

Experimental determination of some geochemical parameters relating to conditions of equilibration of peridotite in the upper mantle

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Abstract

Three natural peridotite nodules have been subjected to pressure and temperature conditions corresponding to supersolidus conditions of a hydrous upper mantle. The bulk chemistry of the nodules covers a wide range for peridotite in the upper mantle.

The chemistry of the residual phases during partial melting has been determined as a function of temperature and pressure. The diopside content of orthopyroxene coexisting with clinopyroxene increases with increasing temperature and with decreasing pressure. The diopside content of the clinopyroxene is insensitive to pressure and bulk chemistry. The relation between diopside content and temperature of equilibration results in a temperature calibration that is within ± 3 percent (relative) of the values predicted from the data of Davis and Boyd (1966).

The partition coefficient, $K_D = (Al^{VI}/Cr)^{opx}/(Al^{VI}/Cr)^{cpx}$ is calibrated as a function of temperature using all nodules and a pressure range of 7.5–30 kbar. Least-squares fitting of a $\ln K_D$ vs. $1/T$ plot results in a straight line with 2 percent uncertainty (relative) in the temperature interval between 700° and 1120°C. Estimates of temperatures of equilibration of some natural peridotites based on Al^{VI} –Cr partitioning between clino- and orthopyroxenes result in values that agree with those predicted by the geothermometer of Davis and Boyd (1966).

Introduction

Ever since Yoder *et al.* (1957) experimentally determined the compositions of coexisting feldspars as an indicator of their temperature of equilibration, considerable time and energy has been devoted to relating the composition of mineral assemblages to their equilibrium physical conditions. Experimental determinations have been concentrated on simple model systems because of the more rigorous physiochemical control of a three- or four-component system compared with multicomponent natural rocks. However, data from simple systems are applicable to natural rocks only after the effect of chemical variables not included in the calibration experiments is assessed on the geothermometer or geobarometer. Unfortunately many such assessments are only semiquantitative and result in considerable variation of determined physical conditions of equilibration of natural rocks, depending on the geothermometer and geobarometer chosen. One solution to such problems is to calibrate the physiochemical indicators with natural rock compositions (*e.g.*, Akella and Boyd, 1974). These studies

have shown, however, that attainment of equilibrium during calibration experiments is a problem that is not yet overcome, and there is still a need for testing the geothermometers and geobarometers already suggested. Consequently, natural peridotites have been subjected to pressure and temperature conditions corresponding to those of the upper mantle in an effort to evaluate the accuracy of pressure and temperature indicators used for peridotite rocks in the upper mantle.

Experimental method

Three peridotite nodules from nephelinite tuff of the Honolulu series, Hawaii, have been used in these experiments (Table 1). The compositions were selected to cover the compositional range of most mantle-derived peridotite xenoliths.

All experiments were accomplished in a solid-media, high-pressure apparatus similar to that described by Boyd and England (1960), using 0.5" diameter furnace assemblies. Rock powder + H₂O were contained in sealed Ag50Pd50 sample containers. This container material was used to reduce iron

Table 1. Composition of starting material

	A	B	C
SiO ₂	43.7	45.10	44.82
TiO ₂	0.20	0.13	0.52
Al ₂ O ₃	4.0	3.92	8.21
Fe ₂ O ₃	0.89	1.00	2.07
FeO	8.09	7.29	7.91
MgO	37.4	38.81	26.53
CaO	3.50	2.66	8.12
Na ₂ O	0.38	0.27	0.89
K ₂ O	0.01	0.02	0.03
H ₂ O ⁺	0.14	0.07	0.11
H ₂ O ⁻	0.10	0.12	0.15
P ₂ O ₅	<0.01	0.01	0.04
MnO	0.123	0.14	0.19
CO ₂	...	0.01	0.01
C	...	0.00	0.00
F	...	0.01	0.01
S	...	0.02	0.04
Cr ₂ O ₃	0.40	0.31	0.20
NiO	0.24	0.25	0.20
Subtotal	99.17	100.14	100.05
Less O	...	0.01	0.02
Total	99.17	100.13	100.03
MgO/(MgO + FeO + 0.9Fe ₂ O ₃)	0.88	0.89	0.83
CaO/Al ₂ O ₃	0.88	0.68	0.99

A. 618-138b. 1, peridotite (spinel lherzolite), Hawaii (White, 1966). Analyst, N. H. Suhr, The Pennsylvania State University.

B. 66PAL-3, peridotite (spinel lherzolite), Hawaii. Provided by E. D. Jackson. See Jackson and Wright (1970, Table 4).

C. 66SAL-1, peridotite (garnet lherzolite), Hawaii. Provided by E. D. Jackson and Wright (1970, Table 4).

loss to the capsule (Muan, 1963). Details of the sample preparation are described by Mysen and Boettcher (1975a, b). Temperatures were measured with Pt-Pt90Rh10 thermocouples. Reported temperatures are accurate to within $\pm 10^\circ\text{C}$. All experiments were done with the piston-in technique and -10 percent friction correction (Boettcher, in Johannes *et al.*, 1971).

Run durations were 24 hours above 1000°C , 48 hours between 900° and 1000°C , and more than 48 hours at lower temperatures. The run duration below 800°C was about 72 hours.

Run products were analyzed with the MAC automated electron microprobe at the Geophysical Laboratory (Finger and Hadidiacos, 1971). The presence of H₂O vapor and hydrous silicate liquid in most runs enhanced crystal growth, thus facilitating chemical

analysis. However, the large crystal size (30–50 μm) commonly resulted in chemical zoning within individual grains. This problem was evaluated by analyzing along line traverses across all grains used for calibration. Generally, 5–10 points per grain and about 5 grains of each mineral in a given run product were averaged for each analysis used in the calibration. The uncertainties given in the figures are the standard deviations ($\pm 1\sigma$) of such averages.

Results

The phase relations of these peridotites in the *P-T* range investigated here are published elsewhere (Mysen and Boettcher, 1975a). Geochemical parameters such as $\text{Mg}/(\text{Mg} + \Sigma\text{Fe})$, $\text{Al}^{\text{IV}}/\text{Al}^{\text{VI}}$, and $\text{Ca}/(\text{Ca} + \text{Na})$ of crystalline phases increase isobarically with increasing temperature and decrease isothermally

with increasing pressure. However, these ratios are also positively correlated with those of the starting materials (Mysen and Boettcher, 1975b). Consequently, they can be used for pressure and temperature estimation only under very restricted conditions and are of limited value for geothermometry and geobarometry.

The pyroxene solvus has been redetermined a number of times (Davis and Boyd, 1966; Boyd, 1970; Hensen, 1973; Akella and Boyd, 1974; Nehru and Wyllie, 1974; Warner and Luth, 1974; Råheim *et al.*, 1975; Howells and O'Hara, 1975). The data of Hensen (1973) suggested that the solubility of $\text{CaMgSi}_2\text{O}_6$ in orthopyroxene decreases with increasing pressure, a contention also supported by the data of Akella and Boyd (1974). The present data are plotted together with those of Davis and Boyd (1966) in Figure 1. It is evident that the solubility of clinopyroxene in orthopyroxene decreases with increasing pressure in the pressure range 7.5–30 kbar. However, because of the moderate slope of the $\text{Ca}/(\text{Ca} + \text{Mg})$ isopleths in Figure 1, high-quality analytical data are required when the diopside content of orthopyroxene is used for estimating pressure or temperature of equilibration.

The clinopyroxene limb of the pyroxene solvus is less steep than the orthopyroxene limb (Davis and Boyd, 1966) and is therefore a more promising means of measuring temperatures of equilibration. Warner and Luth (1974) extrapolated their ≤ 10 kbar data and suggested that the solubility of orthopyroxene in clinopyroxene increases slightly with increasing pressure at low temperatures, whereas the solubility decreases with increasing pressure at high temperatures (above $\sim 1200^\circ\text{C}$). Råheim *et al.* (1975) reported "pronounced" pressure dependence of the position of the clinopyroxene limb on the CaSiO_3 – MgSiO_3 join; they did not elaborate on the kind of pressure dependence.

The simple ratio $\text{Ca}/(\text{Ca} + \text{Mg})$ of clinopyroxene in equilibrium with orthopyroxene of all the present experiments is plotted (curve A) together with the curve of Davis and Boyd (1966) (curve B) in Figure 2. Three features of Figure 2, given the present limits of analytical precision, appear to be important: (1) The $\text{Ca}/(\text{Ca} + \text{Mg})$ ratio of clinopyroxene in equilibrium with orthopyroxene in peridotite is not pressure-dependent, at least in the range 7.5–30 kbar. (2) The $\text{Ca}/(\text{Ca} + \text{Mg})$ ratio is not dependent on the bulk chemistry of peridotite. (3) The new curve calibrated with natural peridotite compositions and the original curve of Davis and Boyd (1966) are in close agree-

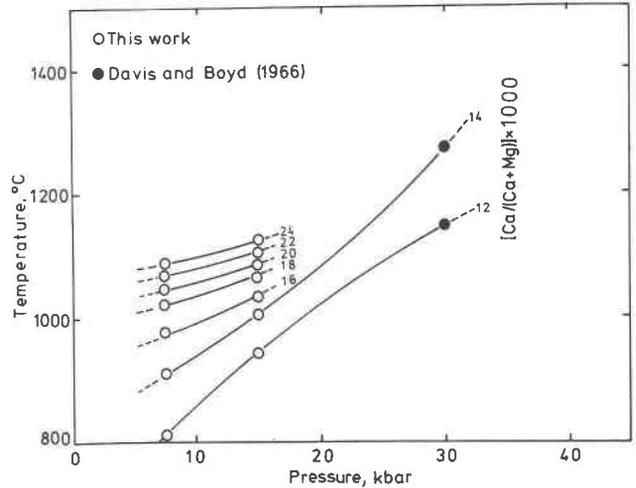


FIG. 1. $[\text{Ca}/(\text{Ca} + \text{Mg})] \times 1000$ isopleths of orthopyroxene in equilibrium with clinopyroxene as a function of pressure and temperature.

ment. If the correction of the original curve as suggested by Boyd (1970) is applied to the data of Davis and Boyd (1966), the curve obtained here (curve A, Fig. 2) is identical with their curve. This close agreement suggests that the temperature calibration of the clinopyroxene limb by Davis and Boyd (1966) is quantitatively applicable to peridotite in the upper mantle without consideration of the pressure of equilibration and the detailed chemistry of the peridotite itself.

The $\text{Ca}/(\text{Ca} + \text{Mg})$ ratio of clinopyroxene on the join $\text{CaMgSi}_2\text{O}_6$ – MgSiO_3 is proportional to the mole

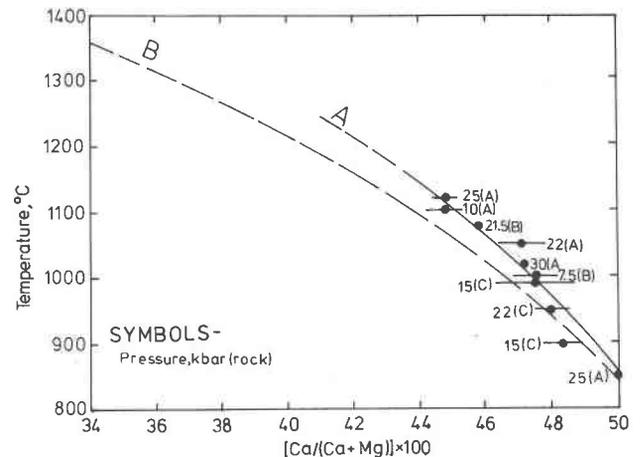
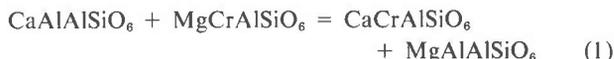


FIG. 2. $[\text{Ca}/(\text{Ca} + \text{Mg})] \times 100$ of clinopyroxene as a function of temperature (curve A). Pressure range, 7.5–30 kbar (numbers refer to pressure of equilibration). Curve B from Davis and Boyd (1966). Error bar, $\pm 1\sigma$.

fraction of $\text{CaMgSi}_2\text{O}_6$ in the clinopyroxene. However, this ratio of natural clinopyroxenes does not account for small, but significant amounts of Tschermak's molecule. An alternative to the molar $\text{Ca}/(\text{Ca} + \text{Mg})$ ratios is to subtract Ca of the clinopyroxene formula needed to account for Ca-, Ca-Ti, and Ca- Fe^{3+} Tschermak's molecules. The ferric iron content of the clinopyroxenes analyzed here is not known, but Mysen and Boettcher (1975b) estimated it to be less than 10 percent of the total iron. The Ca correction would therefore be very small, considering the small amount of total iron present in these clinopyroxenes. Because of the lack of a ferric iron determination, Ca- Fe^{3+} Tschermak's molecule is excluded in the calculation of the $\text{Ca}'/(\text{Ca}' + \text{Mg})$ vs. temperature plot in Figure 3. The new Ca content of clinopyroxene, Ca' , is corrected by the simple relation $\text{Ca}' = \text{Ca} - \text{Al}^{\text{IV}}$, taking into account the calcium for Ca- and Ca-Ti Tschermak's molecules (curve C). Also included in Figure 3 are the data of Akella and Boyd (1974) obtained with a reconstituted peridotite composition and corrected for Ca- and Ca-Ti Tschermak's molecules. Both sets of data are in close agreement. The clinopyroxene limb of the pyroxene solvus obtained by correcting the Ca content for other Ca molecules is shifted about 5 percent (relative) toward the orthopyroxene end of the join (curves A and C). The original determination by Davis and Boyd (1966) lies between those two extremes (curve B). Boyd (1970) suggested that solution of Al_2O_3 in clinopyroxene decreases the solubility of the MgSiO_3 molecule in the same phase. By recalculating

the clinopyroxene composition at the garnet-clinopyroxene-orthopyroxene invariant point in the system $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ at 1200°C and 30 kbar (Boyd, 1970), the uncorrected $\text{Ca}/(\text{Ca} + \text{Mg})$ ratio falls within 0.2 percent of curve A in Figure 2. Subtraction of the amount of Ca corresponding to Al^{IV} in the chemical formula gives a $\text{Ca}'/(\text{Ca}' + \text{Mg})$ ratio that is 2 percent (relative) different from that of curve C in Figure 3.

The excellent agreement between the experimental data reported here and those for the pyroxene solvus by Davis and Boyd (1966) and Boyd (1970) supports the curve of Davis and Boyd as a suitable reference curve for testing other geothermometers. Partitioning of Al^{VI} and Cr between orthopyroxene and clinopyroxene is potentially useful for geothermometry because of the close similarity between six-coordinated aluminum and chromium. It is therefore expected that the activity coefficients of Al^{VI} and Cr are close to 1. For the exchange reaction



$$K_D = (\text{Al}^{\text{VI}}\text{Cr})^{\text{opx}}/(\text{Al}^{\text{VI}}/\text{Cr})^{\text{cpx}} \quad (2)$$

The data used to calibrate the geothermometer $\ln K_D$ vs. $1/T$ (Fig. 4) cover the entire compositional range and a pressure of 7.5–30 kbar. Least-squares fitting of a straight line through the data points results in the equation

$$1/T = (0.26 \pm 0.01)\ln K_D + (0.67 \pm 0.01) \quad (3)$$

where T is the absolute temperature and the uncer-

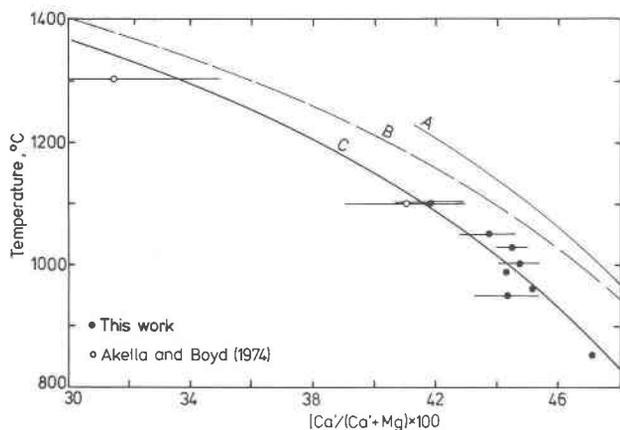


FIG. 3. Percent diopside in clinopyroxene in equilibrium with orthopyroxene in the pressure range 7.5–30 kbar. Percent diopside = $[\text{Ca}'/(\text{Ca}' + \text{Mg})] \times 100$, where $\text{Ca}' = \text{Ca} - \text{Al}^{\text{IV}}$. Curve A, from Fig. 2. Curve B, from Davis and Boyd (1966). Curve C, data corrected by subtracting Ca from the chemical formula that corresponds to Al^{IV} . Error bar, $\pm 1\sigma$.

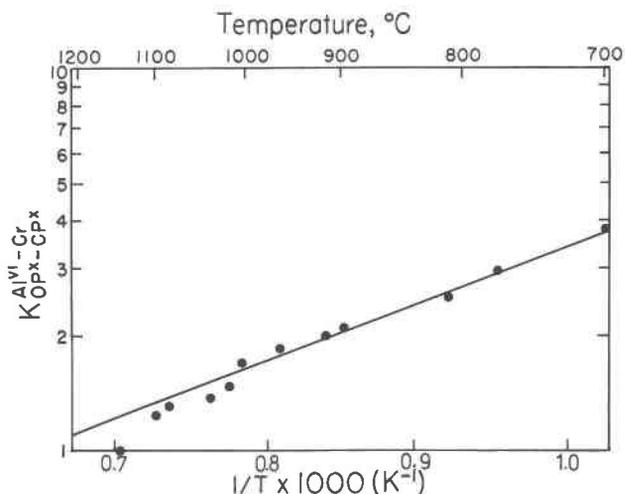


FIG. 4. Al^{VI} -Cr geothermometry of coexisting orthopyroxene and clinopyroxene. $K_D = (\text{Al}^{\text{VI}}/\text{Cr})^{\text{opx}}/(\text{Al}^{\text{VI}}/\text{Cr})^{\text{cpx}}$. Pressure range, 7.5–30 kbar.

tainty in $1/T$ is about 2 percent. The enthalpy and entropy of the exchange reaction (1) are 7.8 ± 0.3 cal/mole and 1.33 ± 0.02 cal/mole deg., respectively. These values are 30 and 50 percent lower than the respective values for the exchange of the enstatite molecule between orthopyroxene and clinopyroxene (Nehru and Wyllie, 1974), supporting the contention that the Al^{VI} -Cr solid solutions at this concentration level approximate ideal solutions better than those involving the enstatite molecule.

The ortho- and clinopyroxenes used in the calibration curve shown in Figure 4 contain ≤ 1.0 weight percent Cr_2O_3 and ≤ 6.0 weight percent Al_2O_3 . Most of the experiments were in the spinel peridotite field with ≥ 90 mole percent spinel (pleonaste + hercynite) and the remaining ≤ 10 mole percent, $MgCr_2O_4$ and $FeCr_2O_4$ molecules. The few experiments in the garnet peridotite stability field produced garnet with ≤ 3 weight percent Cr_2O_3 .

Some temperatures of equilibration of various peridotites obtained with both the Davis and Boyd (1966) and the Al^{VI} -Cr geothermometers are shown in Figure 5. The two sets of temperatures are in good agreement, suggesting that the Al^{VI} -Cr geothermometer is applicable to natural rocks. The two geothermometers are interchangeable in peridotitic rocks. It has been pointed out, however (Boyd, 1970; Boyd and Nixon, 1973), that the data for the pyroxene solvus cannot be extended to other rock types having mineral assemblages different from that for which the geothermometer was calibrated. Mysen and Boettcher (1976) mentioned that the Al^{VI} -Cr geothermometer can also be applied to websterite rock types, on the basis of experiments in the supersolidus region of garnet websterite + H_2O . This result is understandable in view of the lower concentrations of Al^{VI} and Cr compared with Ca and Mg in clinopyroxenes.

According to D. H. Eggler (personal communication, 1975) use of the Al^{VI} -Cr geothermometer on Cr-rich peridotites such as those described by Eggler and McCallum (1974) results in unreasonable temperatures. The value of the Cr/Al ratio of the peridotite may thus be a limiting factor in the application of the geothermometer curve shown in Figure 4.

Application of the geothermometer expressed by equation (3) to natural rocks requires analytical data on both ortho- and clinopyroxenes. In an attempt to reduce these analytical requirements, possible relations between Cr and Al^{VI} of the two pyroxenes have been explored. Chemical data on experimentally equilibrated, coexisting ortho- and clinopyroxenes are plotted in Figures 6 and 7. The data are plotted

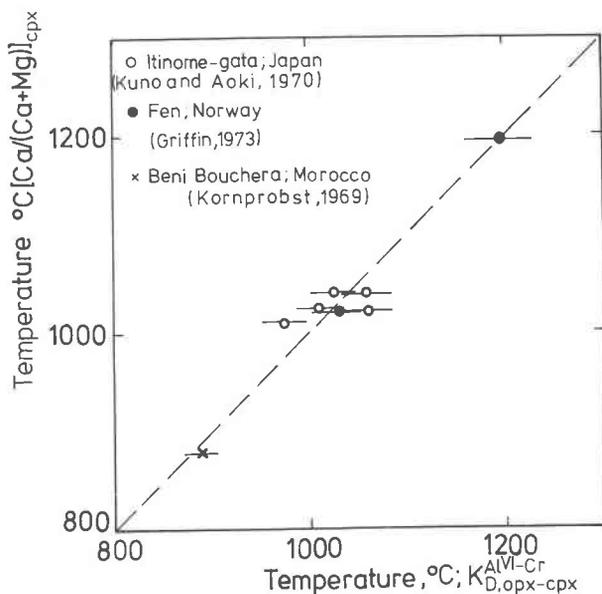


FIG. 5. Determined temperatures of equilibration of some natural peridotites using the geothermometer curve in Figure 4 (K_D) and the pyroxene solvus of Davis and Boyd (1966).

without regard for pressure of equilibration, and they suggest that Al^{VI} and Cr of one of the pyroxenes are approximately linearly related to those of the other (Figs. 6 and 7). The heavy lines in Figures 6 and 7 are least-squares fitted curves that can be described by the equations

$$Cr_{opx} \times 10^3 = 0.58 \pm 0.02 Cr_{epx} \times 10^3 - 1.20 \pm 0.35 \quad (4)$$

$$Al^{VI}_{opx} \times 10^3 = 0.72 \pm 0.05 Al^{VI}_{epx} \times 10^3 + 13.4 \pm 5.2 \quad (5)$$

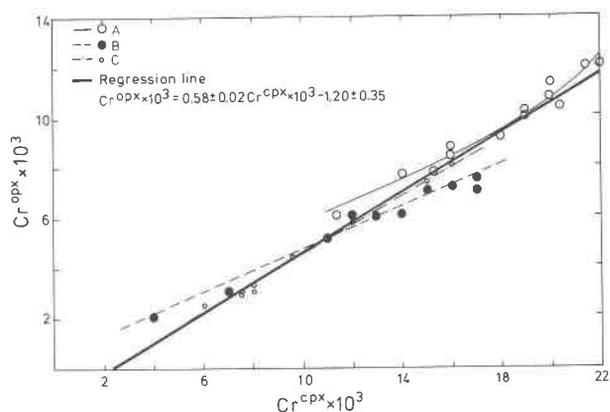


FIG. 6. Chromium content (atom proportion) of coexisting clinopyroxene and orthopyroxene. Equation expresses least-squares fit of all data points. Pressure range, 7.5–30 kbar.

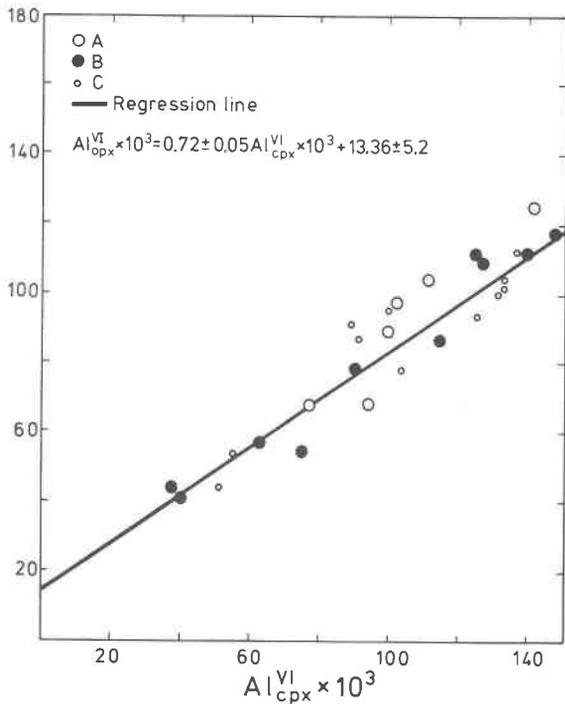


FIG. 7. Six-coordinated aluminum in coexisting clinopyroxene and orthopyroxene. Equation expresses least-squares fit of all data points. Pressure range, 7.5 to 30 kbar.

By substituting these expressions in equation (3), the following geothermometer expressions are obtained.

For clinopyroxene:

$$1/T = 0.26\{Cr/Al^{VI}[(0.72Al^{VI} + 0.01336)/(0.58 - 0.00128)] + 0.67\} \quad (6)$$

For orthopyroxene:

$$1/T = 0.26\{Cr/Al^{VI}[(1.72Cr + 0.00128)/(1.39Al^{VI} - 0.0136)] + 0.67\} \quad (7)$$

However, temperatures obtained with either equation (6) or (7) are somewhat more uncertain than those from equation (3) owing to the relatively large scatter of the analytical points in Figures 6 and 7. Subsequent refinements of experimental data on coexisting clinopyroxene and orthopyroxene may reduce the uncertainty considerably.

Conclusions

Determination of the pyroxene solvus in natural peridotite compositions shows that the solvus determined in the simple system $CaO-MgO-SiO_2$ by Davis and Boyd (1966) can be applied quantitatively and without corrections to natural peridotite formed

in the upper mantle. The geothermometer is insensitive to bulk rock chemistry and to pressure.

A geothermometer based on partitioning of six-coordinated aluminum and chromium between coexisting ortho- and clinopyroxenes gives temperatures that agree closely with those based on the pyroxene solvus. The $Al^{VI}-Cr$ geothermometer has a potentially wider applicability than the pyroxene solvus because of the smaller enthalpy and entropy of the exchange reaction.

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