_3 content of the orthopyroxene coexisting with clinopyroxene + garnet \pm rutile \pm ilmenite in the system $\text{CaSiO}_3\text{--MgSiO}_3\text{--FeSiO}_3\text{--CaTiAl}_2\text{O}_6$ was also determined in the 31–44 kbar pressure range and at 1100°C (Akella and Boyd, 1973). These results are compared with the data from other synthetic systems (Table 6). The alumina solubilities obtained for the orthopyroxene in the system $\text{CaSiO}_3\text{--MgSiO}_3\text{--Al}_2\text{O}_3$ are slightly less than those in the $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ system. A significant drop in the Al_2O_3 content of the orthopyroxene occurs in the system to which FeO was added. As the alumina solubilities in orthopyroxenes determined in the Fe-bearing system are nearly the same as those for the natural mineral mixture, a direct application of equilibria from simplified iron-free synthetic systems to natural garnet-bearing assemblages should result in estimates of equilibration pressure that are too high.

Estimation of equilibration pressure—a comparison

Wood and Banno (1973) and Wood (1974) have derived a thermodynamic model for the solution of

Al_2O_3 in enstatite coexisting with garnet from which the effect of contaminating ions can be calculated. Wood and Banno have pointed out that application of their model to the pyrolite data of Green and Ringwood (1967) produces a much improved agreement with the results obtained for the pure $\text{MgSiO}_3\text{--Mg}_3\text{Al}_2\text{Si}_8\text{O}_{12}$ system.

In the present study, a natural mineral mixture of diopside + enstatite + garnet + olivine was equilibrated under controlled pressure and temperature conditions. Using the chemical composition of these equilibrated phases (Table 7), the equilibration pressure and temperature were estimated by direct application of the phase data for the $\text{MgSiO}_3\text{--Al}_2\text{O}_3(\text{EnCo})$ and $\text{CaSiO}_3\text{--MgSiO}_3\text{--Al}_2\text{O}_3(\text{WoEnCo})$ systems and the model of Wood and Banno (Table 8).

The equilibration pressures estimated by direct application of the phase data for both WoEnCo and EnCo are all higher than the measured equilibration pressures. Nevertheless, there appears to be an inconsistency between the EnCo data (MacGregor, 1974) and the WoEnCo data (present study) at 1100°C . For two runs at this temperature (Table 8) the pressures estimated from the WoEnCo data are higher than those estimated by direct application of the EnCo data. This discrepancy is due to the low Al_2O_3 contents in enstatite reported by MacGregor (1974) at and below 1100°C for the EnCo system compared with the present data. The model of Wood and Banno (1973) appears to work well for the results at 31 kbar and 1100° and 1300°C , but corrections obtained are 4–5 kbar for runs at 38 kbar and 1100°C and 44 kbar and 1300°C (Table 8). This discrepancy is not understood.

TABLE 8. Experimental and calculated* equilibrium temperatures and pressures for a natural enstatite + diopside + garnet assemblage

Run No.	Al_2O_3 in Ent	Temperature, $^\circ\text{C}$		Pressure, kbar			
		Exp.	Calc.	Exp.	EnCo	WoEnCo	Wood
N-7	3.54	1300	1285	31	40	38	31
N-10	2.43	1300	1325	44	47	45	40
N-8	2.48	1100	1145	31	35	37	29
N-13	1.69	1100	1040	38	42	43	33

*Temperature calculated from $\text{Ca}/(\text{Ca} + \text{Mg})$ using the diopside solvus (Boyd, 1973). Pressure calculation: EnCo, from $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ (MacGregor, 1974); WoEnCo, from $\text{CaSiO}_3\text{--MgSiO}_3\text{--Al}_2\text{O}_3$ (Akella, this paper); Wood, from a theoretical relation described by Wood (1974). The measured temperature was used in the pressure calculations.

†See Table 7 for the analysis of all the coexisting phases.

Conclusion

The results reported here suggest that estimates of equilibration conditions can now be made with sufficient accuracy to be useful in understanding the origin of the ultramafic nodules associated with kimberlites. It is clear, however, that modifications and refinements of this pressure-temperature estimation procedure will probably be made as more data are available.

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