

The Compositions of Coexisting Pyroxenes and Garnet in the System $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ at $900^\circ - 1,100^\circ \text{C}$ and High Pressures

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Abstract. The compositions of coexisting orthopyroxene, clinopyroxene and garnet in the $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system are fixed at any given P and T . Reversed hydrothermal experiments over the P/T range 15–40 kb/ $900^\circ - 1,100^\circ \text{C}$ indicate that the garnet composition is nearly constant at $\text{Py}_{86}\text{Gr}_{14}$; the Al-content and $\text{Ca}/\text{Ca} + \text{Mg}$ values of the pyroxenes vary significantly, however:

T $^\circ \text{C}$	P kbar	Wt. % Al_2O_3		$\frac{\text{Ca}}{\text{Ca} + \text{Mg}} \times 100$	
		in opx	in cpx	in opx	in cpx
900	15	3.55	2.92	0.72	47.05
900	30	1.62	0.92	0.81	47.30
1,100	20	1.11	0.92	1.22	45.20
1,100	40	1.26	0.88	0.81	45.64

The significant variation of Al_2O_3 content with pressure supports its use as a geobarometer. The $\text{Ca}/\text{Ca} + \text{Mg}$ values of coexisting ortho- and clino-pyroxene have been used as a geothermometer. However, the present results show that the presence of Al_2O_3 in the pyroxenes decreases significantly the mutual solubility of the pyroxenes, which may cause errors of up to 200°C if the Al_2O_3 effect is ignored.

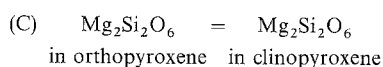
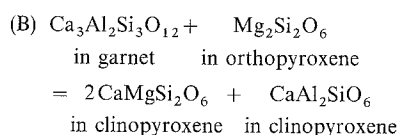
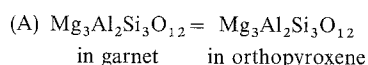
Thermodynamic analyses of the experimental results for the reaction $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}(\text{gar}) = \text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}(\text{opx})$ yield average values of ΔH° and ΔS° of 7.4 Kcal and 5.7 eu, respectively, which are in marginal agreement with calorimetric results. Similar analysis of our results for the reaction $\text{MgSiO}_3(\text{cpx}) = \text{MgSiO}_3(\text{opx})$ support earlier conclusions that MgSiO_3 substitution in clinopyroxene behaves as a regular solution (Holland et al. 1979) and that Al substitution is quasi-ideal (Wood 1979).

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Application of the present results to garnet lherzolites from southern Africa yields a geotherm which is parallel to those previously proposed, although the indicated heat flow is greater. Similar rocks, from the Solomon Islands, show a much steeper geothermal gradient, as expected for an oceanic plate.

Introduction

In the four-component system $\text{CaO} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$, the compositions of coexisting orthopyroxene, clinopyroxene and garnet are fixed at a given temperature and pressure by the buffering reactions:



Reaction (A), which controls the Al content of orthopyroxene in equilibrium with garnet, forms the basis of the most widely used geobarometer for deep-seated mantle samples from kimberlite pipes. It has been studied experimentally in the system $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$, by Boyd and England (1964), MacGregor (1974), Howells and O'Hara (1978), and Lane and Ganguly (1980). MacGregor (1974), Fujii (1977), Arima and Onuma (1977), and Danckwerth and Newton (1978) determined the compositions of enstatite in the $\text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system at various P , T points in equilibrium with the lower-pressure assemblage spinel + forsterite. Reaction (B), which

controls the Al-content of clinopyroxene in equilibrium with orthopyroxene and garnet, was studied experimentally by Akella (1976) and Howells and O'Hara (1978). Reaction (C) was studied experimentally in the system $\text{CaO}-\text{MgO}-\text{SiO}_2$ by numerous investigators, most recently Lindsley and Dixon (1976). Whereas earlier investigators relied heavily on synthesis or unreversed experiments, the Lindsley and Dixon (1976) runs approached equilibrium compositions from two directions. They analyzed their run products with the electron microprobe. Thus, the equilibrium compositions were determined more definitively than in previous studies. The Lindsley-Dixon work has been used to constrain a widely-used geothermometer based on the diopside-enstatite solid solution relations (Wells 1977).

Previous experimental studies of pyroxene compositions in the four-component system buffered by garnet or by spinel + forsterite (Boyd 1970; Herzberg 1978; Akella 1976; Fujii 1977; Finnerty 1978; Dixon and Presnall 1977; Howells and O'Hara 1978) have lacked either clear-cut demonstration of equilibrium compositions or microanalysis of the pyroxenes. In this study we use the method of Lindsley and Dixon (1976) and Danckwerth and Newton (1978), that of an H_2O vapor flux. Though H_2O at high pressures and temperatures produces fast reaction rates, it effectively confines the experimental temperature range below $1,100^\circ\text{C}$ at pressures below 25 kbar, in order to avoid hydrous melting. Even with the H_2O flux, reaction rates are not fast enough below 900°C to secure definitive reversals in feasible run times of at most several days duration. Pressures are limited by the formation of amphibole below 14–15 kbar.

A number of attempts were made in the present study to produce reversal of the pyroxene compositions in dry and slightly moist (breathed-upon) charges at $1,400^\circ\text{C}$ – $1,500^\circ\text{C}$. The results were discour-

aging – samples were of insufficient grain size for reliable analysis and showed poor equilibration compared to the hydrothermal data below $1,100^\circ\text{C}$. The attempts at higher temperatures were therefore abandoned and concentration was put on the hydrothermal study.

In spite of the limited temperature range of the present study, the number of valid reversals obtained makes possible a thermodynamic analysis of reactions (A), (B) and (C) and allows calibration of a garnet lherzolite geobarometer based on the Al content of orthopyroxene in the temperature range of the most common deep mantle samples, the granular lherzolites. The effect of Al on the mutual solubility of diopside and enstatite is assayed in the present study over temperature and pressure ranges large enough to draw general conclusions of importance for geothermometry.

Experimental Methods

Sensu stricto it is not possible to reverse the compositions of phases with two degrees of compositional freedom. In order to demonstrate equilibrium compositions of garnet, orthopyroxene and clinopyroxene, equilibrium was, however, approached from two directions for all three phases. Synthetic starting materials were used in all experiments (Table 1) and care was taken to assure that the materials were homogeneous. Starting garnets, were crystallized from glasses made by G.M. Chinner (Chinner et al. 1960) with the exception of pyrope₆₀grossular₄₀, which was supplied by H.T. Haselton (Haselton and Westrum 1980). The orthopyroxene and clinopyroxene compositions were prepared from reagent grade CaCO_3 , $\text{Al}(\text{OH})_3$, H_2SiO_3 and MgO crystal. The MgO was heated to high temperature just prior to weighing and a slight correction was made for the weight gained (due to absorption of H_2O) on the balance. Both the CaCO_3 and the $\text{Al}(\text{OH})_3$ were checked by firing loss to confirm that they contained the theoretical amounts of CO_2 and H_2O . After prolonged grinding under acetone the reagent mixes were fired at $1,350^\circ\text{C}$ to remove H_2O and CO_2 . The MgSiO_3 mix was converted to clinoenstatite by firing at $1,400^\circ\text{C}$ for several days, and then to enstatite at high pressures (Table 1).

Table 1. Compositions (wt. %) and synthesis conditions of reactant materials used in this study

#	Composition	P	T	Total time (hours)	Remarks
1	MgSiO_3 (100%), opx	20	1,500	1	from clinoenstatite
2	MgSiO_3 (81.69%)– $\text{CaMgSi}_2\text{O}_6$ (9.31%)– Al_2O_3 (9.00%), opx	20	1,500	20	initially from glass, five successive runs of 4 h each, reground each time
3	$\text{CaMgSi}_2\text{O}_6$ (100%), cpx	20	1,500	1	from glass
4	$\text{CaMgSi}_2\text{O}_6$ (60%)– MgSiO_3 (40%), cpx	30	1,600	2	from glass
5	$\text{CaMgSi}_2\text{O}_6$ (68.97%)– MgSiO_3 (22.03%)– Al_2O_3 (9.00%), cpx	20	1,500	4	initially from glass, three successive runs, reground each time
6	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (100%), Gt	30	1,300	1	crystallized glass from G.A. Chinner
7	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (80%)– $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (20%), Gt	30	1,300	1	crystallized glass from G.A. Chinner
8	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (60%)– $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (40%), Gt	45	1,300	1	synthesized by H.T. Haselton

The clinopyroxene mixes were melted at 1,465°C and quenched to produce glasses. Syntheses were performed in the piston-cylinder apparatus in graphite capsules. Numerous runs of 1–4 h each at 1,500°C and 20 kb, separated by fine-grinding, were necessary to get homogeneous Al-bearing clinopyroxenes and orthopyroxenes (Table 1). All materials were analyzed with X-ray diffraction and electron microprobe to check homogeneity.

Experiments were conducted in a 1/2" or 3/4" diameter piston-cylinder apparatus with NaCl pressure media. The smaller pressure chamber was used at 40 kbar. At the conditions of the present runs NaCl has been shown to provide an essentially hydrostatic pressure source with no friction correction needed (Holland 1980). Temperatures were determined using side-by-side chromel-P-alumel and W-3% Re vs W-25% Re thermocouples. Details of run techniques and temperature measurement have been described elsewhere (Danckwerth and Newton 1978).

Each experimental run in the 3/4" assembly consisted of two capsules, one with garnet, aluminous intermediate orthopyroxene and clinopyroxene; the other with end-member pyroxenes and garnet. Runs in the 1/2" assembly contained only one capsule. Starting mixes were sealed in 1/16"-diameter Pt tubes with approximately 40 wt.% H₂O. The total weight of sample + H₂O was about 8 mg. After the run, the charges were checked for the presence of pyroxenes and garnet with X-ray diffraction, and then mounted in an epoxy disc for microprobe analysis.

Energy-dispersive microprobe analyses were conducted with an ARL-EMX electron microprobe analyzer. All analyses were made at 15 kV with a beam diameter of approximately 1 µm. The standards used (pyrope glass, pyrope₈₀grossular₂₀ glass, enstatite₉₀corundum₁₀ glass, synthetic diopside and synthetic enstatite) were sufficiently close to the unknowns to insure that any errors in correction procedure were negligible.

The typical grain sizes of run products were 10–40 µm for garnet and orthopyroxene and 5–20 µm for clinopyroxene. Most grains of orthopyroxene and garnet showed core to rim zonation with the rims closer to final inferred equilibrium compositions. Occasionally in 900°C runs the cores retained the original starting compositions. Rare grains of olivine and of quartz were found in most runs – probably the result of the breakdown of Mg₂Si₂O₆ to Mg₂SiO₄ + SiO₂ by a metastable solution, transport, and redeposition process across a small temperature gradient.

At least ten analyses of each phase in each run were made. An analysis was rejected, and repeated, if it did not total to 100 ± 2% or if its stoichiometry was not within 2% of an ideal garnet or pyroxene.

Experimental Results

Overlap Problem

A problem encountered in this study, especially at low pressures, and in other hydrothermal studies (Lindsley and Dixon 1976; Danckwerth and Newton 1978; Lane and Ganguly 1980), is the overlap or crossover of pyroxene analyses in reversal experiments. Typical analytical results from the paired capsules of a simple run, plotted in Fig. 1, bottom, show that one or both of the pyroxene compositions have overstepped equilibrium. This is probably the result of path looping; that is, nucleation of a pyroxene on the opposite side of the equilibrium boundary from the starting composition. Lane and Ganguly (1980) reported inverse Al-zonation of some orthopyroxenes

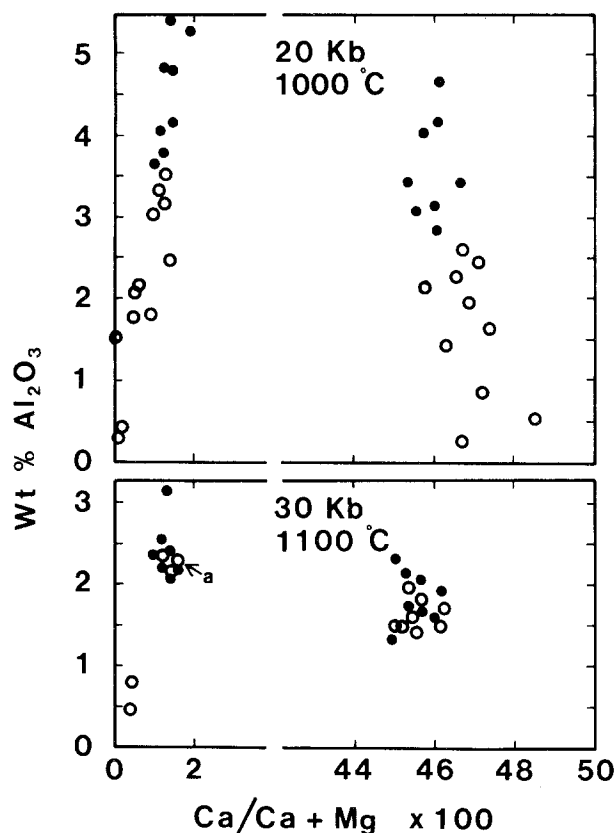


Fig. 1. Typical results of experiments which partially equilibrated (top) and one that approached nearly complete equilibrium (bottom). Open circles converged from diopside and enstatite compositions; closed circles started as intermediate Ca–Mg–Al pyroxenes. Note that in both experiments the values of Ca/Ca + Mg overlapped while Al₂O₃ contents only overlapped in the bottom figure. The cluster of points denoted with an "a" only represent a third of the analyses which fall in that region

which indicated path-looping, and a few such grains were found in the present study. If path looping took place in both runs of a reversal pair, the equilibrium composition must lie within the region of overlap. If, however, only one of a pair of reversal runs underwent path looping, the crossover region is not a true reversal bracket. The assumption made in the earlier studies, and the one made here, is that the equilibrium point lies within the crossover region. This is justified by the observations that a continuum of analyses approaching the crossover region from opposite directions was generally found, inversely zoned pyroxenes were quite rare, and the crossover regions, where present, were generally quite small.

Orthopyroxene and Clinopyroxene in the CaO–MgO–SiO₂ System

Experimental results for the Al-free system on mixes of diopside + enstatite (materials #s 1 and 3 in Tab-

Table 2. Experimental results for orthopyroxene-clinopyroxene equilibrium (reaction 2) in the CaO–MgO–SiO₂ system

Run	P	$T_{\text{Cr-Al}}$	$T_{\text{W-Rh}}$	$\frac{\text{Ca}}{\text{Ca}+\text{Mg}} \times 100$		Run duration (hours)
				opx ^a	cpx ^a	
1	20	900	900 ± 2	1.5–0.6	46.5–47.3	74
2	25	900	903 ± 2	1.0–0.8	46.9–47.3	51
3	30	900	896 ± 2	0.6–0.5	47.0–47.0	48
4	20	1,000	none	1.5–1.5	45.5–45.7	28
5	25	1,000	1,000 ± 4	1.5–1.2	45.5–45.8	36
6	30	1,000	991 ± 2	1.6–0.9	45.2–45.8	51
7	25	failed	1,100	1.4–1.1	43.5–44.2	22
8	30	1,100	failed	1.4–1.3	43.3–44.6	6

^a All composition ranges are overlaps (see text). Starting materials were diopside, enstatite and clinopyroxene of composition Di₆₀En₄₀

Table 3. Experimental determination of garnet composition at equilibrium with clinopyroxene and orthopyroxene

Run	P	T _{Cr–Al}	Final mole % pyrope ^a			Run duration (hours)
			From Py	From Py ₆₀	From Py ₈₀	
9	20	900	85.6	84.2	—	68
10	30	900	90.0	—	85.8	78
11	20	1,000	86.0	85.5	—	46
12	25	1,000	85.3	84.3	—	52
13	30	1,000	86.5	—	85.2	46
14	20	1,100	86.4	83.7	—	27
15	30	1,100	86.9	—	86.1	30
16	40	1,100	87.0	86.2	—	5

^a The garnet was equilibrated with clinopyroxene and orthopyroxene whose initial compositions were pure diopside and enstatite, respectively

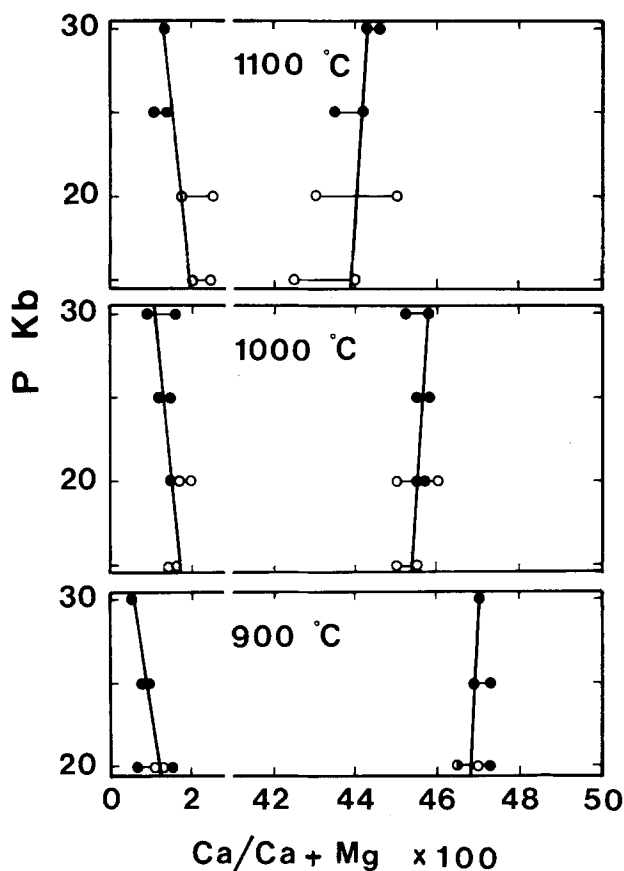


Fig. 2. Results of experiments on reaction (C) (clinopyroxene-orthopyroxene equilibrium) in the Al-free system. Open circles represent the data of Lindsley and Dixon (1976); closed circles are the present results. The straight lines have been drawn to fit all the present reversed data, to show a smooth change of slope from 900° to 1,100° C, and to be consistent with the experiments for the Al-bearing system (shown in Fig. 5). In this and several of the next figures, single symbols indicate that the two halves of a reversal experiment converged on the same point. Also in this and several of the next figures, a few points have been shifted slightly right or left for clarity

le 1) + water in one capsule and clinopyroxene (#4) + water in the mate are given in Table 2 and plotted in Fig. 2. The reversal results are in excellent agreement with those obtained by Lindsley and Dixon (1976).

The Composition of Garnet in Equilibrium with Orthopyroxene and Clinopyroxene

A series of experiments were made in order to determine the composition of garnet in equilibrium with orthopyroxene and clinopyroxene (Table 3). All runs were made with two capsules. In most runs, the first contained pyrope₁₀₀ + diopside + enstatite (starting materials #'s 1, 3 and 6) + water, and the second contained pyrope₆₀grossular₄₀ + diopside + enstatite (starting materials #'s 1, 3 and 8) + water. The equilibrium garnet composition indicated by all of these experiments was 85 ± 1.5% pyrope. Two runs were made using intermediate Ca–Al–Mg pyroxenes (starting materials #'s 2, 5 and 6 or 8) in the starting mix which yielded the same results. Thus it appears that even if the original pyroxenes are initially off equilibrium compositions, they buffer the garnet at the equilibrium composition.

Orthopyroxene and Clinopyroxene Compositions in Equilibrium with Garnet

The compositions of orthopyroxene and clinopyroxene in equilibrium with garnet were determined in a third series of experiments. Paired reversal capsules contained: (1) Py₈₀Gr₂₀ garnet, enstatite and diopside; (2) Py₈₀Gr₂₀ garnet, clinopyroxene (material #5, Table 1) and orthopyroxene (material #2, Table 1). With the exception of 40 kbar runs in the 1/2"-diameter apparatus, the two reversal-pair capsules were run side-by-side in the same assembly.

Table 4. Reversed compositions of orthopyroxenes and clinopyroxenes at equilibrium with garnet. Unless indicated by a footnote, the values represent the range of composition overlap when equilibrium was approached from two directions (see text). The values denoted with a footnote approached, but did not overlap, equilibrium

Run	<i>P</i>	<i>T</i> _{Cr-Al}	<i>T</i> _{W-Rh}	Orthopyroxene				Clinopyroxene				Run duration (hours)
				CaO	MgO	Al ₂ O ₃	SiO ₂	CaO	MgO	Al ₂ O ₃	SiO ₂	
17	15	900	901 ± 3	0.33 0.45	38.24 38.56	4.06 3.04	57.37 57.96	23.37 24.15	19.33 19.10	3.45 2.40	53.86 54.35	60
18	20	900	none	0.34 0.50	38.89 39.05	2.43 1.77	58.34 58.67	24.19 24.64	19.37 19.11	1.65 1.35	54.79 54.90	90
19	25	900	904 ± 2	0.45 0.45	39.06 39.31	1.77 ^a 1.17 ^a	58.71 59.08	24.31 24.62	19.47 19.25	1.15 1.05	55.07 55.08	93
20	30	900	none	0.33 0.56	39.36 39.30	1.27 ^a 0.96 ^a	59.04 59.18	24.02 24.72	19.78 19.25	1.00 0.85	55.21 55.18	98
21	16	1,000	failed	0.78 0.81	36.81 38.01	6.69 3.65	55.72 57.53	23.41 24.06	18.59 18.73	5.20 3.50	52.80 53.71	82
22	20	1,000	1,010 ± 10	0.53 0.75	38.18 38.00	3.80 ^a 3.79 ^a	57.49 57.46	23.14 23.63	19.76 19.46	2.85 ^a 2.60 ^a	54.25 54.32	27
23	22 ¹ / ₂	1,000	1,001 ± 4	0.53 0.64	38.36 38.39	3.34 3.04	57.76 57.92	23.31 23.93	19.82 19.32	2.35 2.30	54.52 54.45	74
24	25	1,000	996 ± 3	0.50 0.64	38.86 38.62	2.18 2.48	58.46 58.26	23.45 24.09	19.95 19.68	1.73 1.09	54.87 55.14	42
25	30	1,000	1,003 ± 2	0.45 0.67	38.88 38.80	2.23 1.98	58.44 58.56	23.80 24.39	19.76 19.53	1.50 0.85	54.95 55.24	48
26	40	1,000	1,001 ± 5	0.22	39.60	0.91 ^a	59.27	24.07	19.91	0.54	55.48	12
27	40	1,000	1,003 ± 2	0.56	39.44	0.61 ^a	59.40	24.41	19.55	0.74	55.30	14
28 ^b	25	1,100	1,098 ± 3	0.47 0.86	38.33 38.51	3.55 2.28	57.65 58.34	22.48 23.83	20.49 19.87	2.40 1.15	54.63 55.15	57
29 ^c	30	1,100	1,105 ± 2	0.50 0.86	38.73 38.58	2.48 2.13	58.28 58.43	23.02 23.19	20.22 20.36	1.95 1.25	54.81 55.20	27
30	40	none	1,100	0.39	39.21	1.52	58.88	23.54	20.19	0.95 ^a	55.32	10
31	40	1,098 ± 3	1,100	0.50	39.32	1.01	59.16	23.67	20.13	0.82 ^a	55.38	11

^a Values marked with in table indicate that compositions converged but did *not* overlap (see text); all other composition ranges are overlap ranges. Paired reversal capsules contained: (1) Py₈₀Gr₂₀ garnet, enstatite and diopside; (2) Py₈₀Gr₂₀ garnet, clinopyroxene (material #5, Table 1) and orthopyroxene (material #2, Table 1).

^b Large amount of melt present; garnet embayed

^c Minor amount of melt

Results for these runs are given in Table 4. Apart from the overlap problem, equilibration of the Ca/Ca + Mg values and of Al₂O₃ concentrations was generally definitive and nearly complete for all except the lowest-pressure experiments. Occasionally, pyroxene compositions were spread out between the final and starting compositions. The clinopyroxene compositions did not equilibrate as completely as the orthopyroxene compositions (Fig. 1). The Al₂O₃ content of the pyroxenes buffered by the presence of garnet decreases their mutual solubility significantly, as shown in Fig. 3. The effect on the clinopyroxene limb is pronounced, while that on the orthopyroxene limb is quite small. The garnet-saturated Al₂O₃ content of clinopyroxene in equilibrium with orthopyroxene at 1,000° C decreases the Mg content of the clinopyroxene over that in the garnet-free system by an amount

equivalent to a temperature decrease of about 100° C, as shown in Fig. 3.

Discussion

Al₂O₃ Contents of Orthopyroxene and Clinopyroxene

The only extensive study in the temperature and pressure range of the present study is that of Akella (1976). His unreversed syntheses from glass generally showed one to two weight percent more Al₂O₃ in pyroxenes than in the present reversals at the same nominal *P*–*T* conditions. In contrast to the assumption commonly made by others (e.g., Obata 1976), we find the clinopyroxene to have significantly less Al₂O₃ than coexisting orthopyroxene.

The present results for the Al₂O₃ content of orthopyroxene may be extended somewhat and com-

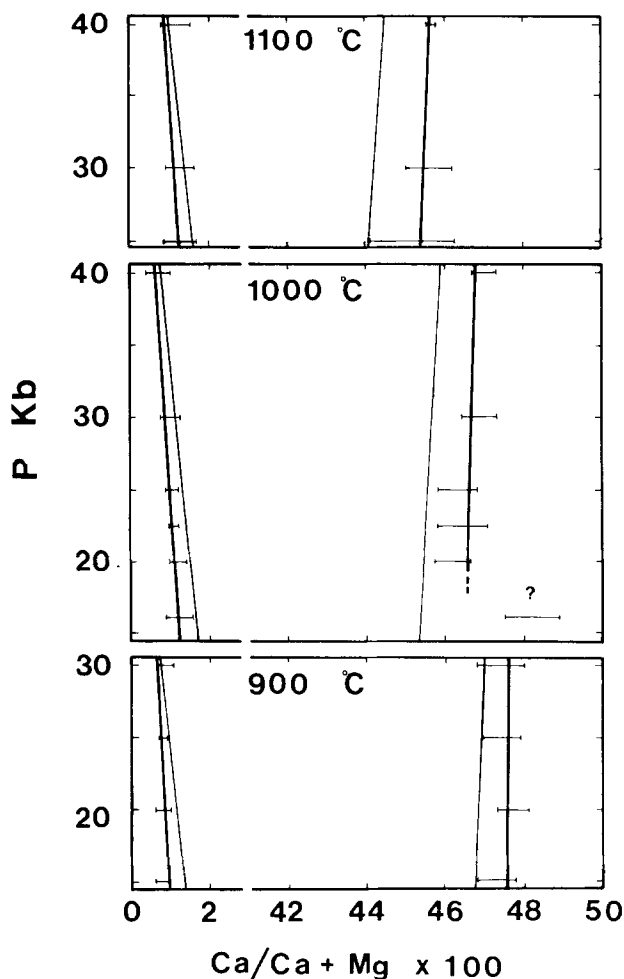


Fig. 3. Experimental results for reaction C in the Al-bearing system (brackets and bold lines). For comparison, the fine lines show the results for the Al-free system (from Fig. 2). The bold lines were drawn so as to fit all reversals, to show a smooth change in slope from 900° to 1,100° C and to converge on the Al-free results at high pressures

pared with the results of other investigators on garnet-pyroxene equilibrium in the system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ through a thermodynamic analysis. For equilibrium in reaction (A), we have:

$$\ln K^0 = -\frac{\Delta H_A^0}{RT} + \frac{\Delta S_A^0}{R} \approx \ln \frac{a_{\text{opy}}^{\text{opx}}}{a_{\text{py}}^{\text{gt}}} + \frac{P\Delta\bar{V}_A}{RT} \quad (1)$$

where K^0 is the one-bar equilibrium constant, and ΔH^0 , ΔS^0 and $\Delta\bar{V}$ are, respectively, the standard enthalpy, standard entropy, and partial molal volume change. $a_{\text{opy}}^{\text{opx}}$ denotes the activity of the $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ component in orthopyroxene, following Lane and Ganguly (1980). Following Wood and Banno (1973), rather than Lane and Ganguly (1980), we adopt a one-bar standard state, so as to make use of measured partial molar volumes (Danckwerth and Newton 1978; Haselton and Newton 1980). It is

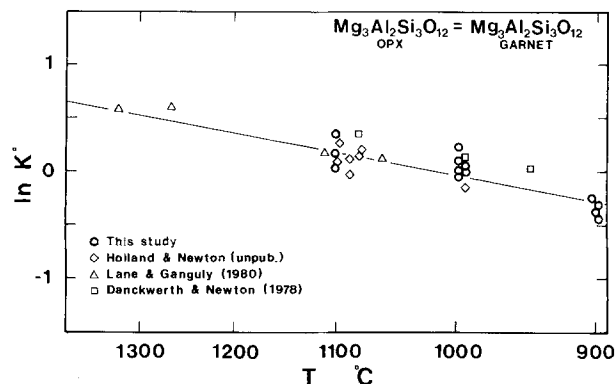


Fig. 4. $\ln K^0$ versus reciprocal temperature for reaction A, opy = pyrope. All reversed experimental results for the Ca-free system (Danckwerth and Newton 1978; Lane and Ganguly 1980; Holland and Newton, unpublished) and the Ca-bearing system (this study) have been shown

assumed that the small amount of Ca in the orthopyroxene does not significantly effect the partial molal volume of reaction, which ranges from 8.4 to 8.9 cm^3 over the composition range considered here. The approximation sign is used in expression (1) because of neglect of differential thermal expansion and compressibility in the last term.

The activity of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ in orthopyroxene is evaluated as:

$$a_{\text{opy}}^{\text{opx}} = (X_{\text{Mg}}^{\text{M2}})^2 \cdot X_{\text{Al}}^{\text{M1}} \cdot 2 \quad (2)$$

following Ganguly and Ghose (1979), where $X_{\text{Mg}}^{\text{M2}}$ is the mole fraction of Mg on the M2 octahedral site and $X_{\text{Al}}^{\text{M1}}$ is the mole fraction of Al on the M1 octahedral site. The substitution of Ca on M2 is quite nonideal, but the amounts of Ca present are so small that the activity coefficient is essentially unity. The activity of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ in garnet in the four-component system is given by:

$$a_{\text{py}} = (\gamma X_{\text{Mg}})^3 \quad (3)$$

where γ is the activity coefficient and X_{Mg} is the Mg/Mg+Ca ratio. The calorimetry-based activity functions of pyrope-grossular (Haselton and Newton 1980) give γ very close to one at $X_{\text{Mg}} = 0.85$.

Figure 4 is a plot of $\ln K^0$ versus reciprocal temperature for reaction (A). Included are all reversed data for the $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system as well as the present results for the Ca-bearing system. A linear least-squares fit to all the data yields values of ΔH^0 and ΔS^0 of 7,370 cal/mole and 5.7 cal/K-mole. The ΔH^0 value does not agree well with the 3.1 ± 2.0 kcal which may be deduced from the solution calorimetry on synthetic pyrope, enstatite, and $\text{En}_{90}\text{Al}_{10}\text{O}_{30}$ orthopyroxene of Charlu et al. (1975). However, the calculation requires 10-fold multiplica-

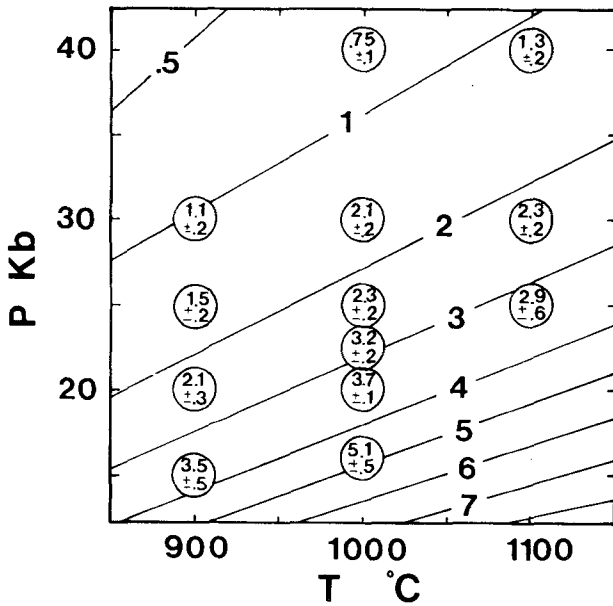


Fig. 5. Experimental determined alumina contents of orthopyroxene buffered by clinopyroxene and garnet. Smoothed isopleths were calculated from the thermochemical parameters given in text

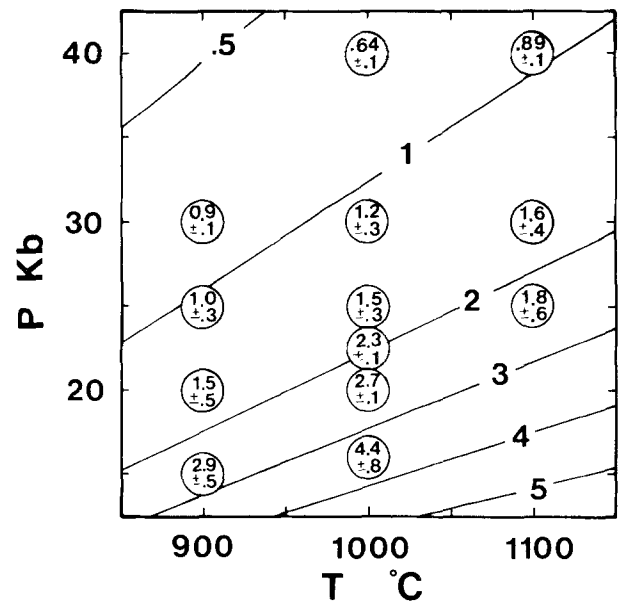


Fig. 6. Experimentally determined alumina contents of clinopyroxene buffered by orthopyroxene and garnet

tion of the heat of solution difference between enstatite and $\text{En}_{90}\text{Al}_2\text{O}_{310}$, and is correspondingly uncertain.

The ΔS^0 value from Fig. 4 may be used to derive a value of S^0_{opy} . At 1,000 K, the entropy of pyrope from Haselton and Westrum (1980) and Newton et al. (1977) yields a value of $S^0_{\text{opy}} = 190.95$. This value is greater than $3S^0_{\text{MgSiO}_3} + S^0_{\text{Al}_2\text{O}_3}$, which may be ascribed to the Al-coordination change from six to four in forming opy from enstatite and corundum.

The derived values of ΔH^0 and ΔS^0 were used to calculate the smooth isopleths shown in Fig. 5. While the simple theory appears to coordinate the experimental data quite well, it must be emphasized that the temperature range of most of the reversals is quite small (900°–1,100° C). Extension to a higher temperature range must be done with caution. The short experimental temperature range does not warrant a more complex analysis, with, perhaps, consideration of heat capacities and thermal expansions, which might produce some curvature in the Al-isopleths similar to those shown for the 3-component system by Lane and Ganguly (1980).

The two reversal experiments of Akella (1976) in the temperature range considered here (1,000° and 1,100° C, both at 44 kbar) each show about 1 wt.% more Al_2O_3 than our isopleth reconstruction indicates. It is difficult to explain this discrepancy on the basis of a difference in pressure calibration between the two studies. Akella (1976) used run-products from other experiments as reactants in his reversal runs,

and these may not have been homogeneous. He did not discuss any zonation in the experimental products or the observation of any incomplete reactions.

The Al contents of clinopyroxene determined in this study are plotted in Fig. 6. These may be systematized by a thermodynamic evaluation of reaction (B) similar to that of reaction (A). The activity of $\text{Mg}_2\text{Si}_2\text{O}_6$ in orthopyroxene is equal to $X_{\text{Mg}}^{\text{M2}} \cdot X_{\text{Mg}}^{\text{M1}}$, following Wood and Banno (1973), and that of $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ in garnet is as determined in the preceding analysis. The activities of $\text{CaMgSi}_2\text{O}_6$ and $\text{CaAl}_2\text{SiO}_6$ in clinopyroxene are given by:

$$a_{\text{CaMgSi}_2\text{O}_6} = \gamma X_{\text{Ca}}^{\text{M2}} \cdot X_{\text{Mg}}^{\text{M1}} \quad (4)$$

$$a_{\text{CaAl}_2\text{SiO}_6} = \gamma X_{\text{Ca}}^{\text{M2}} \cdot X_{\text{Al}}^{\text{M1}} \quad (5)$$

This follows the deductions of Wood (1976, 1978) from high pressure phase equilibrium work that the substitution of Al and Mg on M1 is quasi-ideal, and of Holland et al. (1979) that substitution of Ca and Mg on M2 comprises a regular solution with $W = 5,850$ in calories. In this formulation, $\ln \gamma$ is given by $W(X_{\text{Mg}}^{\text{M2}})^2/RT$. The assumption is implicit that the small amount of Al in the clinopyroxene does not materially affect γ . As in the calculation for reaction (A), partial molal volumes are the one-bar, 298 K values, taken from the molar volume data of Newton et al. (1976), Danckwerth and Newton (1978), and Haselton and Newton (1980). This gives a virtually constant $\Delta \bar{V}_B$ of 4.80 cm^3 . A linear least squares analysis of all 11 data points from the present study

gives $\Delta H_B^0 = 7.34$ kcal and $\Delta S_B^0 = 2.2$ cal/deg. The ΔH_B^0 value agrees very well with the solution calorimetry of Charlú et al. (1978) for $\text{CaMgSi}_2\text{O}_6$, $\text{CaAl}_2\text{SiO}_6$ and $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, and that for $\text{Mg}_2\text{Si}_2\text{O}_6$ (Charlú et al. 1975), which give 7.30 kcal at 970 K. However, ΔS^0 is compared to the value of 4.04 cal/deg from the data of Haselton (1979) for $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, and Robie et al. (1978) for the other three phases of reaction (B). The considerable discrepancy might lie in the tabulated entropy values of $\text{CaAl}_2\text{SiO}_6$, which were derived from high pressure, high temperature phase equilibrium measurements.

The Effect of Al_2O_3 on the Diopside-Enstatite Miscibility Gap

Previous investigators have been unanimous that Al_2O_3 in the pyroxenes decreases their mutual solubility in the spinel+forsterite field (Fujii 1977; Finnerty 1977; Mori 1977). In the garnet field, however, the results of Akella (1976) do not seem to show a consistent Al-effect on the diopside-enstatite solvus, and Mori's (1978) appraisal of the available experimental data suggested a slight decrease of the miscibility gap with Al content in the presence of garnet. The present study shows a considerable widening effect in the garnet field.

The present results in the garnet-saturated pyroxene gap in the four-component system may be compared with the reversals of Lindsley and Dixon (1976) for the Al-free system through the use of an equilibrium constant plot. For reaction (C):

$$\ln K_C^0 = -\frac{\Delta H_C^0}{RT} + \frac{\Delta S_C^0}{R} = \ln \frac{a_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{px}}}{a_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{px}} \cdot a_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{px}}} \quad (6)$$

The activities are evaluated in two-site models:

$$a_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{px}} = (\gamma X_{\text{Mg}}^{\text{M}_2} \cdot X_{\text{Mg}}^{\text{M}_1})^{\text{px}} \quad (7)$$

$$a_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{px}} = (\gamma X_{\text{Mg}}^{\text{M}_2} \cdot X_{\text{Mg}}^{\text{M}_1})^{\text{px}} \quad (8)$$

where $\gamma = \exp \left[\frac{W}{RT} (X_{\text{Ca}}^{\text{M}_2})^2 \right]$ for both pyroxenes; $W_{\text{opx}} = 8,126$ cal and $W_{\text{cpx}}(\text{cal}) = 5,850 + 0.0251 P(\text{bars})$ (Holland et al. 1979).

Fig. 7 is a plot of $\ln K_C^0$ versus reciprocal temperature. The present data are consistent with those of Lindsley and Dixon (1976) and the Holland et al. (1979) formulation. The values of $\ln K_C^0$ are considerably different from those resulting from the ideal solution formulations of Wood and Banno (1973) and Wells (1977). Because Holland et al.'s (1979) calculated W and ΔH^0 are consistent with solution calorimetric data (Newton et al. 1979), the regular solution theory is thermodynamically more correct than the ideal solution formulation. Nonetheless, for Fe-free

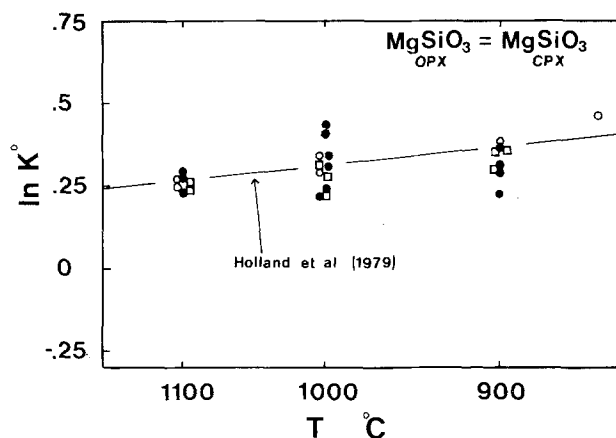


Fig. 7. $\ln K_C^0$ versus reciprocal temperature for reaction C. The straight line is taken from Holland et al. (1979). Solid dots and open squares are from the results of this study for the $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ and the $\text{CaO}-\text{MgO}-\text{SiO}_2$ systems respectively. The open circles are from the data of Lindsley and Dixon (1976) for the Al-free system. Although not shown, if the uncertainties (due to composition overlap) were plotted, every point except the lowest at 900° C agrees with the line of Holland et al. (1979)

pyroxenes, the Wells pyroxene-solvus thermometer gives temperatures almost identical to those of Holland et al. (1979) in the range 900°–1,100° C.

Application to Natural Assemblages

As a practical application of our results we have considered a suite of lherzolite nodules from southern African kimberlites which have been well described by Hervig (1979) and some similar nodules from Malaita (Nixon and Boyd 1979). Temperatures of equilibration of these samples are calculated from the Wells (1977) thermometer because it is consistent with the data of this study and also includes the effect of Fe. For pressure determinations we have used the Al_2O_3 isopleths of orthopyroxene depicted in Fig. 5, and have made no correction for departures from the four-component system, the most important being the FeO contents.

The results for the African kimberlites, shown in Fig. 8, are very similar to the proposed continental shield geotherm of Clark and Ringwood (1964) up to 1,100° C, the highest temperature of the present experiments, and indicate a heat flow slightly greater than 40 mW m⁻² (Pollack and Chapman 1977). Above 1,100° C, extrapolation of our data and application to sheared nodules yields a deflected geotherm. In studies on very similar rocks from the same area, Boyd (1973) and Boyd and Nixon (1975) found a similar deflection using earlier thermometric and barometric calibrations of reactions (A) and (C). However, their calculated geotherms indicate a lower heat flow than ours, and their pressures are 5 to 10 kbar greater than

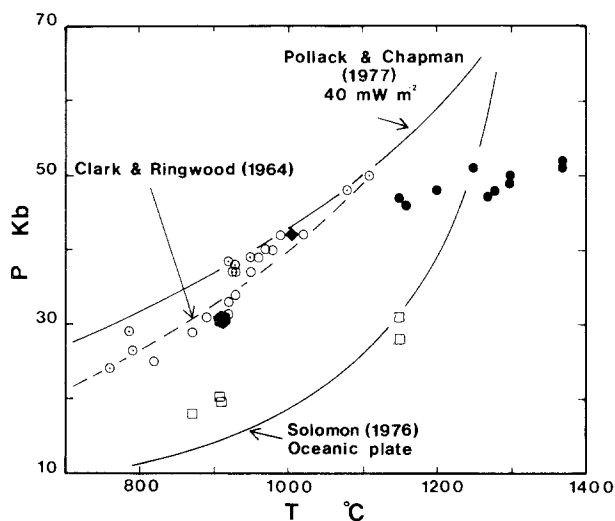


Fig. 8. Calculated pressures and temperatures for a suite of lherzolite nodules from southern African kimberlites and from Malaita, Solomon Islands, basalts. For comparison, the continental shield geotherm of Clark and Ringwood (1964), the 40 mW m^{-2} geotherm of Pollack and Chapman (1977) and the Oceanic Plate geotherm of Solomon (1976) are shown. Symbols: solid dots = sheared nodules from Lesotho; open circles = granular nodules from Lesotho; circles with dots = other southern African kimberlites; diamond = diamond-bearing nodule from Lesotho; hexagon = graphite-bearing nodule from Lesotho; open square = lherzolite nodule from Malaita. All data are from Hervig (1979) except those pertaining to Malaita, which are taken from Nixon and Boyd (1979).

ours over all temperature. This disagreement is largely due to the fact that they used the Al_2O_3 isopleth data of MacGregor (1974), with and without the corrections of Wood and Banno (1973) for Fe. Because MacGregor's data apply to a Ca-free system, they yield significantly higher pressures for a given Al_2O_3 content. For temperature estimation, Boyd (1973) and Boyd and Nixon (1975) used the two-pyroxene thermometers of Davis and Boyd (1966) and of Wood and Banno (1973) which give higher temperatures than the Wells (1977) thermometer.

The Wells (1977) thermometer and the present Al-enstatite barometer were applied to several samples from Malaita (Solomon Islands) based upon the analyses of Nixon and Boyd (1979). As expected for an oceanic regime, there is a hotter geothermal curve (Fig. 8). For comparison, Fig. 8 shows an estimated geotherm of Solomon (1976) for an oceanic plate. More data are needed before the significance of our results for Malaita can be discussed in detail.

While there are still large uncertainties in calculation of pressure and temperatures due to the effects of additional components, Fig. 8 is presumably a more accurate picture of the southern African geotherm than those calculated previously because it incorporates the effects of Ca on pressure determination.

Careful experiments to determine the effects of Fe, Na, and Cr on garnet-pyroxene and two-pyroxene equilibria are needed before more precise and accurate answers may be obtained.

Conclusions

1. The compositions of coexisting garnet, clinopyroxene and orthopyroxene in the $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system have been reversibly determined over the pressure/temperature range of 15–40 kbar/ 900° – $1,100^\circ\text{C}$. The results are in thermodynamic agreement with earlier studies on 3-component systems;

2. Compositions of coexisting clinopyroxene and orthopyroxene have been determined for the Al-free system which are in agreement with the previous investigation of Lindsley and Dixon (1976);

3. The effect of Al on orthopyroxene-clinopyroxene equilibria is to widen the "solvus" relative to that of the Al-free system. The effect is much more pronounced on the clinopyroxene limb than on the orthopyroxene limb; clinopyroxene Ca/Ca + Mg increases by 1–2 mole-% for a garnet buffered system relative to an Al-free system;

4. The alumina content of orthopyroxene in equilibrium with garnet and clinopyroxene is considerably less than that in a Ca-free system. The Al_2O_3 isopleths shift to lower pressures by as much as 10 kbar in a Ca-saturated system;

5. The Al-content of clinopyroxene in equilibrium with garnet and orthopyroxene is less than that of orthopyroxene for the simple $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. In natural assemblages, however, the effects of additional components, notably Na, lead to strong Al partitioning into clinopyroxene;

6. The geotherms for southern Africa calculated from the present results indicate a steeper gradient than previously proposed by Boyd (1973) and Boyd and Nixon (1975). An apparent deflection of the southern African geotherm near 150 km results from the present calculations, but this could be due to the present linear extrapolation of isopleth data from a lower temperature range. Calculations for the Solomon Islands nodules indicate a much hotter geotherm there than under Southern Africa.

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