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GEOPHYSICAL LABORATORY

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PYROXENES AND GARNETS AS
GEOETHERMOMETERS AND
BAROMETERS

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Most experimental work on pyroxenes and garnets has been concentrated on the study of simple three- or four-component systems, modeling natural rock compositions. Although the data obtained on these simple systems can be usefully applied to natural occurrences, more information is needed on the influence of additional components in order to construct detailed and accurate petrogenetic grids. The present study, using natural starting materials, has been undertaken to obtain data on (1) the orthopyroxene-clinopyroxene two-phase region, (2) the solubility of Al_2O_3 in enstatite, (3) the partition of Mg and Fe^{2+} among garnet and pyroxenes, and (4) the solvus between Ca-rich and Ca-poor (pigeonitic) clinopyroxene.

Experimental Method

In view of the inherent uncertainties associated with synthesis experiments in these systems, the present experiments were carried out on natural minerals that were reequilibrated at high temperatures in experiments of long duration. This method also has the advantage that grain size can be controlled such that the sample is easily amenable to electron microprobe analysis. Because reequilibration experiments require extended run times (e.g., 2-3 weeks at $1100^\circ C$; run times given in Fig. 64), limiting the number of runs that can be carried out, a large sample holder simultaneously containing six samples was used in the experiments in order to improve efficiency. The six-sample assembly can be used in a $\frac{3}{4}$ -inch, solid-media, high-pressure vessel up to a pressure of 30 kbar.

The sample holder consists of two graphite disks with three cylindrical holes (diameter 0.0625 inch; depth, 0.125

inch) drilled in each disk. The holes are closed by fitting lids. The disks are 0.250 inch in diameter and 0.156 inch thick. The thermocouple is separated from the graphite by a thin wall of AlSiMag, a nonconducting, high-temperature ceramic. The measured temperature gradient across the sample is less than $15^\circ C$ (at $1400^\circ C$).

Experiments with two thermocouples (Pt/Pt10% Rh and W3% Re/W25% Re) have been conducted at temperatures of 1100° , 1200° , 1300° , and $1400^\circ C$ (13.5 kbar). Only at 1300° and $1400^\circ C$ was a relative drift between the two thermocouples observed. The relative downward drift in temperature of approximately $2.5^\circ C$ /hour, as read by the Pt/Pt10% Rh thermocouple, is believed to be due to contamination of the couple (cf. Mac and Bell, *Year Book 70*, p. 284). In the runs above $1200^\circ C$, where drift occurred, the power input was adjusted to maintain constant temperature, as read by the tungsten-rhenium couple. The experiments were carried out by the piston-in technique, and the results include a friction correction of -10% (cf. Johannes *et al.*, 1971).

Starting Materials

Five pairs of homogeneous natural pyroxenes and the Salt Lake, Hawaii, spinel hercynite (Kushiro *et al.*, 1972) were used as starting materials for the experiments. The pyroxene pairs are Fe-rich, nonaluminous pyroxenes (nos. 207, 264, 277, and 278) described by Butler (1969, Table 4) and a homogeneous aluminous orthopyroxene (6.6 wt % Al_2O_3) and aluminous clinopyroxene (5.3 wt % Al_2O_3) from the Delegate breccia pipe, Australia. The position of the pairs in the pyroxene quadrilateral is shown in Fig. 64A. Originally the minerals were ground under acetone to an average grain size of $20 \mu m$. After it was found that diffusion rates were a major problem, a finer grain size of 5-10 μm was used. At $1100^\circ C$ a small amount (approx-

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mately 5 wt %) of oxalic acid was added to promote reaction.

Results

The results of the experiments are shown diagrammatically in Fig. 64 A-F. Each point on these diagrams represents one (or in some cases more than one) spot analysis carried out with the electron microprobe analyzer (Finger and Hadidiacos, *Year Book 71*, p. 598). Only analyses with structural formulae within 2% of the ideal values are shown. No analyses have been excluded on other criteria; the diagrams show all data points obtained. The points from the alumina-bearing compositions have been projected through Al_2O_3 .

Considerable compositional inhomogeneity is found in most runs (Fig. 64) and overall equilibrium was not reached in the experiments. It is common to find

unreacted material in the cores of grains of more than 15 μm . This lack of overall equilibrium is discouraging, but as the initial compositions of the minerals are known, the direction of reaction can be clearly established. The compositional range shown for each mineral must lie within its stability field. Those compositions farthest removed from the original composition are believed to be approaching equilibrium most closely. The averages of three to eight analyses (per run) of each mineral selected on this basis show low standard deviations (Table 12).

The alumina content of enstatite in equilibrium with pyrope has been studied experimentally by Boyd and England (*Year Book 63*, p. 157) and more recently by I. D. MacGregor (in preparation). Data on natural ultramafic compositions have been reported by MacGregor and Ringwood (*Year Book 63*, p. 161) and Green and Ringwood (1970).

TABLE 12. Analytical Results: Average Values with Standard Deviations

T, °C	P, kbar	Mg/(Mg+ Fe ²⁺), mole %	Ca/(Ca+ Mg), mole %	Al ₂ O ₃ wt %	P _{obs} , kbar	P _{calc} , kbar
Orthopyroxene Analyses						
1110	22.5 D*	0.80 (0.00)†	0.034 (0.00)	3.0 (0.23)	-8.5	-10.8
1110	40.5 D	0.83 (0.00)	0.024 (0.00)	1.3 (0.25)	--~10.0	-12.4
1410	27.0 S	0.86 (0.00)	0.047 (0.00)	5.9 (0.24)	--9.0	-6.5
1410	40.5 S	0.89	0.034	3.1		
Clinopyroxene Analyses						
1110	22.5	0.82 (0.00)	0.45 (0.00)	3.6 (0.11)		
1110	40.5	0.84 (0.01)	0.44 (0.01)	3.0 (0.71)		
1410	27.0	0.85 (0.00)	0.26 (0.01)	6.5 (0.23)		
1410	40.5	0.88	0.30	5.8(?)		
Garnet Analyses						
1110	22.5	0.67 (0.01)	0.23 (0.01)		Gross, mole %	
1110	40.5	0.68 (0.01)	0.21 (0.01)		16.6	
1410	27.0	0.80 (0.01)	0.71 (0.02)		15.2	
1410	40.5	0.85	0.08		14.4	
<i>K_D</i> Values (using average compositions)				<i>K_D</i> (Ga-Cpx)	<i>K_D</i> (Cpx-Opx)	
1110	22.5			0.43	1.13	
1110	40.5			0.41	1.11	
1410	27			0.71	0.88	
1410	40.5			0.65	0.87	

* Starting material: D, Deltex (Fig. 64B); S, Salt Lake Crater, Hawaii, spinel ilmenite.

† Standard deviations in parentheses.

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 lack of overall
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 minerals are
 reaction can be
 compositional
 eral must lie
 use composi-
 the original
 approach-
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 (12).
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 (12).
 in
 studied
 England
 and more
 prepara-
 Fe com-
 Mac-

P_{calc} , kbar

-10.8
 -12.4
 -6.5

mole %
 6.6
 5.2
 4.4

(Cpx-Opx)
 .13
 .11
 .88
 .08

0.00

The alumina content of orthopyroxene, in equilibrium with garnet and clinopyroxene, obtained in the present experiments is considerably lower than that reported by MacGregor for the same pressure and temperature (Table 12). Recently S. Banno and B. J. Wood (in preparation) have used a thermochemical calculation to evaluate the effect of Ca and Fe^{2+} substitution in garnet and orthopyroxene on the pyrope-enstatite equilibrium. The calculated pressure difference by the method of Banno and Wood is in reasonable agreement with the observed pressure shift (difference between the present data and the data by MacGregor, in preparation, Table 12).

The influence of chromium is expected to be in the same direction as that of Ca and Fe^{2+} ; that is, the stability field of garnet is extended, and the stability of aluminous enstatite is restricted. The data of Akella and Boyd (this Report, Table 10) on synthesis experiments at 1100°C in Ti-rich compositions show Al contents in the orthopyroxene comparable to those obtained here.

The alumina content of clinopyroxene is higher than that of the coexisting orthopyroxene (Table 12). The clinopyroxenes, however, contain about 1 wt % Na_2O , and when the Al_2O_3 content is subtracted as jadeite component the clinopyroxene contains slightly less Al_2O_3 than the orthopyroxene.

The Orthopyroxene-Clinopyroxene Two-Phase Region

In the Mg-rich portion of the two-pyroxene field in the temperature range 1100°–1200°C and down to $Mg/(Mg + Fe^{2+}) = 0.80$, the clinopyroxene solvus [Cpx(Opx)] projects towards the Fs corner of the pyroxene quadrilateral. The use of $Ca/(Ca + Mg)$ in applying the Di(En) solvus (Boyd and Schairer, 1964; Davis and Boyd, 1966) to determine temperature for Fe-bearing compositions is in order under these condi-

tions because the Fe-bearing pyroxene composition is projected from Fs onto the Di-En join.

At 1400°C and 13.5 kbar the solvus under discussion is absent for compositions with $Mg/(Mg + Fe^{2+}) \leq 0.90$ because of the appearance of pigeonite (Fig. 64F). The topology of the phase diagram indicates that even minor amounts of Fe cause errors in temperatures estimated from the Di(En) solvus. At 1400°C and 27 kbar the temperature of a pyroxene pair with $Mg/(Mg + Fe^{2+}) = 0.85$ would still be overestimated by 50°C or more. At 45 kbar only one measurement could be made, and the value obtained suggests that as the Ca-poor clinopyroxene (pigeonite) field contracts with increasing pressure (see later section of this Report), the Cpx(Opx) solvus boundary rotates, projecting more and more in the direction of the Fs corner of the quadrilateral.

The behavior of the Opx(Cpx) solvus with varying pressure, temperature, and Fe/Mg ratio is complicated. As shown in Fig. 65 the $Ca/(Ca + Mg)$ of orthopyroxene increases with temperature and decreases with pressure. The pyroxenes with low Ca contents at high pressure, however, contain the highest $Mg/(Mg + Fe)$, suggesting the possibility of control by this chemical variable.

Comparison with the empirical curve of Boyd and Nixon (this Report, Fig. 6) and the experimental data of Boyd (1970) on the system En-Di-Py and Akella and Boyd (this Report) indicates that the effects on Ca in orthopyroxene of pressure and $Mg/(Mg + Fe^{2+})$, on the one hand, and temperature, on the other, are of the same order of magnitude and of opposite sign.

The Distribution of Fe and Mg between Garnet and Pyroxenes

The experimentally determined K_D values for garnet-clinopyroxene and clinopyroxene-orthopyroxene pairs are

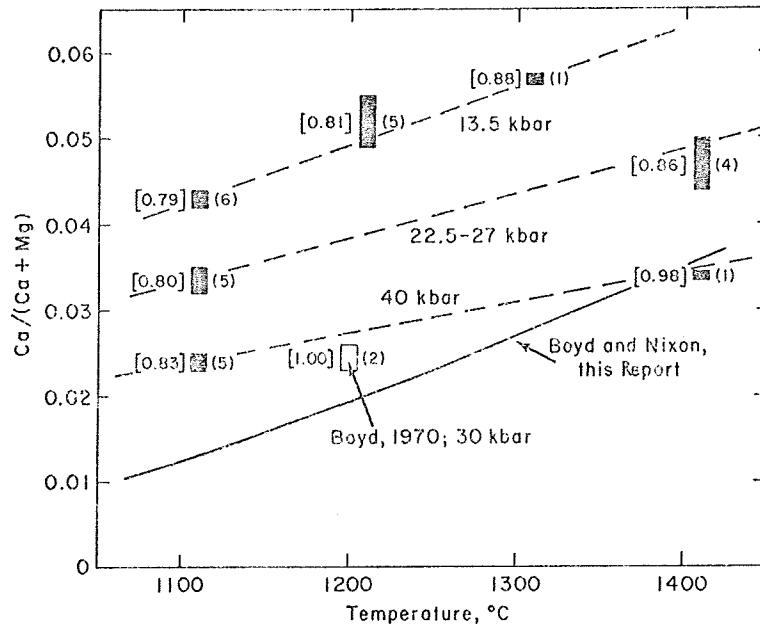


Fig. 65. Variation of $\text{Ca}/(\text{Ca} + \text{Mg})$ ratio in orthopyroxene in equilibrium with clinopyroxene as a function of temperature and pressure. Empirical curve for ultramafic nodules (Boyd and Nixon, this Report) is shown for comparison. Figures in parentheses indicate number of analyses; figures in brackets indicate the $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratio of the orthopyroxene.

given in Table 12. The data show a clear-cut influence of temperature on the partition coefficients for exchange equilibria between Ga-Cpx and Cpx-Opx.

Comparison with the experimental data of Akella and Boyd (this Report, Tables 10 and 11) at 1100°C indicates that K_D is approximately constant for garnet (with Cpx) with a $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ of 0.70 to 0.40.

The effect of pressure on K_D (garnet-clinopyroxene) has been variously estimated at about 3% per kbar (Evans, 1965) to about 1% per kbar at 1100°C (Banno, 1970). The observed decrease in K_D at 1100°C from 0.43 at 22.5 kbar to 0.41 at 40.5 kbar is insignificant and suggests that the pressure effect on K_D may be much smaller than theoretically predicted.

The values obtained here have a special interest because of the possible comparison with the large amount of data on garnet ilmenites and related garnet-

clinopyroxene-orthopyroxene bearing nodules from kimberlites collected by Boyd and Nixon (this Report). Figure 66 shows the K_D values of garnet-clinopyroxene pairs plotted against temperature, estimated from the Di(En) solvus (Boyd and Nixon, this Report). The diagram shows a correlation of K_D with estimated temperature and with several exceptions (7 out of 28) the points lie on a straight line between 950° and 1420°C . The points obtained in this study plot close to or on the line, as do the data of Akella and Boyd (this Report). It is concluded, therefore, that the K_D (garnet-clinopyroxene) is a potentially useful geothermometer and that the curve in Fig. 66 can be used as a first approximation for high-temperature, high-pressure ultrabasic rocks.

The grossular content of garnet in the three-phase assemblage varies with the estimated temperature (Fig. 66). The decrease of grossular_{ss} in the garnet must

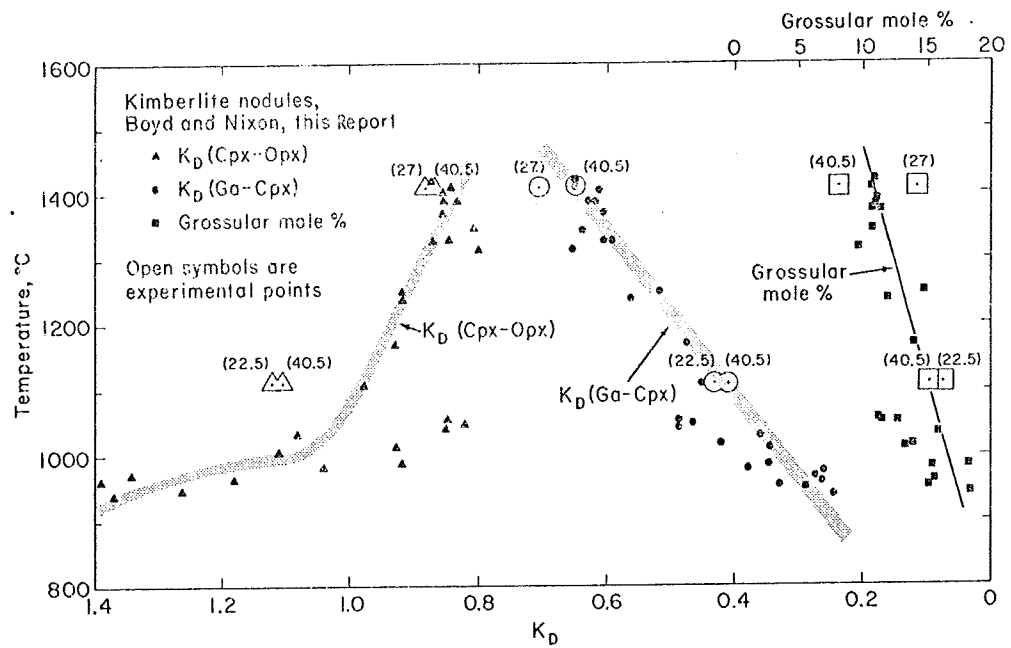


Fig. 66. Variation of K_D (Ga-Cpx), K_D (Cpx-Opx), and grossular content of garnet in ultramafic nodules from kimberlites as a function of temperature (derived from Di(En) solvus; Boyd and Nixon, this Report). Experimentally determined values are shown for comparison. Also shown are the data of Boyd (1970) for the system $MgSiO_3$ - $CaSiO_3$ - Al_2O_3 . The pressures of the experimental runs are given in parentheses.

be attributed mainly to an increase in temperature, with increasing pressure as a secondary factor. The influence of the Mg/Fe ratio can probably be disregarded here in view of the small compositional range of the garnets. However, a possible effect of the Mg/Fe on the grossular content of the garnet cannot be discounted. Note that the data of Boyd (1970) on the system $MgSiO_3$ - $CaSiO_3$ - Al_2O_3 at 1200°C fall on the curve in Fig. 66. The grossular contents of the garnets in the present experiments compare reasonably well with those from natural specimens formed under similar physical

conditions (Fig. 66). The data of Kushiro, Syono, and Akimoto (1967) for the Fe-free system are apparently inconsistent with the temperature effect observed here.

The distribution of Mg and Fe^{2+} between clinopyroxene and orthopyroxene shows a nonlinear correlation with estimated temperature (Fig. 66). At low temperatures (1100°C and below) Mg favors clinopyroxene over orthopyroxene, but at high temperature this relationship is reversed. This unusual behavior, exemplified by the data of Boyd and Nixon (this Report), has been repro-

duced experimentally (Table 12, Fig. 66). The inflection point lies close to 1100°C. Above 1100°C the value of K_D departs increasingly from unity, and a near linear correlation with estimated temperature is evident. The experimental values are very close to those from natural specimens at 1410°C but plot slightly off the empirical curve at 1100°C, possibly suggesting that reequilibration of the pyroxenes was not complete.

Extrapolation of the K_D (Ga-Cpx) curve to lower temperature is not possible at present. Theoretically the curves of K_D versus temperature should not produce straight lines even when mixing in the phases is ideal (in the ideal case $\ln K$ versus $1/T$ should be linear). The value of K_D (Ga-Cpx) for eclogite from high-grade metamorphic terranes ranges from 0.1 to 0.2 (Banno, 1970). Because these eclogites probably formed in a temperature range of 550°–800°C, considerable curvature of the K_D line in Fig. 66 must occur below 900°C.

The Stability Field of Ca-Poor Clinopyroxene

The results of the experiments relevant to the stability of Ca-poor clinopyroxene* are shown diagrammatically in Fig. 64 A–F. The results illustrate the expansion of the Ca-poor clinopyroxene stability field with increasing temperature and its contraction with increasing pressure.

The wollastonite content of Ca-poor clinopyroxene in the experiments shows a wide spread, and the data do not indicate the first composition to become stable relative to orthopyroxene + clinopyrox-

ene with increasing temperature. Comparing the results at 15 kbar of Smith (1972), Grover, Lindsley, and Turnock (1973), and Kushiro and Yoder (*Year Book 68*, p. 228), it appears that the apex of the pigeonite field decreases in Wo content from about Wo₁₅ (mole %), in the range En₁₅Fs₈₅ to En₄₀Fs₆₀, to Wo₈ on the diopside-enstatite join. Natural pigeonites from volcanic rocks, probably formed at very low pressure, typically contain Wo₁₀, whereas the Wo content of pigeonite on the Di-En join at atmospheric pressure is between 4 and 5 mole % (Kushiro, 1972c). The foregoing observations suggest that the wollastonite content of the pyroxene forming the apex of the Ca-poor clinopyroxene field, i.e., the Ca-poor clinopyroxene in the three-phase assemblage two clinopyroxenes + orthopyroxene (Fig. 64), is displaced toward lower Ca content with increasing Mg content (and temperature) and toward higher Ca content with increasing pressure. The latter effect may explain the phase relations at 1100°C and 22.5 kbar. The topology of the diagram suggests that at 22.5 kbar the composition of the Ca-poor clinopyroxene in the three-phase assemblage may have moved to Wo₂₂. The data of Brown (*Year Book 66*, Fig. 10) indicate that the composition Wo_{7.6}En_{40.7}Fs_{51.7} is not stable at 1100°C and 22.5 kbar. This result is consistent with the phase boundaries of Fig. 64B. To obtain the dashed hypothetical phase boundaries in Fig. 64 A–F, the data of Ross, Huebner, and Dowty (1973) have been extrapolated to higher pressures using the slope of the orthopyroxene-to-clinopyroxene inversion curve of Brown (*Year Book 66*, Fig. 10). This slope is almost identical with that obtained by Kushiro and Yoder for the lower stability of Ca-poor clinopyroxene on the Di-En join (*Year Book 68*, Fig. 18). The extrapolated results are shown to be consistent with the present data and provide a self-consistent set of phase diagrams.

* At room temperature most natural Ca-poor clinopyroxenes have $P2_1/c$ symmetry (pigeonite). Recent workers (Prewitt, Brown, and Papike, 1971) have shown that these same pyroxenes have $C2/c$ symmetry at high temperature. Therefore it is not deemed necessary to distinguish between structural types in discussing clinopyroxene phase equilibria at high temperatures.