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GARNET PERIDOTITES AND THE SYSTEM $CaSiO_3$-$MgSiO_3$-Al_2O_3

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Abstract

Analytical data for diopsides, enstatites, and garnets from kimberlites are reviewed with particular reference to the garnet-lherzolite assemblage. The diopsides show a pronounced bimodal distribution in their solid solution toward $MgSiO_3$, which is not understandable in terms of existing phase studies. The enstatites show very restricted solid solution toward $CaSiO_3$ and Al_2O_3, consistent with experimental work on the systems $MgSiO_3$-$Mg_3Al_2Si_3O_{12}$ and $MgSiO_3$-$CaMgSi_2O_6$. The garnets are relatively constant in their Mg, Fe, and Ca contents but show a wide variability in Al and Cr.

A new determination of phase relations in the system $CaSiO_3$-$MgSiO_3$-Al_2O_3 at 1200°C and 30 kbar shows extensive solid solutions along the garnet join and in a diopside field extending toward $CaAl_2SiO_6$ and $MgSiO_3$. There are four three-phase fields, one of which ($Di_{ss}+En_{ss}+$Mg-Gt) models the essential features of the garnet-lherzolite assemblage rather well. Compositions of coexisting phases have been determined by electron-probe analysis.

Introduction

Most petrologic models of the upper mantle include garnet peridotite as a major constituent. The physical properties of this rock type are compatible with those derived from seismic measurements for the mantle above the transition zone, and peridotites appear to be possible parents for basaltic magmas. Moreover, garnet peridotites are abundant among the ultramafic xenoliths that have been erupted in kimberlite. These xenoliths may not be representative of primeval mantle rock, but there is reason to believe that they have equilibrated at considerable depth in the mantle and been erupted with little fundamental alteration.

Considerable attention has been directed in recent years to the mineralogy of these kimberlite xenoliths. At the same time, laboratory studies of phase relations in pyroxene and garnet systems have provided a partial understanding of the mineral assemblages found in these rocks. The phase relations of ultramafic rocks in general are simpler than those of most rocks of crustal origin, and there is hope that with sufficient laboratory investigation the mineral assemblages and equilibration conditions of the ultramafic suite can be understood in considerable detail.

The purpose of the present paper is to review recent mineralogical and experimental studies relevant to the garnet-peridotite xenoliths in kimberlite and to present a new determination of the phase relations in the system $CaSiO_3$-$MgSiO_3$-Al_2O_3 at 1200°C and 30 kbar. Subsolidus phase relations in this system form a useful model of the garnet-pyroxene assemblages found in garnet lherzolites and other xenoliths.

Mineralogical Review

The major primary phases in the peridotite xenoliths in kimberlite are forsterite, enstatite, pyrope, and diopside. Phlogopite and chrome spinel are commonly present in subordinate amounts, but sometimes it is difficult to be certain whether they are primary or secondary. The fabric is very coarse, and disequilibrium features such as exsolution lamellae and compositional zoning are rare. Alteration to secondary minerals such as serpentine and carbonate varies from slight to complete. The primary minerals appear to have equilibrated below the solidus at considerable depth in the mantle, and in most cases there appears to have been little or no reaction between them during eruption.

The equilibria between enstatite and diopside and between these pyroxenes and garnet are of paramount interest because these equilibria have been shown to be sensitive functions of temperature and pressure. Forsterite is almost ubiquitous, but in a discussion of subsolidus equilibria its presence can be ignored because it does not form significant solid solutions wlth the other primary phases. The solid solutions between the two pyroxenes and garnet are interdependent, and for this reason it is important to focus attention on xenoliths that contain all three. In the pure system $CaSiO_3$-$MgSiO_3$-Al_2O_3 the assemblage Ca-rich clinopyroxene + Mg-rich orthopyroxene + garnet is invariant at constant temperature and pressure. This relationship cannot be strictly applied to the peridotite xenoliths because the natural minerals contain small but significant amounts of Fe, Cr, Na, etc. Nevertheless these extraneous solid solutions are of secondary importance in many cases. In a few cases described hereafter their effects are undoubtedly considerable.

Garnet lherzolites, which contain both pyroxenes with garnet and forsterite, are one of the most abundant rock types found as kimberlite xenoliths. A considerable body of analytical data exists for minerals from these lherzolite xenoliths, although there are only two xenoliths for which analyses have been made of both pyroxenes and garnet (A−3, O'Hara and Mercy, 1963; E−3, Nixon, Von Knorring, and Rooke 1963). Analyses for pyroxene and garnet from many harzburgite xenoliths are also available. Much of the analytical work on kimberlite minerals has been carried out on individual coarse crystals which are commonly dispersed through kimberlite. Whether these crystals are cognate phenocrysts, xenocrysts, or both is a matter that needs clarification. In many cases the crystals appear to be disaggregated xenoliths, and it is likely that they have come from harzburgite and lherzolite assemblages. Analytical data for xenocrysts as well as a variety

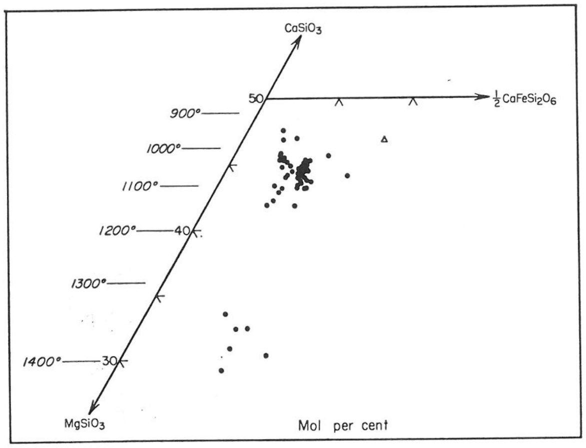

FIG. 1. Electron-probe analyses of diopsides from kimberlite in a portion of the pyroxene quadrilateral. Solid points are from Boyd and Nixon (1970) and Boyd (1969); open triangle is an analysis of a diopside included in diamond (Meyer and Boyd, 1969). Temperatures are for the Di(*en*) solvus in the system MgSiO$_3$-CaMgSi$_2$O$_6$ at 30 kbar (Davis and Boyd, 1966).

of peridotite xenoliths are combined in this review, but pyroxenes and garnets that are known to have equilibrated in the lherzolite assemblage will be distinguished.

The electron-probe and wet-chemical analyses of xenolith minerals that are discussed in this paper are primarily from African localities. A few analyses for kimberlite xenoliths from the United States and the Soviet Union are included. The mineralogical data described herein are not a complete coverage of all sources but should provide a representative picture.

Diopside. Bright green chrome diopsides are characteristic minerals in kimberlite, and their presence in alluvial deposits is often used as an indicator in prospecting for kimberlite pipes. In the lherzolite xenoliths, the diopside is often finer grained than the enstatite and olivine and sometimes is found in interstitial intergrowths with phlogopite and spinel. Sparse wet-chemical analyses of these diopsides show a wide range of solid solution toward enstatite (Davis and Boyd, 1966), suggesting a considerable range in equilibration temperature. To augment these data, electron-probe analyses have recently been made on a large number of kimberlite diopsides from about fifteen pipes in South Africa, Lesotho, Uganda, and Tanzania (Boyd, 1969; Boyd and Nixon, 1970).

The electron-probe analyses show a distribution that was quite unexpected from the earlier wet-chemical studies. Results for sixty-three analyses are plotted in a portion of the pyroxene quadrilateral in Figure 1. There are two well-defined groups. A calcic group containing about 90 percent of the analyses shows variable but restricted solid solution toward enstatite and ferrosilite, whereas a subcalcic group with a smaller number of analyses shows a very large solid solution toward enstatite. Two of the earlier wet-chemical analyses that had indicated compositions intermediate between these groups have been checked by probe and found to fall in the calcic group (Boyd and Nixon, 1970).

These analyses are projected onto the join MgSiO$_3$-CaMgSi$_2$O$_6$ in Figure 2, and a distinction is made between those known to have come from the garnet-lherzolite assemblage and those from other, mostly unknown, assemblages. The subset of diopside analyses from garnet-lherzolite xenoliths shows essentially the same distribution as the

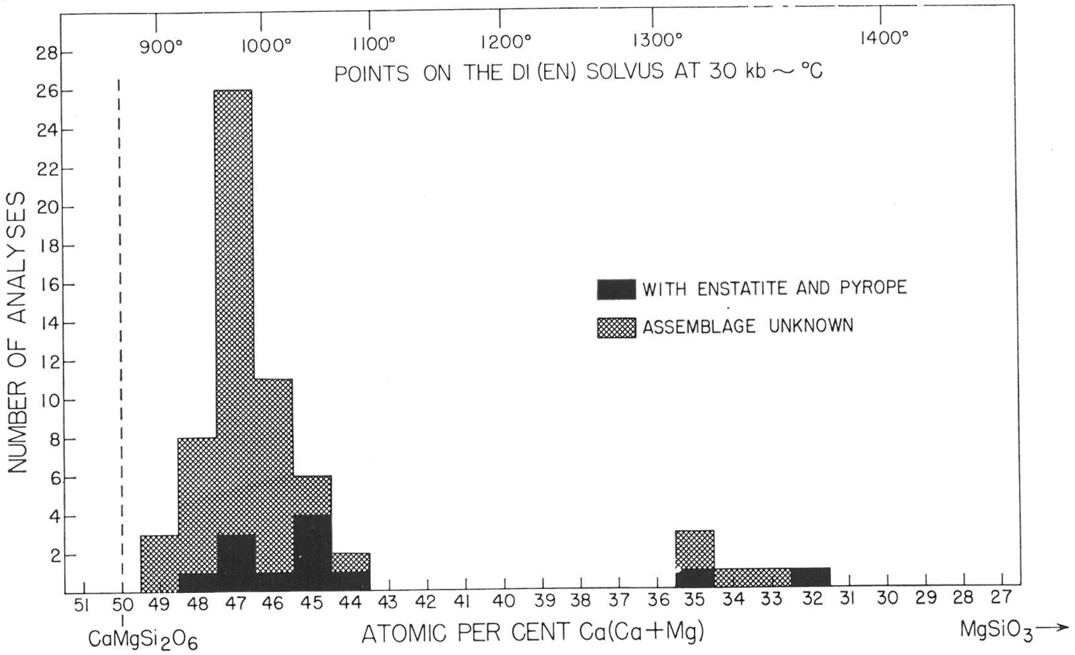

FIG. 2. Ca/(Ca+Mg) ratios of the diopsides in Fig. 1. A distinction is made between diopsides from garnet-lherzolite xenoliths those that occur as xenocrysts.

whole group. Both calcic and subcalcic diopsides are found coexisting with garnet and enstatite.

The Al_2O_3 contents of these diopsides average 2.1 percent and practically all fall in the range 1.0–2.5 percent Al_2O_3 (Fig. 3). Cr_2O_3 ranges up to a little over 3 percent (Fig. 4) and averages 1.3 percent. Ferric iron determinations cannot be readily made with an electron probe, and in their absence it is difficult to distinguish quantitatively between solid solution toward garnet and solid solution toward Na pyroxene. Nevertheless, in Figure 5 the sum of Al and Cr is plotted against alkalis (atomic proportions) for the limited number of diopsides that have been analysed for Na and K. These analyses approach a 1:1 relationship for Al+Cr to Na+K, indicating that the solid solution is largely toward jadeite and ureyite. Wet-chemical analyses show on the order of 1 percent Fe_2O_3, so there is clearly some solid solution toward garnet, but it is restricted. Solid solution toward the components of Na pyroxene makes up 10–20 atomic percent of these diopsides and is thus significant.

The subcalcic diopsides contain less Cr_2O_3 and slightly more Al_2O_3 than the average values for all the analyses. However, there is no sharp differentiation in R_2O_3 contents or in the minor elements, mirroring the relationship shown in Figures 1 and 2. The only essential chemical difference between the calcic and subcalcic groups is in the degree of solid solution they show toward $MgSiO_3$.

There do appear to be some differences in provenance in that subcalcic diopsides have thus far been found in only three localities—Thaba Putsoa and Solane in Lesotho (formerly Basutoland) and Shinyanga (probably Kizumbi) in Tanzania. The Lesotho and Tanzania localities are 1800 miles apart, so that the occurrence of the subcalcic diopsides is clearly more than local. The calcic diopsides are primarily from the Kimberley pipes, but they also occur at many other localities; at Solane both calcic and subcalcic varieties have been found together in the same pipe (Boyd and Nixon, 1970).

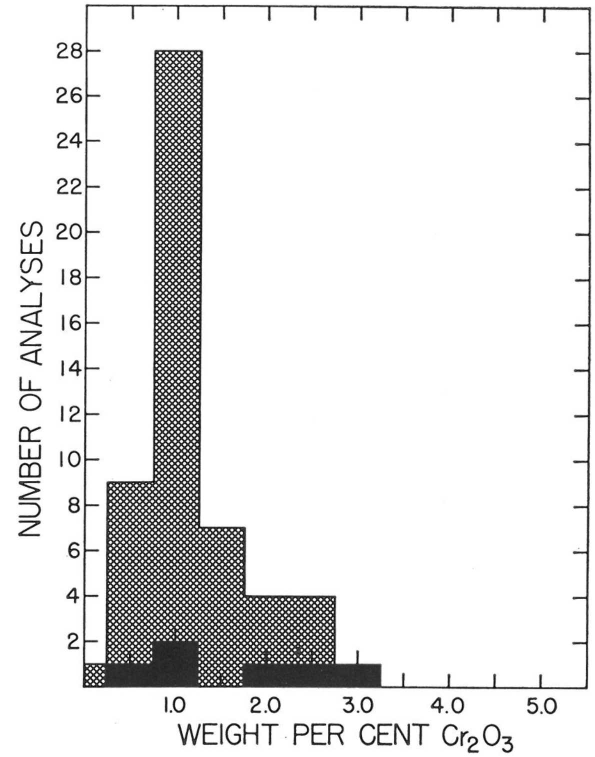

FIG. 4. Cr_2O_3 contents of the diopsides in Fig. 1. Diopsides from garnet-lherzolite nodules are shown in black

The solvus curve limiting the solid solution of $MgSiO_3$ in diopside has been determined at atmospheric pressure and at 30 kbar (Boyd and Schairer, 1964; Davis and Boyd, 1966). Kushiro (1969) has studied the system $MgSiO_3$-

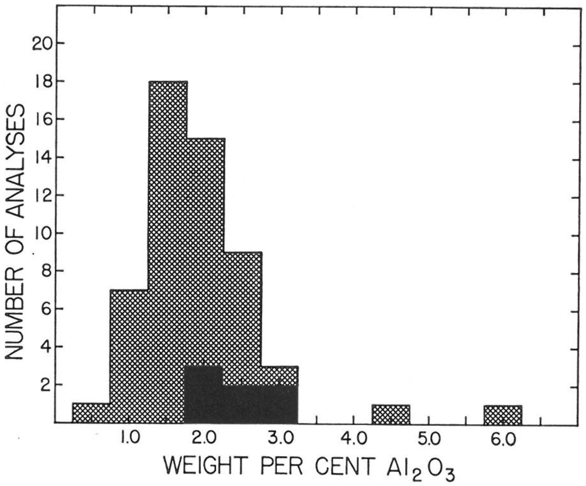

FIG. 3. Al_2O_3 contents of the diopsides in Fig. 1. Diopsides from garnet-lherzolite nodules are shown in black.

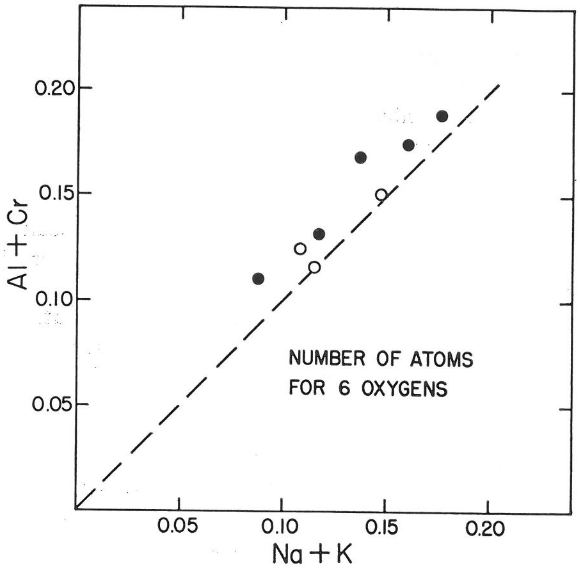

FIG. 5. A plot of alkalis against Al+Cr for the diopsides in Fig. 1.

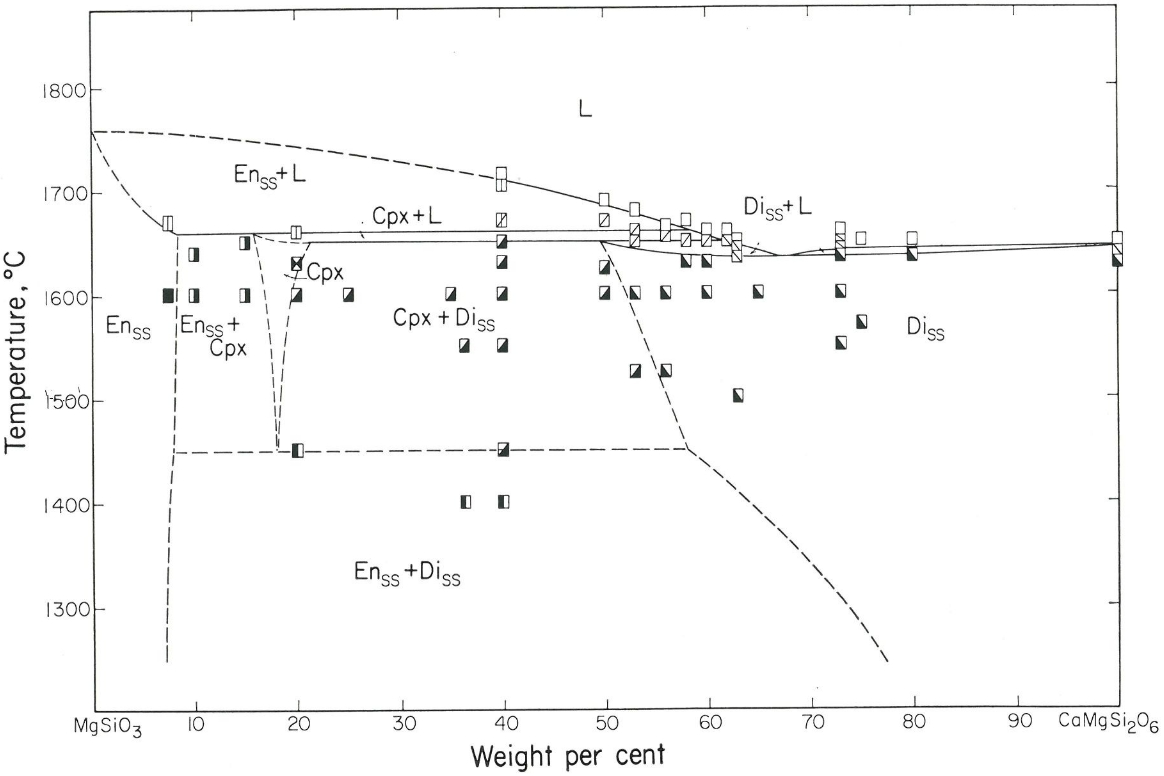

FIG. 6. A portion of the system $MgSiO_3$-$CaMgSi_2O_6$ at 20 kbar showing the field for pigeonite (Cpx) after Kushiro (1969).

$CaMgSi_2O_6$ above 1400°C at 20 kbar. The composition of diopside in equilibrium with enstatite is sensitive to temperature in the range 1000°–1400°C, but it appears to be relatively insensitive to pressure. Points from the solvus at 30 kbar are shown in Figures 1 and 2. The calcic diopsides appear to have formed at temperatures around 1000°C, whereas the subcalcic diopsides appear to have equilibration temperatures on the order of 1350°C.

These temperatures are not improbable for the upper part of the mantle, but the total lack of diopsides of intermediate compositions makes it very awkward to interpret the bimodal distribution shown in Figures 1 and 2 by means of the continuous solvus curve determined by experiment. If the subcalcic diopsides have indeed formed at higher temperature and presumably greater depth in the mantle than the calcic group, then it is very difficult to understand why the kimberlites in which they occur did not include diopsides with intermediate compositions during eruption. A well-differentiated, bimodal distribution is obviously hard to explain in terms of a continuous solvus curve and a continuous geothermal gradient of whatever curvature.

The experimental studies of the system $MgSiO_3$-$CaMgSi_2O_6$ presently extend up to a pressure at 30 kbar. The presence of diamond among the primary minerals in kimberlite suggests that these minerals have equilibrated at pressures of at least 50 kbar. Hence there is a possibility that the bimodal distribution of diopside analyses reflects features in the pyroxene phase diagram which appear at pressures above those at which these pyroxenes have thus far been studied.

The narrow field for pigeonite in the system $MgSiO_3$-$CaMgSi_2O_6$ at 20 kbar discovered by Kushiro (1969) may relate to this problem. Kushiro's diagram is reproduced in Figure 6, and it can be seen that this field is limited to Mg-rich compositions and to temperatures above 1450°C. There is a broad field where an Mg-rich $P2_1/c$ clinopyroxene coexists with a Ca-rich $C2/c$ clinopyroxene. These relations were not observed by Davis and Boyd (1966) in their study of this join at 30 kbar, and their diagram needs reinvestigation in the light of Kushiro's discovery.

The pigeonite field in Figure 6 is considerably more Mg-rich than the subcalcic diopsides described above, but it is conceivable that this field shifts toward diopside with increased pressure. If so, it appears that the pyroxene assemblages found in kimberlites could be modeled by the phase relations shown in Figure 6. Within a narrow temperature range across 1450°C it is possible to have either a Ca-rich clinopyroxene ($C2/c$) coexisting with enstatite or a considerably less calcic clinopyroxene ($P2_1/c$) co-existing with enstatite of nearly the same composition.

X-ray studies of two of the subcalcic diopsides described above show that they have $C2/c$ symmetry (Joan R. Clark, pers. commun.). However, recent high temperature-X-ray studies of Ca-poor clinopyroxenes (Smyth, 1969; Smith, 1969) show that those with $P2_1/c$ symmetry at room temperature undergo a displacive transformation to $C2/c$ at high temperatures. Hence, it is possible that the clinopyroxenes in Kushiro's pigeonite field (Fig. 6) actually have $C2/c$ symmetry at high temperatures. If so the two-pyroxene field shown at "Cpx+Di_{ss}" (Fig. 6) would be a true miscibility gap in a structurally continuous series. The tendency of $C2/c$ pyroxenes to invert to $P2_1/c$ on cooling may be a function of Ca content, and the inversion may be inhibited in more Ca-rich pyroxenes.

It must be emphasized that these suggestions are entirely hypothetical. But it seems more likely that an explanation of the bimodal distribution of these diopside compositions will be found in pyroxene phase relations than in awkward constraints on the depths of origin and mode of eruption of kimberlites.

Enstatite. Electron-probe data on enstatites from kimberlites are not as yet available, but a small number of wet-chemical analyses have been published. They are plotted in a portion of the pyroxene quadrilateral and also in a portion of the system $CaSiO_3$-$MgSiO_3$-Al_2O_3 in Figure 7. These enstatites show a small solid solution toward $FeSiO_3$, but their solid solutions toward $CaSiO_3$ and toward Al_2O_3 are very restricted. Histograms for the R_2O_3 oxides are given in Figure 8. Al_2O_3 and Fe_2O_3 each average about 1 percent, and Cr_2O_3 with a mean of 0.3 percent is considerably lower than in the coexisting diopsides. Alkalis are very low in these enstatites, and the trivalent elements form solid solutions of the Tschermak type, toward garnet.

These reduced solid solutions toward $CaSiO_3$ and garnet are compatible with phase studies on synthetic systems. Although diopside exhibits a large solid solution toward $MgSiO_3$ at high temperatures, coexisting rhombic enstatites dissolve very little $CaSiO_3$. As shown by data presented hereafter, enstatite in equilibrium with diopside on the join $MgSiO_3$-$CaMgSi_2O_6$ at 1200°C and 30 kbar contains 2.7 mole percent $CaSiO_3$, compared with a mean of 1.4 mole percent for the enstatites from garnet-lherzolite xenoliths shown in Figure 7. It is interesting to note the enstatite in Figure 7 that shows the largest solid solution toward $CaSiO_3$ (2.9 mole percent) coexists with a subcalcic diopside. The origin of these subcalcic diopsides is presently enigmatic, but there is reason to believe they have formed at higher temperatures than the more common calcic type, and the composition of this associated enstatite would support this view.

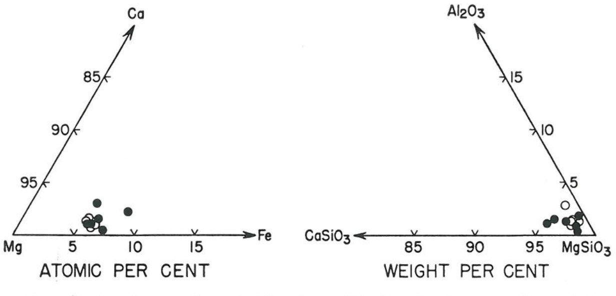

FIG. 7. Analyses of enstatites from kimberlite in a portion of the pyroxene quadrilateral (left) and in the system $CaSiO_3$-$MgSiO_3$-Al_2O_3 (right). Solid points are enstatites from garnet-lherzolite xenoliths. Data are from Nixon, Von Knorring, and Rooke (1963), O'Hara and Mercy (1963), Banno, Kushiro, and Matsui (1963), and MacGregor and Ringwood (1964).

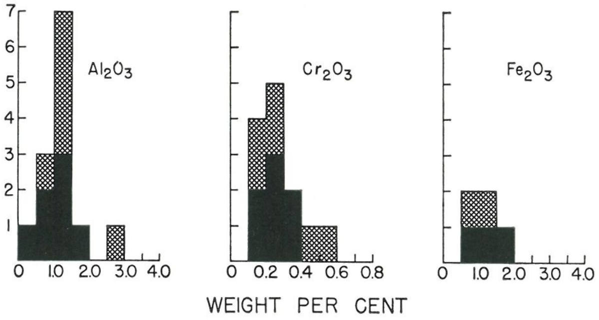

FIG. 8. R_2O_3 contents of the enstatites from Fig. 7. Solid points are enstatites from garnet-lherzolite xenoliths.

Rhombic enstatite can dissolve large quantities of Al_2O_3 (or garnet) under certain P-T conditions. Phase relations for the system $MgSiO_3$-$Mg_3Al_2Si_3O_{12}$ (Boyd and England, 1964) at 30 kbar show that enstatite in equilibrium with pyrope at 1600°C contains about 15 weight percent Al_2O_3. Within the pyrope stability field, increase of pressure reduces the solubility limit of Al_2O_3 in enstatite, because it exsolves to form more dense garnet. Figure 9 shows isotherms for this solvus at 1100°C and 1600°C modified after Boyd and England (1964). High values of Al_2O_3 in enstatite in equilibrium with pyrope at 20–30 kbar are greatly reduced at higher pressures. At 60 kbar the solubility limit of Al_2O_3 in enstatite is less than 2 weight percent in the temperature range up to 1600°C. Most enstatites from kimberlites have probably equilibrated in the diamond stability field where the pressures were greater than 50 kbar, and their low solid solution toward garnet is thus consistent with experiment.

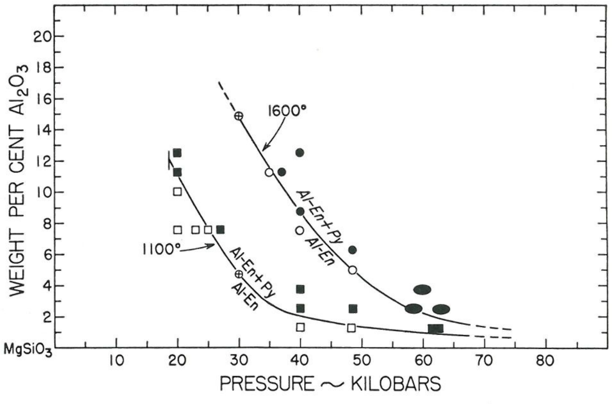

FIG. 9. Isotherms for the solvus En(*co*) in the system $MgSiO_3$-$Mg_3Al_2Si_3O_{12}$ after Boyd and England (1964) with additional data at 60 kbar. Open circles with crosses are points taken from an isobar at 30 kbar (Boyd and England, 1964, Fig. 54); open points are for Al enstatite and solid points are for Al enstatite+pyrope.

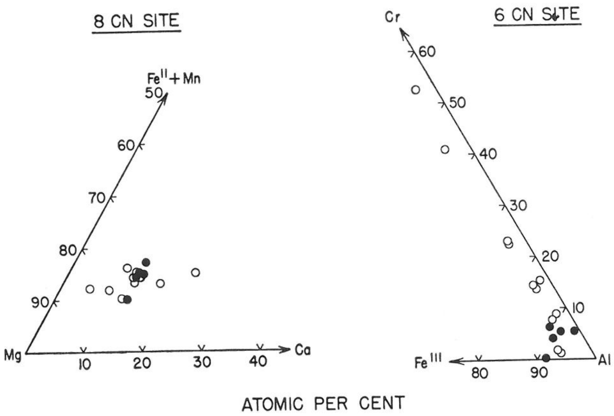

FIG. 10. Analyses of garnets from kimberlites plotted in diagrams for the eight-coordinated site and for the six-coordinated site. Solid points are garnets from lherzolite xenoliths. Data are from Nixon, Von Knorring, and Rooke (1963), O'Hara and Mercy (1963), MacGregor and Ringwood (1964), Brookins (1967), Nixon and Hornung (1968), and Sobolev (1969).

Garnet. The garnet structure contains a six-coordinated site usually occupied by trivalent ions and an eight-coordinated site usually occupied by divalent ions. These sites permit a wide range of ion substitutions and there are a large number of garnet end-members. The end-member concept in garnets has a limited utility because substitutions in the six-coordinated site are not generally coupled to substitutions in the eight coordinated-site. Recalculation of garnet analyses into end-members leads to ambiguities because the results depend on the order of the calculation. A simple and unambiguous method of showing the compositional variation in kimberlite garnets is to plot the occupancy of each of these sites on a ternary diagram. The components of eight-coordinated site are Fe^{2+}, Mg, and Ca; Mn may be ignored or included with Fe^{2+} because its concentration is usually in the range 0.1–0.5 weight percent MnO. The components of the octahedral site are Fe^{3+}, Cr, and Al; Ti, which does form a coupled substitution, is ignored because its concentration is normally less than 0.5 weight percent TiO_2.

Figure 10 shows a plot of analyses of kimberlite garnets. The eight-coordinated site is predominantly occupied by Mg, but there are substantial amounts of Ca and Fe. There is very little Fe^{3+} in the octahedral site in any of these garnets, and a majority of them contain over 80 percent Al in this site. Nevertheless some are very rich in Cr, and one contains over 50 percent Cr in the octahedral site. Analyses of garnets from the lherzolite assemblage group closely in both diagrams (Fig. 10). Undoubtedly this reflects the reduced variance of the three-phase assemblage, but inasmuch as the number of analyses is small this relationship may be partly an accident of sampling.

Experiments described hereafter show that the observed Ca/(Ca+Mg) ratio of the garnets from lherzolite xenoliths is duplicated very closely by garnets crystallized in the synthetic system $CaSiO_3$-$MgSiO_3$-Al_2O_3 at high pressures. Apparently this ratio is not much affected by variation in equilibration conditions. However, the significance of the wide range in Cr in these garnets is not now understood. Similar Cr-rich garnets have been found as inclusions in diamond (Meyer and Boyd, 1970). As yet few phase studies at high pressures have been made with Cr_2O_3 as a component.

THE SYSTEM $CaSiO_3$-$MgSiO_3$-Al_2O_3

Phase studies on the joins $MgSiO_3$-$CaMgSi_2O_6$ and $MgSiO_3$-$Mg_3Al_2Si_3O_{12}$ have been used in the previous section to interpret compositional variations in kimberlite pyroxenes. Nevertheless, such application is only an approximation because the solid solutions of diopside and enstatite toward each other and toward garnet are interdependent. For example, the solid solution of diopside toward $MgSiO_3$ will be changed by solution of Al_2O_3 in the diopside, and similarly the solid solution of enstatite toward garnet will be changed by solution of $CaSiO_3$ in the enstatite. These relationships have been stressed by a number of authors, including O'Hara and Mercy (1963) and Banno (1965). O'Hara and Yoder (1967) have provided experimental data in support of the theoretical treatments.

The system $CaSiO_3$-$MgSiO_3$-Al_2O_3 (Boyd, 1970) models pyroxene-garnet relations in ultramafic rocks rather well. This ternary system contains the garnet join $Mg_3Al_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$ and the pyroxene join $MgSiO_3$-$CaMgSi_2O_6$ and illustrates the solid solutions between them. It also contains the pyroxene $CaAlSi_2O_6$, "calcium Tschermak's molecule" or CaTs for short, which is stable under limited conditions of high temperature and pressure (Hays, 1966; Hijikata and Yagi, 1967).

The ternary system fails to model the natural assemblages in that the natural pyroxenes and garnets show small but significant solid solutions toward Fe analogues. The garnets and diopsides may also contain considerable Cr_2O_3, and the diopsides normally show 10–20 mole percent solid solution toward Na pyroxene.

Within this system at high pressures, there is a three-phase field: enstatite+diopside+garnet. All three phases are parts of solid-solution series, but at a given temperature and pressure their compositions are invariant. Ideally we should like to know the compositional coordinates of this three-phase field as a function of pressure and temperature over the range in which natural garnet peridotites have equilibrated.

The present study provides such a determination for a single temperature and pressure, 1200°C and 30 kbar. These conditions were selected because pyrope is a stable phase and because previous work on binary joins that bound the ternary system indicated that the pyroxenes and garnets could be crystallized sufficiently coarse to permit analysis by electron probe. Determination of the subsolidus phase relations in a complex ternary system by optical and X-ray methods would be prohibitively time-consuming and much less accurate than the probe.

The results presented form a synthesis diagram. The various phase assemblages have been crystallized from glass with H_2O as a flux. Nevertheless the phase relations on the bounding joins $MgSiO_3-Mg_3Al_2Si_3O_{12}$ (Boyd and England, 1964) and $MgSiO_3-CaMgSi_2O_6$ (Davis and Boyd, 1966) were reversed within narrow limits at the same pressure and temperature by the same experimental techniques used in the present study. Hence it is believed that the phase relations shown are equilibrium relations. Reversing a ternary solid solution field is a considerably more complex problem than reversing a binary solvus and requires study of the phase relations at a variety of pressure-temperature conditions over which the solid solution fields change.

Phase relations. Equilibria within the system $CaSiO_3$-$MgSiO_3$-Al_2O_3 appear to be truly ternary at 1200°C and 30 kbar. Phase relations for the system as a whole are shown in Figure 11, and portions of this diagram showing the analytical data are expanded in Figures 12 and 13. Table 1 gives a list of abbreviations used in these figures and in the text, and Table 2 gives the electron-probe analyses of coexisting phases in runs on various bulk compositions. Experimental and analytical methods used in determining these phase relations are described in the appendix.

These phase relations are dominated by two intersecting solid solution fields, one along the join pyrope-grossularite and the other along the join diopside-CaTs. There are four invariant assemblages (three-phase fields)—two predominantly above the garnet join involving corundum, garnet, and clinopyroxene: and two below the garnet join involving (1) clinopyroxene, garnet, and wollastonite, and (2) clinopyroxene, garnet, and orthopyroxene.

The clinopyroxene solid solution "finger" (Di_{ss}) that extends from diopside toward CaTs pierces the garnet join interrupting the solid solution between pyrope and grossularite (Figs. 11, 12). CaTs is not a stable phase at 1200°C and 30 kbar, although it becomes stable at higher temperatures and lower pressures (Hays, 1966; Hijikata and Yagi, 1967). This solid solution terminates at a composition of

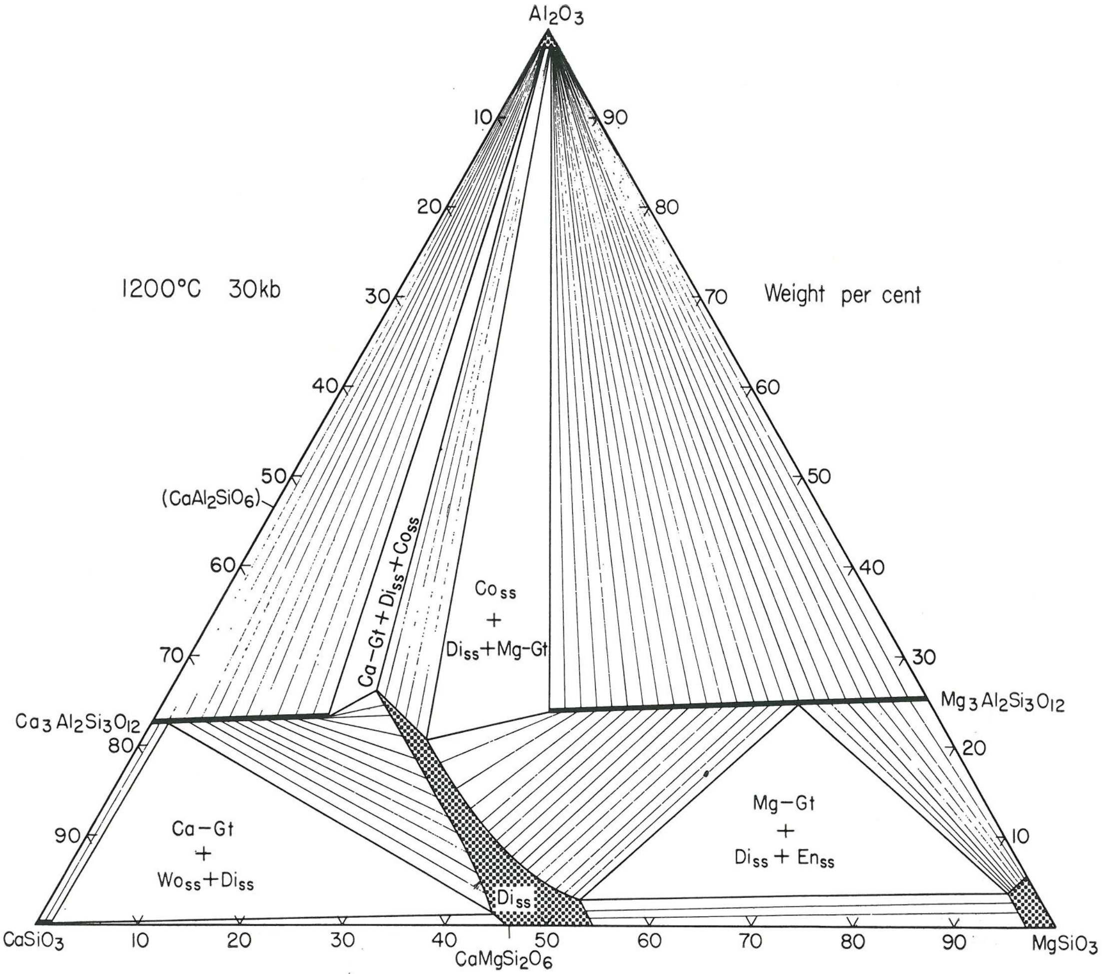

FIG. 11. Synthesis diagram for phase relations in the system $CaSiO_3$-$MgSiO_3$—Al_2O_3 at 1200°C and 30 kbar. Data points are shown in Figs. 12 and 13.

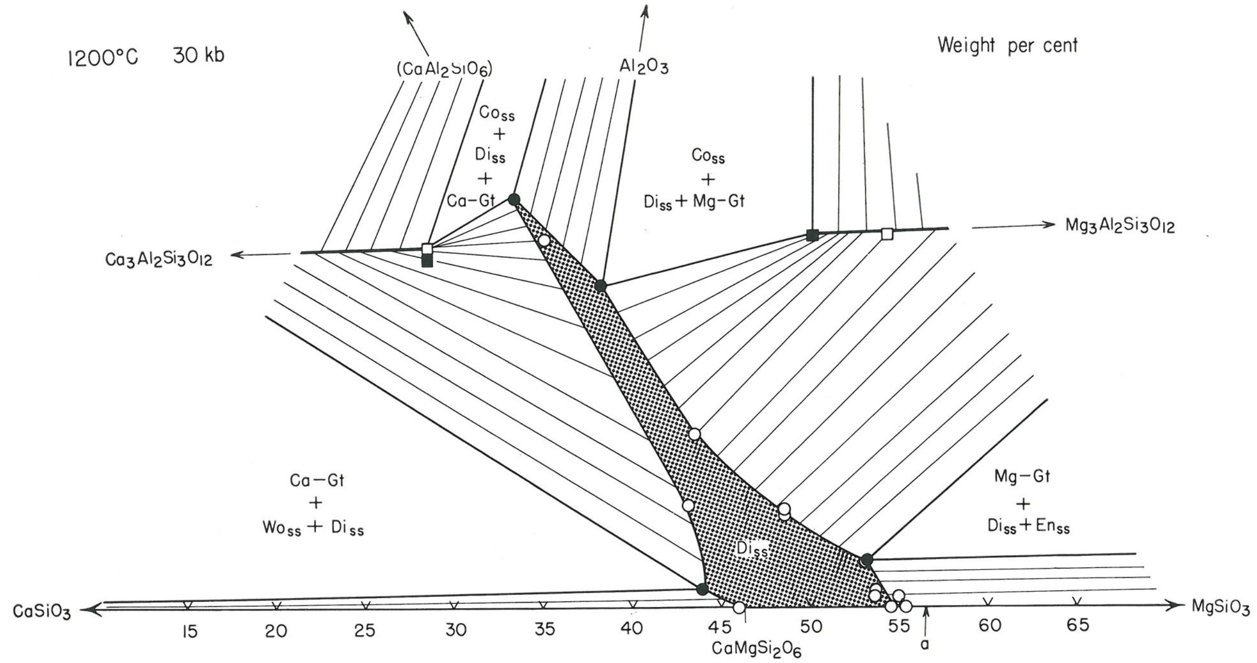

FIG. 12. A portion of the system $CaSiO_3$-$MgSiO_3$-Al_2O_3 at 1200°C and 30 kbar showing the solid-solution field for diopside. Open points represent analyses of phases in two-phase assemblages, and solid points are for phases in three-phase assemblages. Circles are pyroxenes, and squares are garnets. Point *a* is the Di(*en*) solvus in the system $CaMgSi_2O_6$-$MgSiO_3$ determined by Davis and Boyd (1966).

56 weight percent CaTs. Pyroxenes along the join $CaMgSi_2O_6-CaAlSi_2O_6$ also dissolve $MgSiO_3$, the solubility limit toward $MgSiO_3$ decreasing as the alumina content increases. There appears to be little or no solid solution from this join toward $CaSiO_3$, reflecting the fact that the large Ca ion will not readily enter the M_1 site. Four of the five analyses for pyroxenes in equilibrium with phases more Ca-rich than compositions on the join $CaMgSi_2O_6-CaAlSi_2O_6$ lie exactly on the join, within reasonable analytical uncertainty. The clinopyroxene in the three-phase field $Di_{ss}+Wo_{ss}+Ca-Gt_{ss}$ does show some solid solution toward $CaSiO_3$, but this result is somewhat suspect. Compositions within this three-phase field are extremely difficult to grow sufficiently coarse for probe analysis. The analyses were necessarily carried out on very fine-grained samples in which there is a particular danger of unobserved intergrowths.

Solid solution along the garnet join is interrupted in the interval 23–51 weight percent (25–54 mole percent) pyrope by the clinopyroxene solid solution field. At 20 kbar and 1300–1400°C, CaTs is a stable phase and a solid solution field extends all the way from diopside to CaTs (Clark, Schairer, and de Neufville, 1962). When CaTs breaks down to grossularite+corundum with increasing pressure (14 kbar at 1200°C; Hays, 1966) the solid solution field along the join $CaAlSi_2O_6-CaMgSi_2O_6$ begins to retreat toward diopside. At 30 kbar it still pierces the garnet join, but at pressures above 30 kbar it will retreat below the garnet join and a complete solid solution between pyrope and grossularite will eventually become stable.

Present data on the garnet join are seemingly in conflict with earlier work by Chinner, Boyd, and England (1960), who reported a complete solid solution between pyrope and grossularite at 1250°C and 30 kbar. However, they made a −8 percent friction correction to their pressure measurements, whereas those given here are reported as load pressures. Using the load pressure convention, Chinner *et al.* made their runs at 32.3 kbar. It is possible that only a small increment of pressure above 30 kbar is sufficient to stabilize the garnet join.

→

FIG. 13. Portions of the system $CaSiO_3$-$MgSiO_3$-Al_2O_3 showing the analytical data. (A) The garnet join with weight percentage of Al_2O_3 plotted against the weight ratio Mg/(Mg+Ca) in order to expand the Al_2O_3 axis. Vertical bars on the points are error limits of ±2 relative percent Al_2O_3. (B) The wollastonite solid solution field. (C) The enstatite solid solution field. Point *b* is the En(*wo*) solvus in the system $CaMgSi_2O_6$-$MgSiO_3$ determined by Davis and Boyd (1966), and point *c* is the En(*co*) solvus in the system $MgSiO_3$-$Mg_3Al_2Si_3O_{12}$ determined by Boyd and England (1964).

All the electron-probe analyses of garnets made in this investigation are plotted in Figure 13 with the coordinates weight percentage Ca/(Ca+Mg) and weight percentage Al_2O_3. With this type of plot the Al_2O_3 axis can be expanded and the fit of the garnet analyses to the pyrope-grossularite join can be examined. A majority of the analyses fall on the join within reasonable analytical uncertainty (Fig. 13), but there are a number that fall below the join; and if best-fit curves were drawn through all the analyses, the curves would lie below the join. Ringwood (1967) has shown that an extensive solid solution of garnet toward pryoxene develops at pressures on the order of 100 kbar. Present results might be taken as evidence of the onset of this type of solid solution, but the scatter in these results (Fig. 13) makes it seem more likely that the garnets in some runs incorporated minute inclusions of pyroxene that could not be seen and avoided during analysis.

There is an appreciable solid-solution field for rhombic enstatite that extends toward diopside and toward Mg-rich garnet. The solid solution toward garnet is considerably reduced from that which prevails at lower pressures and higher temperatures (Fig. 9 and text above). Solution of Al_2O_3 in the enstatite does not have a measurable effect on the Ca/(Ca+Mg) ratio, but the Al_2O_3 content of enstatite in equilibrium with diopside and garnet is significantly less than the Al_2O_3 content of enstatite in equilibrium with pyrope on the join $MgSiO_3-Mg_3Al_2Si_3O_{12}$ (Fig. 13).

TABLE 1. ABBREVIATIONS USED IN THIS PAPER

Di	Diopside, $CaMgSi_2O_6$
En	Orthorhombic enstatite, $MgSiO_3$
Wo	Wollastonite, $CaSiO_3$
Mg-Gt	Mg-rich garnet on the join $Mg_3Al_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$
Ca-Gt	Ca-rich garnet on the join $Mg_3Al_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$
CaTs	Ca-Tschermak's molecule, $CaAl_2SiO_6$
Co	Corundum, Al_2O_3
$wo_x en_y co_z$	Composition ($x+y+z=100$ wt %)
ss	Subscript denoting solid solution
En(*co*)	Notation indicating the solvus for the component Al_2O_3 in enstatite

The wollastonite and corundum show very limited solid solutions. Under the conditions of this study wollastonite (Fig. 13) dissolves 1–2 weight percent $MgSiO_3$ and 0.1–0.2 weight percent Al_2O_3. The corundum proved too fine-

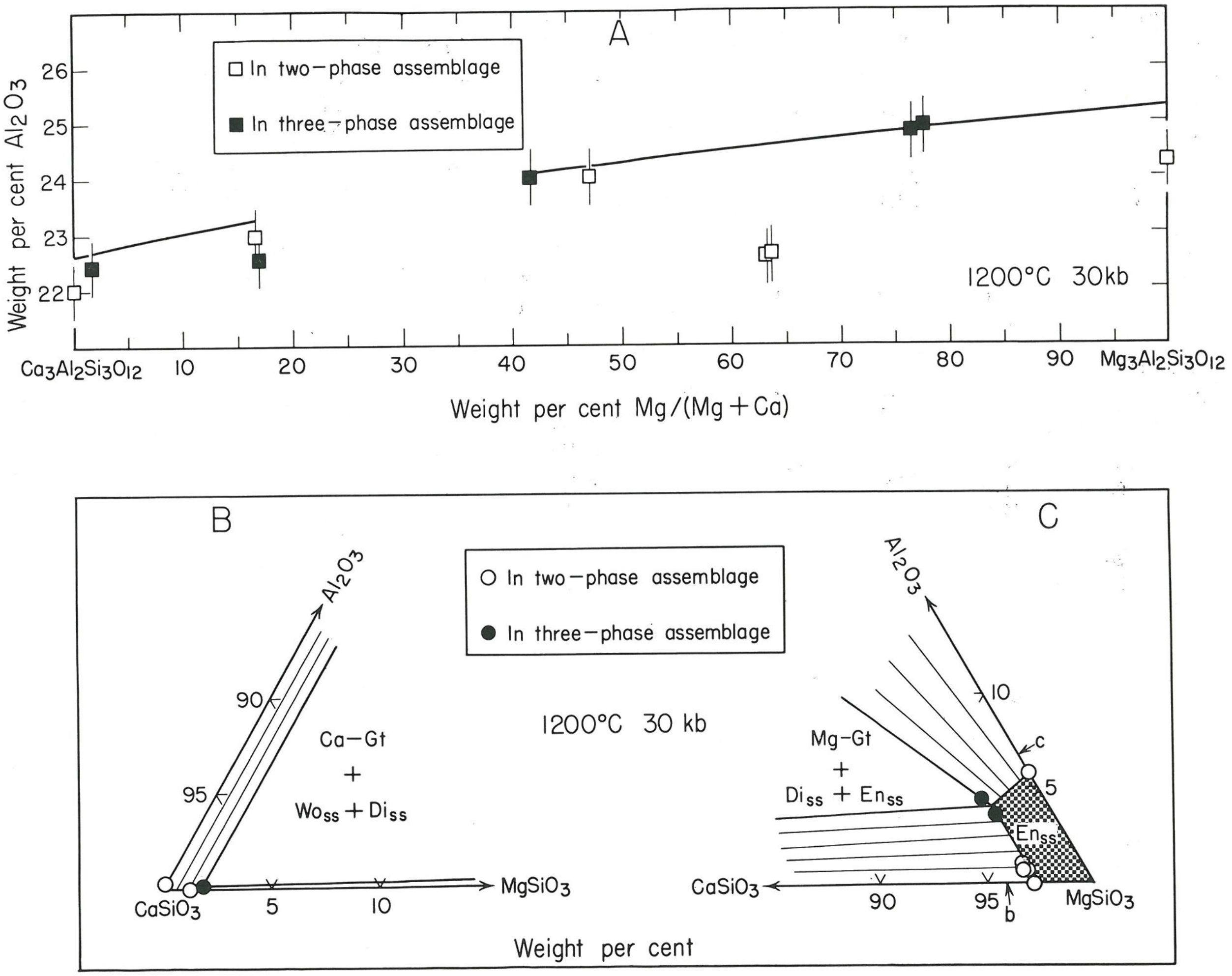

TABLE 2. ELECTRON-PROBE ANALYSES OF QUENCHED SAMPLES HELD 2–5 HOURS AT 1200°C AND 30 kbar

Run No.	Phase	Composition (Wt. %)[a]			
		$CaSiO_3$	$MgSiO_3$	Al_2O_3	Total
1	*Starting glass*	—	*90.0*	*10.0*	—
	Mg-rich pyroxene	—	94.9	5.9	100.8
	garnet	—	75.6	24.3	99.9
2	*Starting glass*	*21.5*	*78.5*	—	—
	Mg-rich pyroxene	2.9	99.3	—	102.2
	Ca-rich pyroxene	46.1	55.2	—	101.3
3	*Starting glass*	*28.4*	*71.6*	—	—
	Mg-rich pyroxene	2.6	98.8	—	101.4
	Ca-rich pyroxene	44.9	55.9	—	100.8
4	*Starting glass*	*76.8*	*23.2*	—	—
	wollastonite	96.2	1.2	—	97.4
	Ca-rich pyroxene	53.8	45.7	—	99.5
5	*Starting glass*	*94.7*	—	*5.3*	—
	wollastonite	97.8	—	0.2	98.0
	garnet	77.0	—	22.0	99.0
6	*Starting glass*	*19.7*	*78.4*	*1.9*	—
	Ca-rich pyroxene	45.5	52.8	0.7	98.9
	Mg-rich pyroxene	2.9	96.2	0.6	99.8
7	*Starting glass*	*32.3*	*66.6*	*1.1*	—
	Ca-rich pyroxene	45.0	55.2	0.7	100.8
	Mg-rich pyroxene	2.7	98.4	0.8	101.8
8	*Starting glass*	*25.9*	*71.9*	*2.3*	—
	Ca-rich pyroxene	45.6	53.0	1.1	99.7
	Mg-rich pyroxene	2.8	96.8	1.1	100.7
9	*Starting glass*	*39.5*	*48.7*	*11.9*	—
	Ca-rich pyroxene	48.6	45.6	6.3	100.5
	garnet	22.5	55.9	22.6	101.0
10[b]	*Starting glass*	*39.5*	*48.7*	*11.9*	—
	Ca-rich pyroxene	48.1	45.2	5.9	99.2
	garnet	22.8	56.1	22.6	101.5
11	*Starting glass*	*45.6*	*39.4*	*15.0*	—
	Ca-rich pyroxene	51.3	38.2	11.2	100.7
	garnet	33.9	43.0	24.0	100.9
12	*Starting glass*	*54.2*	*22.4*	*23.4*	—
	Ca-rich pyroxene	52.1	23.0	23.2	98.3
	garnet	59.6	17.0	23.0	99.6
13	*Starting glass*	*53.4*	*16.2*	*30.4*	—
	Ca-rich pyroxene	53.3	20.3	26.2	99.8
	garnet	60.8	17.6	22.5	100.9
	corundum	—	—	—	—
14	*Starting glass*	*46.6*	*29.9*	*23.7*	—
	Ca-rich pyroxene	50.9	27.6	20.5	99.0
	garnet	38.2	38.9	24.0	101.1
	corundum	—	—	—	—
15	*Starting glass*	*72.1*	*21.9*	*6.0*	—
	garnet	75.9	1.8	22.4	100.1
	Ca-rich pyroxene	53.7	44.0	1.1	98.8
	wollastonite	—	—	—	—
16	*Starting glass*	*83.8*	*12.1*	*4.1*	—
	wollastonite	97.8	1.8	0.1	99.7
	Ca-rich pyroxene	—	—	—	—
	garnet	—	—	—	—
17	*Starting glass*	*19.5*	*67.5*	*13.4*	—
	Ca-rich pyroxene	45.5	52.0	3.1	100.6
	Mg-rich pyroxene	2.9	93.8	4.5	101.2
	garnet	13.8	64.2	24.8	102.8
18	*Starting glass*	*30.0*	*63.0*	*7.1*	—
	Ca-rich pyroxene	45.7	52.0	2.8	100.5
	Mg-rich pyroxene	2.6	94.8	3.7	101.1
	garnet	13.0	63.9	24.9	101.8

[a] Nominal compositions are given for starting glass.

[b] Duplicate of previous run.

grained for accurate analysis, but in one case significant signals for Mg, Ca, and Si were obtained from a granule of corundum 5–6 μm in diameter. The corundum in this run was in the three-phase field $Co_{ss}+Di_{ss}+Ca-Gt$, and it appeared to contain about 1 percent $MgSiO_3$ and 2 percent $CaSiO_3$. Silicon is definitely present in the corundum, but the analysis was not of sufficient accuracy to make it certain that the composition of the corundum is in the plane $CaSiO_3$-$MgSiO_3$-Al_2O_3.

The effect of Al on the solid solution of enstatite in diopside is of particular interest. O'Hara and Mercy (1963) and Banno (1965) have predicted in theoretical treatments that solution of Al_2O_3 in diopside would reduce its solid solution toward $MgSiO_3$. Phase relations determined in this study confirm their prediction. The extension of the clinopyroxene solid solution field toward $MgSiO_3$ decreases as the Al_2O_3 content increases. However, there is an inflection in this field boundary (Fig. 12) at 1200°C and 30 kbar such that aluminous diopside in equilibrium with enstatite and garnet has a Ca/(Ca+Mg) ratio that is only slightly larger than that of an Al-free diopside in equilibrium with enstatite on the join $MgSiO_3-CaMgSi_2O_6$. Specifically, diopside in the three-phase field $Di_{ss}+En_{ss}+Mg-Gt$ contains 3.0 ± 0.1 weight percent Al_2O_3 and has a Ca/(Ca+Mg) ratio of 0.43 ± 0.01 (mole fraction), compared with 0.42 ± 0.01 for diopside in equilibrium with enstatite on the join $MgSiO_3-CaMgSi_2O_6$. These results suggest that application of the pure Di(*en*) solvus to natural peridotites in which the pyroxenes contain only a few percent Al_2O_3 would be in error because of the effect of Al by an amount that is small in relation to other uncertainties.

O'Hara (1967) has proposed a provisional petrogenetic grid for peridotites containing the assemblage Ca-rich

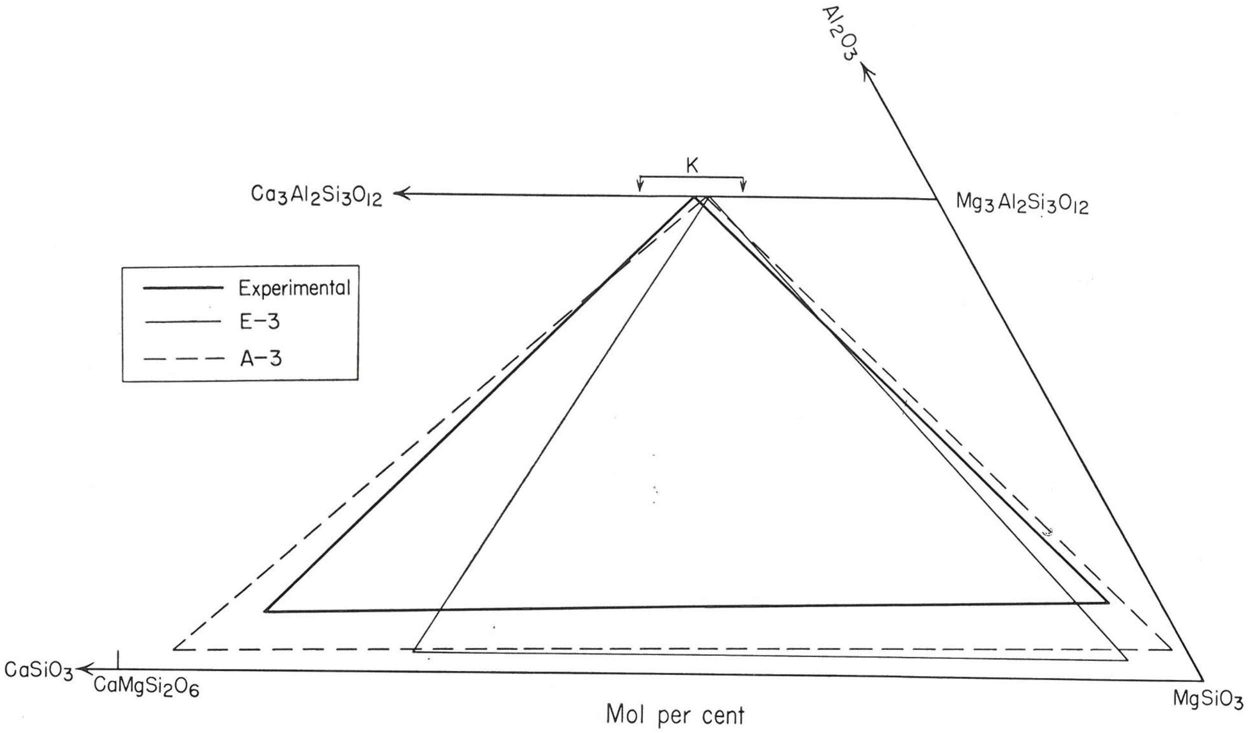

FIG. 14. A portion of the system $CaSiO_3$-$MgSiO_3$-Al_2O_3 showing the experimental determination of the phase field Mg-Gt+Di_{ss}+En_{ss} at 1200°C and 30 kbar together with analytical data for the pyroxenes and garnets of two lherzolite nodules. A-3, O'Hara and Mercy (1963); E-3, Nixon, Von Knorring, and Rooke (1963), Boyd (1969). The range of garnet compositions obtained in experiments by Kushiro, Syono, and Akimoto (1967) is shown as bracket *k*. The two natural garnets are assumed to lie on the join $Ca_3Al_2Si_3O_{12}$-$Mg_3Al_2Si_3O_{12}$. For the natural pyroxenes "Al_2O_3" $=0.5\{Al-Na[Al/(Al+Cr+Fe^{3+})]\}$, where Al, etc., are in atomic proportions.

pyroxene+Ca-poor pyroxene+"Al_2O_3-rich phase." This is based on the $MgSiO_3$ and R_2O_3 contents of the diopside; R_2O_3 contents are corrected for solid solution toward Na pyroxene. O'Hara's grid is constructed from various experimental data, which are considerably more complete where garnet is the "Al_2O_3-rich phase." The pressure-temperature-composition coordinates of the En_{ss}+Di_{ss}+Mg−Gt field in the present study (Fig. 11) fit O'Hara's grid reasonably well. Nevertheless, as more experimental data become available, it is likely that the Al_2O_3 or R_2O_3 content of enstatite will prove to be a more useful pressure sensitive parameter than the corresponding solid solution in diopside because natural enstatites contain virtually no alkalis and much less Cr_2O_3 than coexisting diopsides. These solid solutions toward Na pyroxene and Cr_2O_3 complicate the application of quantitative data from synthetic systems such as that described herein.

Comparison with Natural Assemblages. The three-phase field En_{ss}+Di_{ss}+Mg−Gt determined by experiment (Fig. 11) is plotted in Figure 14 along with analytical data for two natural three-phase assemblages from garnet-lherzolite xenoliths. Data for the E-3 nodule, which contains a subcalcic diopside and which is from the Thaba Putsoa pipe in Lesotho, are from Nixon, Von Knorring, and Rooke (1963) and Boyd (1969). The A-3 assemblage, which includes a calcic diopside, has been described by O'Hara and Mercy (1963).

Experimental data and analytical results for garnet in equilibrium with enstatite and diopside are remarkably concordant. Kushiro, Syono, and Akimoto (1967) have determined the cell dimensions of garnets coexisting with enstatite and diopside in the system $CaSiO_3$-Al_2O_3 crystallized at pressures in the range 18–96 kbar. They found a systematic variation of composition with pressure, ranging from 81 to 88 mole percent pyrope. This range spans the present experimental results and the analytical data for E-3 and A-3. Evidently the point of intersection of the three-phase field with the garnet join is not especially sensitive to variations in temperature and pressure.

The points of intersection of the three-phase fields (Fig. 14) with the solid solution fields for enstatite and diopside show less concordance. The synthetic pyroxenes crystallized with garnet at 1200°C and 30 kbar contain considerably more Al_2O_3 than their natural counterparts. This difference can be interpreted as due to a lower equilibration pressure, higher equilibration temperature, or both. Results for $MgSiO_3$-Al_2O_3 (Fig. 9) show that increase of pressure or decrease of temperature greatly reduces the solubility of Al_2O_3 in enstatite in equilibrium with pyrope, and the effect for diopside should be analogous.

The large difference in Ca/(Ca+Mg) ratio for the calcic (A-3) and subcalcic (E-3) diopsides is not understandable in terms of present phase studies.

CONCLUSION

Analytical studies of pyroxenes and garnets from ultramafic xenoliths and from xenocrysts in kimberlite have revealed a number of characteristics and variabilities. Enstatite shows only slight solid solution toward diopside and also shows little solid solution toward garnet. Kimberlite diopsides contain more R_2O_3 than the enstatites, but the R_2O_3 is primarily in the form of a solid solution toward Na pyroxene (10–20 mole percent), and the solid solution toward garnet is small. The diopsides have Ca/(Ca+Mg) ratios that reveal a wide range in solid solution toward $MgSiO_3$ but with a pronounced bimodal distribution. Most of them are calcic diopsides with restricted $MgSiO_3$ contents, but a small fraction of them form a well-defined subcalcic group. Mg, Ca, and Fe^{2+} in the eight-coordinated site in kimberlite garnets have concentrations that group closely around 74:12:14 (atomic percent); the six-coordinated site is predominantly occupied by Al, but there is a wide range toward Cr.

From phase studies at high temperatures and pressures many of these characteristics can be understood. The reduced solid solution in the pyroxenes toward garnet is reflected in experimental results for the system $MgSiO_3$-$Mg_3Al_2Si_3O_{12}$ at pressures up to 60 kbar. Rhombic enstatite has been shown to dissolve very little $CaSiO_3$ at any temperature in studies of the system $MgSiO_3$-$CaMgSi_2O_6$. New results for the system $CaSiO_3$-$MgSiO_3$-Al_2O_3 support the indications of earlier work on binary systems and very closely duplicate the Ca/(Ca+Mg) ratio for Mg-rich garnet in equilibrium with diopside and enstatite. This ratio appears to be little influenced by variations in equilibration temperature and pressure.

Experimental studies of systems with Cr_2O_3 as a component will be required to understand the large variability in concentration of this oxide in garnet and, to a lesser degree, in diopside. The pronounced bimodal distribution in Ca/(Ca+Mg) in the diopsides remains a puzzle that may be clarified by study of the system $MgSiO_3$-$CaMgSi_2O_6$ at pressures above 30 kbar.

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APPENDIX

EXPERIMENTAL AND ANALYTICAL METHODS

Experimental runs in the system $CaSiO_3$-$MgSiO_3$-Al_2O_3 were made in solid-media, piston-cylinder apparatus (Boyd and England 1960). These runs were brought to temperature at pressure and held for 2–5 hours before quenching. The pressure of these experiments is a "load pressure" calculated from the oil pressure on the hydraulic ram and the known piston areas; it has not been corrected for frictional or other effects. Temperature was measured with Pt/Pt10Rh thermocouples, and the listed temperature is not corrected for the effect of pressure on thermal e.m.f. The accuracy of pressure measurement is believed to be within ±5 percent (Boyd *et al.*, 1966), and the precision of temperature measurement is within ±10°C.

Starting materials were prepared as powdered glass and were moistened with small amounts of H_2O The catalytic effect of H_2O is needed to provide a sufficiently coarse grain size to permit electron-probe analysis, but the amount is critical and difficult to measure. Too much H_2O produces partial or complete melting, and with too little the grain size of the run products is too fine. Breathing on the powdered glass in an agate morter often works well if the humidity in the laboratory is not too low. If the humidity is low it is usually more successful to moisten the powder and allow it to dry until the particles will barely cake. The moistened glass is loaded in platinum capsules with tight, but not welded, lids and the H_2O is gradually driven off during an experiment. With this technique pyroxenes and garnets with a grain size of 50 μm or more are sometimes obtained, but the grain growth is highly erratic. Over 50 runs were made in this investigation and of these only 18 proved satisfactory for electron-probe analysis (Table 2). These were broken into chips mounted on glass slides in epoxy, and polished to as thin a section as practical.

It is sometimes very difficult to distinguish individual grains in these runs during electron-probe analysis. Use of transmitted light is helpful if the section is sufficiently thin. Small differences in crystal habit, cleavage, relief, and cathodoluminescence were also employed. Usually a dozen or more grains of each phase in each assemblage were analyzed for Ca, Mg, and Al with reference to a single standard. The standard used was a glass prepared by J. F. Schairer with the composition 65 percent $CaMgSi_2O_6$-35 percent $NaAlSi_2O_6$. The beam was defocused to 15–20 μm on the standard glass to avoid volatilization of sodium. Analyses were run with a specimen current of about 0.02 μA to enhance resolution. Output was read with a card punch and was processed by computer programs described by Boyd, Finger, and Chayes (1969). An addition to program ABFAN converted the Ca and Mg analyses to $CaSiO_3$ and $MgSiO_3$ and formed a total with Al_2O_3. Thirty-seven of the forty analyses of individual phases total between 98.0 and 102.0, and the remaining three are only slightly outside these limits (Table 2).

The analytical techniques used in this study have been shown to yield an accuracy within ±2 percent of the amount of a major element present in a relatively coarse-grained sample (Boyd, 1969). The fine-grained run products recovered in these experiments are inherently more difficult to analyze, but the reproducibility and internal consistency of a majority of the results shown in Figures 12 and 13 are within error limits of ±2 relative percent. The size of the data points in Figures 12 and 13 (B and C) corresponds to a relative error of ±1 percent for a composition in the center of the ternary.

The procedure of analyzing twelve or more grains of each phase appears to have provided a representative as well as reproducible average in spite of inhomogeneities in most cases. However, runs for aluminous compositions in the two-phase field $Di_{ss}+En_{ss}$ consistently yielded pyroxenes with less Al_2O_3 than the starting compositions (Table 2, runs 6, 7, and 8). The discrepancy is small, but it is clearly larger than the analytical uncertainty. There seems to be no possibility of loss of Al_2O_3 during these experiments, and the compositions of the starting materials (glass) were confirmed by probe analysis. X-ray study of a duplicate of run 8 showed essentially enstatite and diopside with a possible trace of forsterite. The forsterite, if indeed present, coubld have been produced by solution of SiO_2 in the escaping vapor phase. In any event, the presence of forsterite does not affect the equilibria between the pyroxenes, nor will it contain significant Al_2O_3.

The explanation for this discrepancy may be a zoning in Al_2O_3

content with grain size produced by minor melting in the early stages of a run when the H_2O pressure was at a maximum. The liquidus slopes away from the pyroxene join (O'Hara and Yoder, 1967; Boyd and England, 1964) so that Al_2O_3 would be concentrated in the liquid. The coarsest grains (which were those probed) would probably be those that crystallized early in a run when (hypothetical) liquid was present, and they would be depleted in Al_2O_3.

In other portions of the diagram tie lines joining analyses of two-phase assemblages pass through the bulk compositions within reasonable error limits (Table 2, runs 9, 10, 11, and 12).

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