Alumina content of enstatite as a geobarometer for plagioclase and spinel lherzolites[1]

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Abstract

In the system $CaO-MgO-Al_2O_3-SiO_2$, the solidus curve for simplified spinel lherzolite has been determined from 9 to 14 kbar; and at 9 kbar, 1305°C, an invariant point on the lherzolite solidus has been located at which forsterite, enstatite, diopside, anorthite, spinel, and liquid are in equilibrium. The Al_2O_3 content of enstatite on the spinel lherzolite solidus is 8.4 weight percent at 11 kbar, 1350°C. This point, combined with data on Al_2O_3 in enstatite in the garnet lherzolite field and the position of the spinel to garnet lherzolite transition curve, leads to the conclusion that Al_2O_3 isopleths of enstatite in the spinel lherzolite field have gentle and probably negative dT/dP slopes in sharp contrast to the steep positive slopes found by MacGregor (1974) in the system $MgO-Al_2O_3-SiO_2$. Published paleogeotherms for spinel lherzolites therefore need revision to the extent that they depend on the data of MacGregor. Isopleths of Al_2O_3 in enstatite in the plagioclase lherzolite field are more steeply negative and may provide a good geobarometer for this rock type.

Introduction

Until recently, it has been possible to make only very crude estimates of the depth of origin of ultramafic intrusions and ultramafic nodules brought to the surface by volcanic eruptions, these estimates being based on the experimental observation that spinel lherzolite is stable at lower pressures than garnet lherzolite. Boyd (1973) introduced a method that shows promise of revealing much more detailed information about the stratigraphy of the upper mantle. For lherzolite nodules from northern Lesotho containing the assemblage garnet + diopside + enstatite, he used the $Ca/(Ca + Mg)$ ratio of diopside as a geothermometer and the Al_2O_3 content of enstatite as a geobarometer. He was then able to order the nodules according to depth, and to plot them along a paleogeotherm. For determining pressures from the Al_2O_3 content of enstatite, he used the data of MacGregor (1974) for the assemblage forsterite + enstatite + garnet in the system $MgO-Al_2O_3-SiO_2$.

MacGregor (1974) also determined the Al_2O_3 content of enstatite for the assemblage forsterite + enstatite + spinel in the same system, and found Al_2O_3 isopleths with positive dT/dP slopes sufficiently steep to be useful as a geobarometer for spinel lherzolites.

He constructed paleogeotherms for both garnet and spinel peridotite nodule localities, and MacGregor and Basu (1974) used similar paleogeotherms for a more extended discussion of the thermal structure of the lithosphere.

Based on thermodynamic considerations, Wood (1976) criticized MacGregor's Al_2O_3 isopleths in the spinel field, and concluded that the dT/dP slope of the isopleths varies from zero at about 800°C to slightly positive at higher temperatures. Obata (1976) also calculated Al_2O_3 isopleths in the spinel field and obtained a very similar result. It was pointed out by Wood that the Al_2O_3 content of enstatite determined by Anastasiou and Seifert (1972) at 3 kbar, 920°C is in good agreement with the theoretically derived isopleths. MacGregor (1974) also noted the discrepancy between his own data and the results of Anastasiou and Seifert.

An additional data point (Taylor, 1973) not mentioned by Wood is also in good agreement with his theoretically derived isopleths. In Table 2, Taylor listed a run at 15 kbar, 1570°C for the composition 31 percent MgO, 20 percent Al_2O_3, 49 percent SiO_2, in which he made a microprobe determination of the Al_2O_3 content of enstatite (13.4 weight percent Al_2O_3) in equilibrium with liquid. The composition of the starting mixture is very close to the peritectic at which

forsterite, enstatite, spinel, and liquid are in equilibrium, and the temperature of the run is only 5 degrees above his temperature (1565°C) for that peritectic. Thus, he essentially determined the composition of enstatite in equilibrium with spinel and forsterite at the solidus for that assemblage.

Akella (1976) extended the data of MacGregor (1974) in the garnet lherzolite field by adding CaO and determining the Al_2O_3 content of enstatite in equilibrium with garnet and diopside. His Al_2O_3 isopleths are slightly steeper than those of MacGregor. Akella reversed his reactions by approaching the final Al_2O_3 values using enstatites with both high and low Al_2O_3 contents. Obata (1976) calculated Al_2O_3 isopleths for the spinel lherzolite field in the system $CaO-MgO-Al_2O_3-SiO_2$ and found them to have dT/dP slopes ranging from zero at about 800°C to very slightly positive at 1200°C, as in the system $MgO-Al_2O_3-SiO_2$.

In this paper data are presented for the solidus curve of the assemblage forsterite + enstatite + diopside + spinel in the system $CaO-MgO-Al_2O_3-SiO_2$ from 9 to 14 kbar. The composition of enstatite at 11 kbar on this curve has also been determined. These data thus define the high-temperature stability limit of simplified spinel lherzolite and a limiting value for the Al_2O_3 content of enstatite in equilibrium with forsterite, diopside, and spinel. By combining these data with the Al_2O_3 isopleths of Akella (1976) in the garnet lherzolite field and the location of the transition between spinel and garnet lherzolite, it is possible to determine some rough limits for the slope of Al_2O_3 isopleths in the spinel lherzolite field.

Experimental method

The high-pressure experiments have been carried out in a piston-cylinder apparatus (Boyd and England, 1960) with a pressure-cell arrangement identical to that described by Presnall *et al.* (1973, Fig. 1), except that the mullite sleeve around the thermocouple has been replaced by crushable alumina. Both Pt/Pt10Rh and W3Re/W25Re thermocouples have been used with no pressure correction applied to the emf values. Temperatures have been corrected to conform to the International Practical Temperature Scale of 1968 (Anonymous, 1969). All experiments were of the decompression (piston-out) type and no friction correction has been applied. The sources of the starting materials are the same as described by Presnall *et al.* (1972). Glass starting compositions were prepared by firing the oxide mixtures in a gas-air furnace. Mixtures CMAS-4 and CMAS-5 were fired

at 1500–1600°C for 4 hours, and mixture CMAS-6 was fired at 1550°–1670° for 4 hours. Polished thin sections of all runs were made, and phases were identified with a petrographic microscope using both reflected and transmitted light. Analyses were performed with an Applied Research Laboratories model EMX-SM microprobe. Two synthetic glasses ($CaMgSi_2O_6$ and 90 percent $MgSiO_3$, 10 percent Al_2O_3 by weight) obtained from F. R. Boyd of the Geophysical Laboratory were used as standards. Operating conditions were 15 kilovolts accelerating potential, 0.05 microamp beam current, and 150 microamp emission current. The raw data were corrected for fluorescence, absorption, and atomic number effects using the EMPADR VII computer program of Rucklidge and Gasparrini (1969).[2]

Data

In order to determine the solidus for lherzolite at a given pressure (for example 1 atm) a mixture was

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[2] Electron microprobe analytical data reduction, EMPADR VII, Department of Geology, University of Toronto, Toronto, Canada (unpublished manuscript).
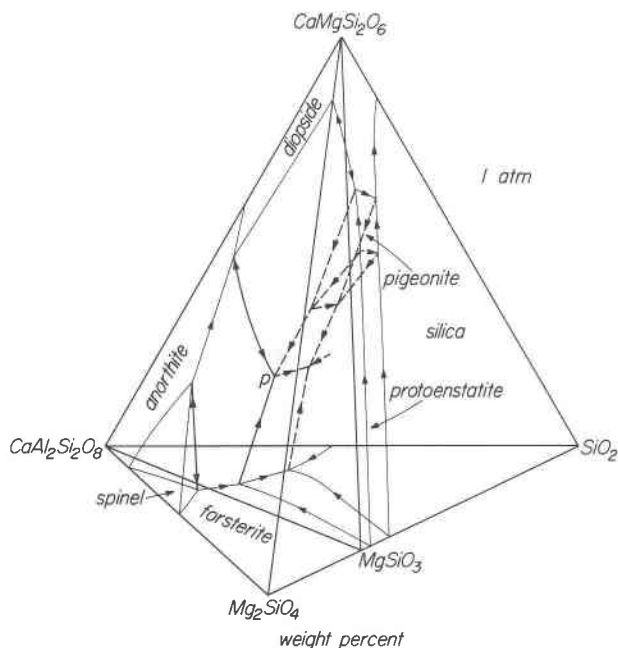

Fig. 1. Liquidus phase relations in the system $Mg_2SiO_4-CaMgSi_2O_6-CaAl_2Si_2O_8-SiO_2$ at 1 atm. Heavy lines are quaternary liquidus univariant lines with arrows indicating directions of decreasing temperature. Compiled from Osborn and Tait (1952), Bowen (1914), Andersen (1915), Kushiro (1972), Hytönen and Schairer (1960), Yang (1973), and Presnall and O'Donnell (unpublished data).

TABLE 1. Compositions in weight percent and CIPW normative mineralogy of starting mixtures

	CMAS-4	CMAS-5	CMAS-6
CaO	14.86	13.89	9.57
MgO	16.16	18.92	28.14
Al_2O_3	19.22	18.26	13.56
SiO_2	49.76	48.93	48.73
fo	3.69	11.51	26.83
di	16.56	14.86	8.16
en	27.31	23.81	28.01
an	52.44	49.82	37.00

chosen that lies close to p (Fig. 1) and on a line between p and forsterite. Runs at temperatures above the invariant point will consist of olivine and liquid. If the mixture does not lie exactly on the line between p and forsterite, some combination of two or less of the additional phases enstatite, diopside, and anorthite could also be present. Exactly at the temperature of p, forsterite, enstatite, diopside, and anorthite would be in equilibrium with liquid. Below the invariant point, the phase assemblage would be either forsterite + enstatite + diopside + anorthite, or enstatite + diopside + anorthite + liquid, depending on the bulk composition. That is, either forsterite or liquid disappears below p.

At higher pressures, the composition of p changes and this necessitated the use of several different mixtures to determine the location of the univariant line in P-T space. Table 1 gives the composition and

normative mineralogy of each of the three starting mixtures used.

Above 9 kbar, anorthite is replaced by spinel, and the assemblage along the univariant solidus curve is forsterite + enstatite + diopside + spinel + liquid. Above the curve, one or more of the phases enstatite, diopside, and spinel is absent, and below the curve forsterite or liquid is absent, depending on the bulk composition of the mixture.

The solidus curve has been reversed at 9.3 and 14 kbar using runs of 6 hours duration (Table 2). This was done by initially bracketing the curve with 6 hour runs. A second set of runs was then made in which the sample was first held for 6 hours on one side of the curve and then held on the other side of the curve for an additional 6 hours. This was accomplished without quenching the sample after the initial 6 hours. Complete conversion of the phase assemblage was not achieved except for the reversal going up-temperature at 14 kbar (Table 2), but in every case the new phase or phases on the other side of the curve were produced. The reversals are thus considered to be valid. However, in order to be sure of the position of the curve and in order to produce more homogeneous enstatites for microprobe analysis, runs of 24 hours duration were made. These are the only runs shown in Figure 2. In every case, the 24 hour runs were consistent with the position of the curve based on the 6-hour reversal experiments. At 9.3 kbar, an apparent inconsistency occurs between the runs at 1315° and 1320°C (Table 3), but when a ± 10° uncertainty is taken into account, the inconsistency disappears.

TABLE 2. Reversal experiments

Initial Conditions			Final Conditions			
T (°C)	P (kbar)	Time (hr)	T (°C)	P (kbar)	Time (hr)	Phases Present*
Composition CMAS-5						
1330**	9.3	6	–	–	–	fo + gl
1330**	9.3	6	1290	9.3	6	fo + en + diop + sp + gl
1290	9.3	6	–	–	–	diop + en + sp + gl
1290**	9.3	6	1330	9.3	6	fo + en + diop + sp + gl
Composition CMAS-6						
1423	14	6	–	–	–	fo + en + gl + q(fo, px)
1423	14	6	1382	14	6	fo + en + diop + sp + gl + q(fo, px)
1399	14	6	–	–	–	fo + en + diop + sp + gl + q
1382	14	6	1423	14	6	fo + en + gl + q(fo, px)

*fo = forsterite, en = enstatite, diop = diopside, px = pyroxene, sp = spinel, gl = glass, q = quench crystals, types of quench crystals in parentheses.
**A Pt/Pt10Rh thermocouple was used for these experiments. For all other experiments a W3Re/W25Re thermocouple was used.
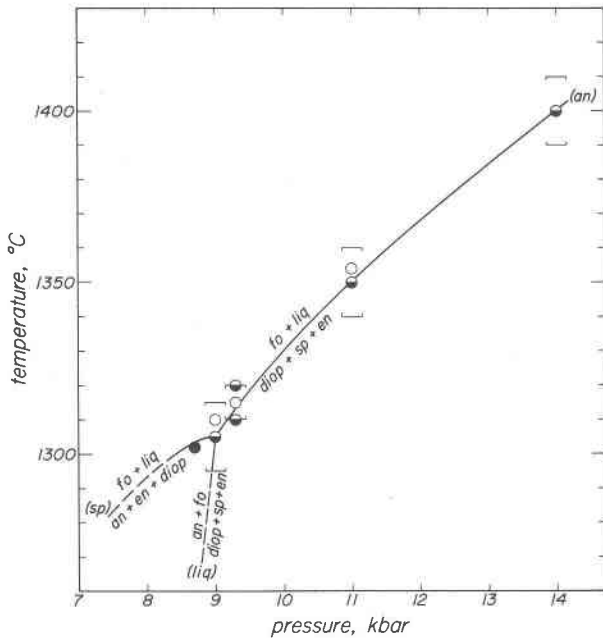
FIG. 2. Univariant solidus curve for plagioclase and spinel lherzolite in the system CaO–MgO–Al$_2$O$_3$–SiO$_2$. Open circles are runs above the solidus, half-filled circles are runs on the solidus, and filled circles are runs below the solidus. Brackets indicate experimental uncertainty in the position of the curve. diop = diopside, en = enstatite, fo = forsterite, sp = spinel, an = anorthite, liq = liquid. Mineral names in parentheses label the univariant curves according to the absent phase.

The solidus curve for the assemblage forsterite + enstatite + diopside + spinel terminates at a quaternary invariant point at which these four phases in addition to anorthite and liquid are in equilibrium. This occurs at 9.0 kbar, 1305°C (Fig. 2), and one run was made at this temperature and pressure in which all the phases at the invariant point were observed. In addition to the solidus curve for spinel lherzolite (anorthite-absent), two other univariant curves are shown. The spinel-absent curve corresponds to the solidus curve for simplified plagioclase lherzolite (forsterite + enstatite + diopside + anorthite) and the liquid-absent curve is the subsolidus transition curve between simplified plagioclase lherzolite and spinel lherzolite. Three other univariant curves originating from the invariant point have been omitted for clarity.

The liquid-absent curve has been determined by Kushiro and Yoder (1965, 1966) using a gas-pressure apparatus, and their curve gives a pressure of 8.9 kbar at 1305°C. This is essentially identical to the value of 9.0 kbar obtained here, suggesting that the piston-out procedure used here requires no pressure correction. This curve has also been determined with piston-cylinder apparatus by Herzberg (1972) and

Herzberg and O'Hara (1972), and the reported pressure using a piston-out technique is 8.9 kbar, independent of temperature. However, data points plotted in Figure 60 of the paper by Herzberg (1972) are compatible with a very steep positive dT/dP slope and permit an uncorrected piston-out pressure of 9.1 kbar at 1305°C. Either of these pressures agrees with the value of 9.0 kbar found here, indicating that uncorrected piston-out pressures in the two laboratories are comparable. Using a gas-pressure apparatus, Herzberg and O'Hara (1972) obtained a pressure for this curve of 8.6 ± 0.15 kbar at 1100°C. Use of the very steep dT/dP slope mentioned above yields a value of 8.8 ± 0.15 kbar at 1305°C, which also agrees with the present determination.

At 11 kbar, 1350°C, a 24 hour run was made containing forsterite, diopside, enstatite, spinel, and glass. Enstatite grains from this run were analyzed with an electron microprobe, and the tests for superior analyses of pyroxenes proposed by Papike et al. (1974) were used as a filter for accepting or rejecting analyses. "Superior" analyses were obtained for seven grains with Al$_2$O$_3$ contents of 8.3, 8.6, 8.5, 8.7, 8.1, 9.6, and 5.5 percent by weight. Assuming all the analyses are good, it appears that 24 hours is not adequate to establish completely homogeneous enstatite compositions throughout the capsule. However, because the first five analyses are closely grouped around an average value of 8.4 percent, I have ignored the last two. Inclusion of the last two would change the average to 8.2 percent, and would cause no important changes in the conclusions of this paper. The complete analysis and structural formula for the average of the first five grains are given in Table 4.

Discussion

In order to determine the general trend of Al$_2$O$_3$ isopleths of enstatite in the spinel lherzolite field, the data point at 11 kbar, 1350°C determined here has

TABLE 3. Quenching experiments all 24 hours in duration

Composition	T (°C)*	P (kbar)	Phases Present**
CMAS–4	1302	8.7	diop + en + an
"	1305	9	fo + diop + en + an + gl
CMAS–5	1305	9	fo + diop + en + an + sp + gl
CMAS–4	1310	9	fo + diop + gl
CMAS–5	1310	9.3	fo + diop + en + sp + gl
"	1315	9.3	fo + en + gl
"	1320	9.3	fo + diop + en + sp + gl
"	1350	11	fo + diop + en + sp + gl + q(en)
"	1354	11	fo + en + gl + q(en)
CMAS–6	1400	14	fo + diop + en + sp + gl + q(en)

*A W3Re/W25Re thermocouple was used for all experiments.
**Abbreviations as in Table 2.

TABLE 4. Enstatite composition at 11 kbar, 1350°C

	Wt. Percent		Number of Cations for 6 Oxygens	
SiO_2	53.3 ± 0.3*	Si	1.82	2.00
Al_2O_3	8.4 ± 0.2	Al	0.18	
MgO	34.7 ± 0.2	Al	0.16	
CaO	2.3 ± 0.1	Mg	1.77	2.01
	98.7	Ca	0.08	

*Standard deviation based on separate analyses of 5 grains ranging from 10 to 20 microns in diameter.

been combined with data on the Al_2O_3 content of enstatite in the garnet lherzolite field (Akella, 1976) and the position of the transition curve between spinel and garnet lherzolite (MacGregor, 1965; Kushiro and Yoder, 1965, 1966; O'Hara et al. 1971; Obata, 1976). Figure 3 shows a compilation of these data, together with extreme positions for the 8.4 percent Al_2O_3 isopleth, depending on which curve for the spinel to garnet lherzolite transition is used.

The solidus curve for spinel lherzolite and the transition curve between plagioclase and spinel lherzolite (liquid-absent) are taken from Figure 2. MacGregor (1965) and Kushiro and Yoder (1965, 1966) both

determined the transition between spinel and garnet lherzolite in the system $CaO-MgO-Al_2O_3-SiO_2$ using piston-in experiments. Uncorrected pressures for the two curves are nearly identical, but MacGregor originally applied no pressure correction while Kushiro and Yoder applied a −13 percent correction (O'Hara et al., 1971, p. 59–60). MacGregor (1974) later decided that a −10 percent correction should be applied to his piston-in experiments, and this correction is used in Figure 3. A correction of −10 percent is about in the middle of the range found in several laboratories for the amount needed to make piston-in measurements agree with piston-out measurements (Johannes et al., 1971). The spinel to garnet lherzolite transition curve in the system $CaO-MgO-Al_2O_3-SiO_2$ determined by O'Hara et al. (1971) is drawn in Figure 3 exactly as they reported it. They used piston-out runs and made no pressure correction, exactly as done in this paper.

In his determination of the Al_2O_3 content of enstatite in the garnet lherzolite field, Akella (1976) made piston-out runs and added a correction of one kbar. To bring his data into correspondence with the other curves in Figure 3, this one kbar correction has been removed. The Al_2O_3 isopleths shown are drawn from his raw data (black dots) and differ slightly from the
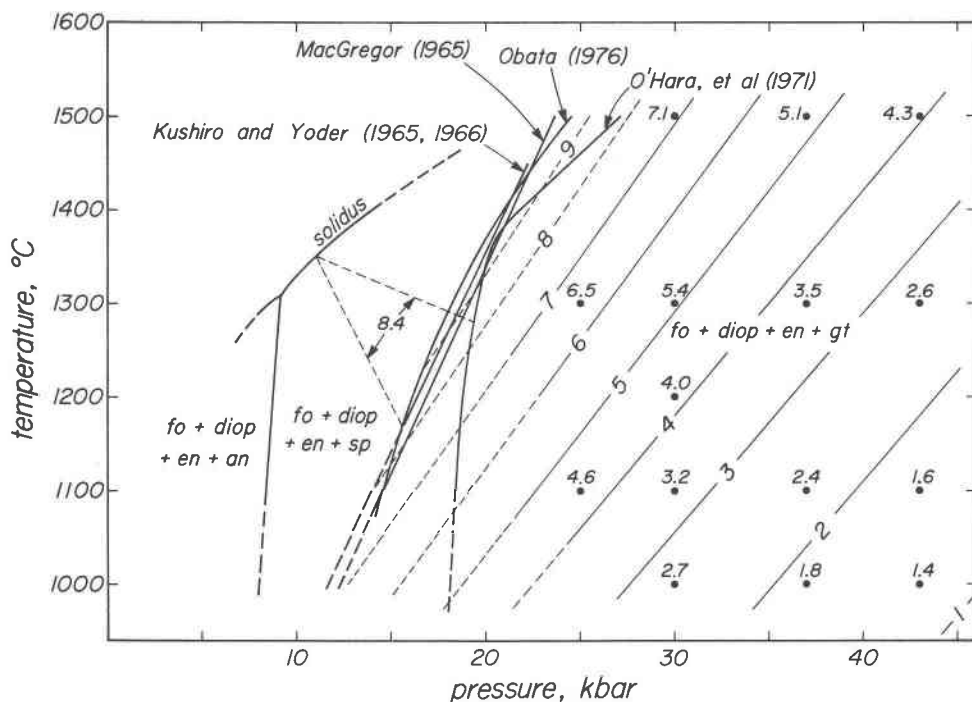

FIG. 3. Stability fields for plagioclase, spinel, and garnet lherzolite in the system $CaO-MgO-Al_2O_3-SiO_2$, with isopleths showing Al_2O_3 content (weight percent) of enstatite. Isopleths in the garnet lherzolite field are constructed from the data of Akella (1976).

curves shown in his Figure 2. His curves would translate into isopleths that are slightly convex upward with slightly steeper slopes (especially in the lower temperature region) than the straight isopleths shown here. Use of his curves along with his +1 kbar correction would cause the 8.4 percent Al_2O_3 isopleth in the spinel lherzolite field to be more steeply negative. In order to determine the 8.4 percent Al_2O_3 intercept on the spinel to garnet lherzolite transition curve, it was necessary to make a small extrapolation of Akella's data to lower pressures. At 1300°C, Akella's data indicate that the difference in pressure between adjacent isopleths increases linearly with pressure, and this relationship was used to construct the approximate positions of the 8 and 9 percent Al_2O_3 isopleths (Fig.3).

The extreme positions shown in Figure 3 for the 8.4 percent Al_2O_3 isopleth in the spinel lherzolite field do not take into account several uncertainties. One of these is the analytical uncertainty in the analysis at 11 kbar, 1350°C (Table 4). Also, the isopleths in the garnet lherzolite field intersect the spinel to garnet lherzolite transition curve at a very small angle. Thus, when the location of the transition curve is shifted only slightly in pressure, there is a large shift in the point at which the 8.4 percent Al_2O_3 isopleth intersects the transition curve.

Another problem is that enstatite with 8.4 percent Al_2O_3 occurs at two points on the transition curve of O'Hara *et al.* (1971). An error must exist either in this transition curve or the isopleths of Akella (1976). The gentle curvature in the spinel to garnet lherzolite curve calculated by Obata (1976) suggests that the bend in the curve by O'Hara *et al.* (1971) at about 21 kbar, 1370°C, is too sharp. A very slight curvature of the 8 and 9 percent Al_2O_3 isopleths above 1400°C would avoid a high-temperature intersection with Obata's transition curve. For all of the transition curves, and especially for that of O'Hara *et al.*, a lower temperature intersection appears to be unavoidable. Thus, I have ignored the high temperature intersection on the curve of O'Hara *et al.* Because of all of these uncertainties, the slope of the 8.4 percent Al_2O_3 isopleth could be steeply negative to approximately horizontal. It seems clear, however, that a steeply positive slope is not possible.

Extension of MacGregor's isopleths in the system $MgO-Al_2O_3-SiO_2$ to the conditions of the data point reported here (1350°C, 11 kbar) would give an extremely high Al_2O_3 content of about 16 weight percent. The addition of CaO would be expected to modify the Al_2O_3 content somewhat, but it seems

unlikely that MacGregor's data are correct, particularly in view of the discrepancies between his data and the data and theoretical calculations of others. The most likely explanation for the high Al_2O_3 contents found by MacGregor is a combination of very small grains and the presence of spinel inclusions in his enstatites. He suggested this himself as a possible problem with the microprobe analyses (MacGregor, 1974, p. 113, 118). In reflected light, the enstatite grains in the runs reported here are typically completely free of spinel inclusions.

Paleogeotherms for spinel and plagioclase lherzolites

At present, the data are insufficient to use Al_2O_3 isopleths in the spinel lherzolite field to infer pressures of formation, and it remains to be seen if these isopleths will ever be useful as a geobarometer. Figure 3 indicates that in the system $CaO-MgO-Al_2O_3-SiO_2$ these isopleths are possibly useful for lherzolites very low in Cr_2O_3, such as are found in high temperature intrusions like the Lizard complex (Green, 1964). Such compositions could be closely approximated by the simplified system. However, most alpine peridotites are rich in Cr_2O_3, and this could strongly affect the positions of the isopleths. It may turn out that Al_2O_3 isopleths in the spinel lherzolite field are more useful as a geothermometer.

Although much more work is required before attempting to use these isopleths, some general consequences for geotherms already published (MacGregor, 1974; MacGregor and Basu, 1974; Mercier and Carter, 1975) can be discussed. Whereas Al_2O_3 isopleths for enstatite in the spinel lherzolite field appear to have gently negative or nearly flat slopes, it appears that these isopleths in the plagioclase lherzolite field must have steep negative slopes. This is suggested by the very low Al_2O_3 content (between 1 and 2 weight percent) of protoenstatite at point *p* in Figure 1 (Presnall and O'Donnell, unpublished data). Also, the Al_2O_3 content of enstatite phenocrysts in a Hawaiian lava that also contains phenocrysts of olivine, diopside, and plagioclase, has been determined by Kuno (1966, Table 1, analysis 1) as 0.75 weight percent (see also Wright, 1971, p. 16 and Tables 7 and 15). Obata (1976) has also calculated steeply negative Al_2O_3 isopleths for enstatite in the plagioclase lherzolite field. Thus, two possible pressures of formation can be indicated by the Al_2O_3 content of enstatite in a lherzolite. Determination of the presence of plagioclase, spinel, or garnet in the rock would generally eliminate the ambiguity. For example, Wilshire and Jackson (1975) noted that uncritical application of

MacGregor's isopleths leads to the absurd conclusion that recrystallized Lizard peridotite formed at a higher pressure (22 kbar) than the primary peridotite (11–16 kbar). The recrystallized peridotite, however, contains plagioclase and could not possibly have formed at this pressure. The rock is easily explained as having formed at low pressures in the plagioclase lherzolite field where the Al_2O_3 content of enstatite is the same as at 22 kbar.

It is hoped that the data presented here might form the beginning of a revised set of data on which pressures or temperatures of formation of spinel and plagioclase lherzolites can be determined. The use of the Al_2O_3 content of enstatite as a geobarometer appears to be the most promising for plagioclase lherzolites, and it is ironic that these are relatively rare rocks.

Acknowledgments

References

AKELLA, J. (1976) Garnet pyroxene equilibria in the system $CaSiO_3$–$MgSiO_3$–Al_2O_3 and in a natural mineral mixture. *Am. Mineral.* **61**, 589–598.

ANASTASIOU, P. AND F. SEIFERT (1972) Solid solubility of Al_2O_3 in enstatite at high temperature and 1–5 kb water pressure. *Contrib. Mineral. Petrol.* **34**, 272–287.

ANDERSEN, O. (1915) The system anorthite–forsterite–silica. *Am. J. Sci.* **39** (Fourth Ser.), 407–454.

ANONYMOUS (1969) The international practical temperature scale of 1968. *Metrologia,* **5**, 35–44.

BOWEN, N. L. (1914) The ternary system diopside–forsterite–silica. *Am. J. Sci.* **38** (Fourth Ser.), 207–264.

BOYD, F. R. (1973) A pyroxene geotherm. *Geochim. Cosmochim. Acta,* **37**, 2533–2546.

―――― AND J. L. ENGLAND (1960) Apparatus for phase equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750°C. *J. Geophys. Res.* **65**, 741–748.

GREEN, D. H. (1964) The petrogenesis of the high-temperature peridotite intrusion in the Lizard area, Cornwall. *J. Petrol.* **5**, 134–188.

HERZBERG, C. T. (1972) Stability fields of plagioclase- and spinel–lherzolite. *Progress in Experimental Petrology,* Natural Environment Research Council, **2**, 145–148.

―――― AND M. J. O'HARA (1972) Temperature and pressure calibration and reproducibility of pressure in solid media equipment. *Progress in Experimental Petrology,* Natural Environment Research Council **2**, 97–98.

HYTÖNEN, K. AND J. F. SCHAIRER (1960) The system enstatite–anorthite–diopside. *Carnegie Inst. Wash. Year Book* **59**, 71–72.

JOHANNES, W., P. M. BELL, H. K. MAO, A. L. BOETTCHER, D. W.

CHIPMAN, J. F. HAYS, R. C. NEWTON AND F. SEIFERT (1971) An interlaboratory comparison of piston-cylinder pressure calibration using the albite-breakdown reaction. *Contrib. Mineral. Petrol.* **32**, 24–38.

KUNO, H. (1966) Review of pyroxene relations in terrestrial rocks in the light of recent experimental works. *Mineral. J. (Japan)* **5**, 21–43.

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

―――― AND H. S. YODER, JR. (1965) The reactions between forsterite and anorthite at high pressures. *Carnegie Inst. Wash. Year Book,* **64**, 89–94.

―――― AND ―――― (1966) Anorthite–forsterite and anorthite–enstatite reactions and their bearing on the basalt–eclogite transformation. *J. Petrol.* **7**, 337–362.

MACGREGOR, I. D. (1965) Stability fields of spinel and garnet peridotites in the synthetic system MgO–CaO–Al_2O_3–SiO_2. *Carnegie Inst. Wash. Year Book,* **64**, 126–134.

―――― (1974) The system MgO–Al_2O_3–SiO_2: Solubility of Al_2O_3 in enstatite for spinel and garnet peridotite compositions. *Am. Mineral.* **59**, 110–119.

―――― AND A. R. BASU (1974) Thermal structure of the lithosphere: a petrologic model. *Science,* **185**, 1007–1011.

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

OBATA, M. (1976) The solubility of Al_2O_3 in orthopyroxenes in spinel and plagioclase peridotites and spinel pyroxenite. *Am. Mineral.* **61**, 804–816.

O'HARA, M. J., S. RICHARDSON AND G. WILSON (1971) Garnet–peridotite stability and occurrence in crust and mantle. *Contrib. Mineral. Petrol.* **32**, 48–68.

OSBORN, E. F. AND D. B. TAIT (1952) The system diopside–forsterite–anorthite. *Am. J. Sci. Bowen Vol.,* 413–433.

PAPIKE, J. J., K. L. CAMERON AND K. BALDWIN (1974) Amphiboles and pyroxenes: characterization of *other* than quadrilateral components and estimates of ferric iron from microprobe data. *Abstracts with Programs 6, Geol. Soc. Am. 1974 Annu. Meet.* 1053–1054.

PRESNALL, D. C., N. L. BRENNER AND T. H. O'DONNELL (1973) Drift of Pt/Pt10Rh and W3Re/W25Re thermocouples in single stage piston-cylinder apparatus. *Am. Mineral.* **58**, 771–777.

――――, C. L. SIMMONS AND H. PORATH (1972) Changes in electrical conductivity of a synthetic basalt during melting. *J. Geophys. Res.* **77**, 5665–5672.

TAYLOR, H. C. J. (1973) Melting relations in the system MgO–Al_2O_3–SiO_2 at 15 kb. *Geol. Soc. Am. Bull.* **84**, 1335–1348.

WILSHIRE, H. G. AND E. D. JACKSON (1975) Problems in determining mantle geotherms from pyroxene compositions of ultramafic rocks. *J. Geol.* **83**, 313–329.

WOOD, B. J. (1976) The application of thermodynamics to some subsolidus equilibria involving solid solutions. *Fortschr. Mineral.* (in press).

WRIGHT, T. L. (1971) Chemistry of Kilauea and Mauna Loa lava in space and time. *U. S. Geol. Surv. Prof. Pap.* **735**, 40 p.

YANG, H.-Y. (1973) Crystallization of iron-free pigeonite in the system anorthite–diopside–enstatite–silica at atmospheric pressure. *Am. J. Sci.* **273**, 488–497.