

Part or all of enstatite may be dissolved in omphacite to make a complex clinopyroxene solid solution. In the present experiment the mole ratio of potassic richterite and garnet is nearly 1:1; potassic richterite is still present after the run, however, probably because of incomplete reaction or the effect of solid solution. Because of the fine-grained nature of the products, electron-probe analysis was not successful in determining in detail the compositions of pyroxene phases. The present experiment suggests that in the presence of garnet, potassic richterite reacts to form phlogopite and clinopyroxene or clinopyroxene + orthopyroxene. In the presence of spinel, potassic richterite may also react to form phlogopite, clinopyroxene, and forsterite. Potassic richterite and Ca-Tschermak's pyroxene component are also isochemical with phlogopite + omphacite. The phlogopite + diopside assemblage is stable in a wide pressure range, as shown elsewhere in this report, and the phlogopite + clinopyroxene (omphacite) assemblage would also be stable in a wide pressure range. It is suggested, therefore, that potassic richterite is not stable in the presence of garnet, spinel, or aluminous pyroxenes. The alumina content of diopside from the Wesselton nodule is only 0.71 wt %. To conclude, potassic richterite would not be expected to occur in eclogites and garnet- or spinel-bearing peridotites under equilibrium conditions. To the best of our knowledge it has not been found in rocks of this type occurring in kimberlite. Potassic richterite may, however, occur in alumina-poor pyroxenites and peridotites or in the rocks in which K is in excess over Al and is still present after forming phlogopite and/or other potassium minerals (e.g., K-feldspar and leucite). The occurrence of potassic richterite in the Wesselton nodule is explained by the presence of excess K over Al.

POTASSIUM CONTENTS OF SYNTHETIC
PYROXENES AT HIGH TEMPERATURES
AND PRESSURES

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Electron-probe analyses of presumed upper-mantle materials, in particular kimberlite nodules, have revealed that olivines, garnets, and orthopyroxenes in general contain <30 ppm potassium and hence do not play an important role in the distribution of potassium in the upper mantle. The K content of clinopyroxenes is considerably larger and is crucial when considering the production of basaltic liquids with K contents varying from 0.05 to 1.5%.

Garnet peridotites, such as those found in kimberlites, are often assumed to be the dominant rock type present in the upper mantle. Chrome diopsides from these nodules generally contain on the order of 100 ppm K or less. The highest concentrations measured to date by electron-probe analysis have been observed in two subcalcic diopsides (Boyd, *Year Book 66*, pp. 331-334); concentrations of 280 and 340 ppm K in these two pyroxenes have been measured in this study. Even allowing for 15% modal abundance for diopsides in garnet peridotite, the K content of the resultant assemblage does not satisfactorily account for the high K contents of alkali basalts, provided at least 1% direct partial melting is involved in the production of the basalt.

Potassium contents of eclogitic omphacites from African kimberlites are more difficult to interpret. Electron-probe analyses given elsewhere in this report demonstrate that the K distribution of omphacites is apparently bimodal, with some containing 20-150 ppm K and others 800-1400 ppm K. The comments expressed above with respect to the diopsides obviously apply to the low K omphacites. The K content of the second group is larger than expected, however,

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and is difficult to explain on crystal-chemical grounds. It is clear that the presence of clinopyroxene with K contents of this order as an upper-mantle phase would be important for controlling the distribution of K in basaltic liquids. Hence, it appeared desirable to seek confirmation for this feature.

We have attempted to determine experimentally the amount of K that could enter the clinopyroxene structure under upper-mantle conditions by reacting together, at high temperatures and pressures, various clinopyroxenes and potassium-rich phases and measuring the potassium content of the resultant pyroxenes by electron-probe analysis. The experiments were made in the pressure range 15 to 32 kb with a piston-cylinder type apparatus similar to that designed by Boyd and England (1960). Sealed Pt tubes were used for the hydrous runs. The starting materials are mechanical mixtures of the following materials: synthetic pure diopside made by Hytönen and Schairer; a mixture of phlogopite composition consisting of forsterite, quench forsterite, and glass; a mixture crystallized at 1 atm from a glass of composition anorthite 50 forsterite 50 (mole %); a natural omphacite from Kaminaljuyu, Guatemala, originally described by Foshag (1957), with a composition close to diopside 45 jadeite 55 (mole %) (Clark and Papike, 1968); and a natural potassic richterite from Wolgidee, Australia, which is similar in composition to that analyzed by Wade and Prider (1940) and is described elsewhere in this report (see Table 17, No. 1).

In all the hydrous runs, diopside and omphacite were recrystallized to euhedral or subhedral crystals even at subsolidus temperatures. During the electron-probe analysis for K the other two spectrometers were set for Ca and Mg, and comparison of the starting materials and reactants indicated the recrystallization of the clinopyroxenes. Additional measurements for Na also revealed the nature of the pyroxenes formed. Phlogo-

pite occurs as hexagonal plates forming thick books; when glass is present, however, it often appears as feathery crystals, believed to be quench crystals. Richterite that had been ground finely was also recrystallized to relatively large, euhedral or subhedral crystals. Because of recrystallization in the presence of excess vapor, equilibrium is believed to have been attained in the hydrous runs. In the anhydrous run made for the 1:1 mixture of diopside and phlogopite composition, the temperature was raised above the solidus to secure equilibrium.

A great deal of difficulty has been experienced in making the electron-probe measurements. The small size of the reaction products necessitated the use of a 1–2 μm electron beam and low sample current (0.025 μa), with resultant low intensity. The main problem has, however, been caused by the presence of minute inclusions and intergrowths of these crystals with K-rich phases (phlogopite and glass), frequently resulting in anomalously high K contents for apparently clear clinopyroxene grains. Consequently several runs have been discarded, and only those measurements in which a fair amount of consistency has been established are reported here. Particular care has been taken in making background measurements, often by using the pure starting materials, which were always mounted together with the reaction products. It is to be noted that the results have been corrected only for background and drift, but it is believed that they are accurate to within 10–20% of their true values; this level of accuracy is adequate for present purposes. A detailed account of the technique used will be given elsewhere.

The assembled data are listed in Table 18. It is immediately apparent that regardless of variation in mineral assemblage, temperature, pressure, and water content, the amount of K that has entered the clinopyroxene reaction products is small, <150 ppm. Even where clinopyroxene has crystallized directly

TABLE 18. Potassium Contents of Synthetic Clinopyroxenes and Garnets

Reactants	P, kb	T, °C	Duration, hours	H ₂ O %	Products	K in Clinopyroxene, ppm
Di + Anhy Phl (1:1)	15	1100	4	11.4	Di, Fo, Phl, Gl, gl	140
	30.5	1150	3½	13.1	Di, Fo, Phl, Gl, gl	90
	32	1000	4	4.6	Di, Phl, gl	70
	21	1450	2¼	...	Di, Fo, Gl	140
Omph + Anhy Phl (1:1)	25	1000	5½	5.0	Omph, Phl	110
	(2:1)	25	1000	6	Cpx, Phl, Fo, gl	50
	(1:1)	26.5	1050	4	Cpx, Phl, Gl	<50
		30	1100	3	Cpx, Fo, Phl, gl	50
Rich + An ₁ Fo ₁ (2:1)	20	1000	3	4.7	Rich, Phl, Cpx	120
Rich + Di (1:1)	24	1000	2	10.4	Rich, Cpx	<50
						K in garnet, ppm
Anhy Phl + An ₁ Fo ₁ (1:4)	30	1100	3	12.6	Gt, Cpx, Phl	<50
Phl*	70	1500	¾	...	Gt, Phl, q-Phl, X	<100

* Run prepared by Kushiro, Syono, and Akimoto (1967).

Abbreviations: Di, diopside; Anhy Phl, anhydrous phlogopite composition; Phl, phlogopite; Fo, forsterite; Gl, glass; gl, glass balls considered to be quenched vapor; Omph, omphacite; Cpx, clinopyroxene solid solution; Rich, potassic richterite; Gt, garnet; An₁Fo₁, crystalline mixture of anorthite and forsterite (1:1 by mole) = pyrope-grossular (2:1 by mole); q-Phl, quench phlogopite; X, unknown phase.

from liquid under anhydrous conditions and in the absence of phlogopite, nearly all the K has remained in the liquid, as measured by the K content of ~13% in the glass. At this stage it is not clear to what extent variations in temperature, pressure, and sodium content affect the substitution of potassium. These results seem in accord with the natural diopsides and low K omphacites previously discussed, and no experimental evidence has been found to explain the presence of 1000–1500 ppm K in omphacite. The most likely explanation appears to be that these high K contents are due to the presence of sub-microscopic intergrowths of amphibole in the omphacite structure, as suggested by J. J. Papike (personal communication, 1968) on the basis of X-ray studies. This possibility has important implications regarding the genesis of eclogites and basaltic lavas, and requires further confirmation. In the runs with amphibole and pyroxene no reaction has occurred between these minerals.

Also given in Table 18 are measurements made on garnets produced in two

runs. Potassium was not detected in either one. One of the runs had previously been analyzed with an electron probe, and up to 5.8% K was reported in the garnets (Kushiro, Syono, and Akimoto, 1967b). The original electron-probe section was available, and further study showed that the earlier analysis was in error. The discrepancy is most likely due to the beam overlapping high K mica in the original analysis. During the analysis of this section, one of the breakdown products of phlogopite was found to have a very high potassium content (phase X in Table 18). Semiquantitative analysis indicates that this phase has on the order of 29% K₂O and 32% MgO but an anomalously low SiO₂ content of 1% or less. Unfortunately, the fine-grained nature of this phase and poor surface of the section prevented proper analysis, and it is not possible at this stage to identify this phase. It seems clear that clinopyroxenes and garnets will not accept sufficient potassium in their structures, even at high temperatures and pressures, to provide that required to form basalt by simple partial

melting. In this case, the rocks that are parental to basalt must contain potassium-rich phases such as phlogopite and/or K-rich amphibole.

HYDROUS SYSTEMS

PHLOGOPITE-H₂O-CO₂: AN EXAMPLE OF THE MULTICOMPONENT GAS PROBLEM

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The study of phlogopite-H₂O by Yoder and Kushiro (1969) revealed extensions of the stability field of phlogopite in the absence of a gas phase and documented the existence of new melting relationships of hydrous phases where gas is absent. It was suggested that melting in the mantle was best approximated by gas-absent conditions rather than gas-present conditions because of the belief that the H₂O content of the mantle was very small and was mainly in hydrous minerals.

Many rocks contain other potentially gaseous components in addition to water, and it is pertinent to investigate the effects of these components on the melting behavior of hydrous minerals. For example, excluding those minerals in rock fragments adventitiously incorporated, the rock kimberlite consists primarily of olivine, phlogopite, and calcite. The presence of the latter two minerals implies H₂O and CO₂ in the magma if such existed. Inclusions in olivine from some nodules in kimberlite contain both liquid and gaseous CO₂, as well as H₂O (Roedder, 1965, p. 1760, 1764). The effect of CO₂ on the melting of phlogopite is, therefore, relevant to the general problem of melting under conditions where the H₂O pressure is less than the total pressure.

Phlogopite-H₂O

The join K₂O·6MgO·Al₂O₃·6SiO₂·H₂O was first restudied in the more H₂O-rich compositions (Fig. 22), following the experimental procedures of Yoder and Kushiro (1969). The boundary be-

tween the forsterite (Fo) + liquid (L) + gas (G) region and the Fo+G region was delineated for $P=10$ kb and $T=1225^{\circ}\text{C}$. The criterion was the presence or absence of interstitial glass, which was presumed to represent in part the more siliceous liquid phase distinct from glass spheres believed to represent a portion of the less siliceous gas phase. The relations deduced from these data are shown in projection on the plane leucite:kalsilite (1:1 mole)-forsterite-H₂O. Only the gas compositions in the G region are believed to lie on the plane. The ratio of dissolved silicate to H₂O in the less siliceous gas in the Fo+L+G region appears to be about 1:1 by weight, whereas the ratio of silicate to water in the more siliceous liquid phase was previously determined to be about 4:1. Partial confirmation of the H₂O content of the more siliceous liquid is obtained from an examination of the inclusions in the larger forsterite crystals. Several types of inclusions were observed, which contained the following phases after quenching to room temperature and an undetermined pressure.

Most of the inclusions consisted of a glass with a very low index of refraction, containing a globule of liquid in which was suspended a small gas bubble in constant thermal motion. The relations in an exceptionally symmetrical inclusion from the Fo+L+G region are shown in the photograph of Plate 1A. Assuming that the inclusion is circular in cross-section, was entrapped at the conditions of the experimental run, and is solely representative of the total fluid phase, the volume proportions of silicate to H₂O can be calculated, neglecting mutual solubility at containment conditions and diffusion through the forsterite crystal. The silicate:H₂O is approximately 56:44 by volume and is approximately 74:26 by weight. In the light of the large possible errors, the agreement with the composition of the more siliceous liquid phase estimated by construction is surprising.