MELTING OF A HYDROUS PHASE: PHLOGOPITE

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ABSTRACT. The upper stability limit of phlogopite has been studied up to 37.5 kb under both gas-present and gas-absent conditions. Reexamination of the curves about the invariant point involving phlogopite (Ph), forsterite (Fo), orthorhombic kalsilite (Ok), leucite (Lc), liquid (L), and gas (G) at about 1160°C and 1 kb indicates that the alleged "breakdown" of phlogopite occurs according to the reaction Ph + G = Fo + Ok + L in the presence of a gas phase and not as a result of Ph → Fo + Ok + L + G. Under gas-absent conditions phlogopite melts incongruently according to the reaction Ph → Fo + Lc + Ok + L up to about 1.7 kb, and then the reaction becomes Ph → Fo + L as the result of a singular point relationship.

The new data indicate that the stability field of phlogopite is greatly expanded in the gas-absent region. Melting of phlogopite in that region is considered analogous to the partial melting of a hydrous parental assemblage in the mantle or lower crust. The liquid generated in the gas-absent region may increase or decrease its H_2O content with increasing temperature, depending on the initial amount of hydrous mineral. The low-H_2O content of liquids in the gas-absent region is comparable to those predicted from field observations. The H_2O content of liquids in the gas-present region is greatly in excess of that believed to exist under the conditions of magma generation.

The highly alkaline character and H_2O content of the liquids in equilibrium with phlogopite, the incongruent melting relationship of phlogopite to forsterite and liquid, and the high-pressure and high-temperature stability of phlogopite have important bearing on the origin at kimberlite.

INTRODUCTION

Present interest in phlogopite arose because of its key role in the formation of kimberlite and its unique chemistry which provides a source of not only potassium but water among the possible mantle minerals. Potassium is essential to heat production and to the generation of the alkali igneous rocks. Water is the obvious propellant in explosive vulcanism and plays a major role in the calcalkaline magma trend (Yoder, 1968). In addition, it contributes in an indirect way to the heat production problem by bringing about drastic lowering of the temperature of beginning of melting.

The major minerals of the mantle—olivine, orthopyroxene, clinopyroxene, garnet, and spinel—are essentially anhydrous except for possible hydrogarnet-type substitution in garnet and pyroxene. There is a growing list of hydrous minerals stable at upper mantle pressures, and phlogopite is one of the most common. Knowledge of the kinds of hydrous minerals in the mantle aids in making estimates of the H_2O content of the mantle. However, it has been noted that the exact H_2O content of the mantle is not really vital; what is important is the H_2O content of the partial melts generated in the mantle (Yoder, 1965). Most experiments bearing on the H_2O content of H_2O-saturated magmas have led to values that appear to be well in excess of those deduced from field studies. Whereas a few percent H_2O is believed to exist in the magma at generation, melting of common anhydrous silicates in the presence of an *excess* of H_2O indicates 10 to 20 percent H_2O dissolved in the liquid at relevant pressures.

The purposes of the present experiments were to (1) evolve some understanding of the melting characteristics of a hydrous phase, especially one believed to be essential in the mantle, in both the gas-present and gas-absent regions, (2) attempt to resolve the difference between laboratory and field estimates of the H_2O content of magmas, (3) provide detailed information on the melting of phlogopite as a principal phase in the formation of kimberlite, and (4) examine the factors that may have led to the wide divergence of results on the upper stability of phlogopite.

EXPERIMENTAL TECHNIQUES

Starting materials.—The anhydrous phlogopite composition, $K_2O \cdot 6MgO \cdot Al_2O_3 \cdot 6SiO_2$, was prepared from pure periclase (Baker's C. P. grade MgO), corundum (tabular alumnia, T61, Aluminum Company of America), and a crystallized glass, $K_2O \cdot 6SiO_2$, made from very pure $KHCO_3$ and purified quartz (Lisbon, Md.). The mixture was sintered and crushed at successively increasing temperatures with a final fusion at 1500°C. The final product consisted of forsterite, quench forsterite, and glass. Complete melting was not considered desirable because of the probable loss of alkali and silica at the excessively high liquidus temperature (>1600°C).[1] The liquidus temperature is not known with certainty because of alkali loss; the vapor pressure is presumably greatly in excess of 1 bar (Luth, 1967a). The fused mixture was used as the starting material in those runs marked "G1" in table 1.

Portions of the fused mixture consisting of forsterite and glass were further treated hydrothermally at 700°C and 5 kb in sealed platinum tubes for periods of 115 to 576 hours for the purpose of preparing synthetic phlogopite. The product was always all 1M (or 3T) phlogopite as determined by optical study and powder X-ray diffraction patterns. No residual or new growth of forsterite was observed. The synthetic phlogopite was dried at 110°C for 24 hours, and the composition was thereafter assumed to be exactly $KMg_3AlSi_3O_{10}(OH)_2$. The crystals consisted of well-formed, colorless, hexagonally shaped books varying up to 60 microns across and were no greater than 10 microns in thickness. This starting material was used in the experiments marked "Xtl" in table 1.

Sample containers and loading procedures.—All starting materials were held in sealed platinum tubes in the two types of apparatus. The tubes were cleaned in hot HCl to remove iron acquired during the extrusion process and were closed by crimping and electric-arc welding at one end. The tubes were then fired at 1250°C for half an hour to recrystallize the platinum, thereby sealing any remaining pin holes and rendering the metal more malleable for the final closure. The sample tubes used in the gas-media apparatus were 2 cm long, 3 mm outside

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[1] The liquidus temperature was reported as 1628°C by Yoder and Eugster (1954, p. 158) on the basis of unpublished work by Dr. J. F. Schairer in the system $KAlSiO_4$–$KAlSi_2O_6$–Mg_2SiO_4. These data were not included in his study of K_2O–MgO–Al_2O_3–SiO_2 (Schairer, 1954), because the data were considered suspect on the basis of alkali volatilization. Luth (1967a) confirmed Schairer's suspicions, using the sealed-tube technique, but did not report the data in his run tables (Doc. 9296, ADI Aux. Pub. Proj., Lib. Cong.).

diameter, and 2.5 mm inside diameter; those used in the solid-media apparatus were 6.5 mm long, 1.8 mm outside diameter, and 1.4 mm inside diameter. After the empty tube was weighed, distilled water was micropipetted into the wedge formed in the bottom of the tube. After the water content was determined by weighing, sufficient starting material was loaded, with frequent tapping to pack the powder, to achieve the desired ratio of water and starting material. The open end, cleaned with a wooden probe, was then crimped, peened, and electric-arc welded in a thin-jawed jeweler's vise, the jaws clamping the walls of the tube tightly together just above the level of the powder so no materials could escape during the brief welding process. The weight was again recorded to ascertain if any material had escaped during the welding process. Usually a negligible loss due to platinum volatilization was noted. In this manner known amounts of water[2] and starting material were contained during the run, and the weight was again recorded after the run to insure no loss of material. The weight percentage of water added in the tube is recorded for each run in table 1. Where no additional water was added to the starting material, the powder was firmly packed with a metal probe, and the crimp made as close to the powder as possible. Care was taken to avoid entrapment of powder in the crimped region where slag may form during the welding.

Apparatus.—The experiments at and below 10 kb were performed in an improved gas-media apparatus similar in basic design to that described by Yoder (1950). The experiments above 10 kb and up to 37.5 kb were carried out in solid-media apparatus similar to that designed by Boyd and England (1960).

In the gas-media apparatus the pressure is measured in the gas to 1 bar; however, uncertainties in the pressure scale itself and the calibration technique and variations in pressure attending temperature regulation suggest that the pressure is probably known only within ± 50 bars at 10 kb. The temperature, measured next to the center of the sample tubes housed in a 30 gram thermal block of platinum by a Pt:Pt 90 Rh 10 thermocouple, is believed to be accurate within ± 5°C. A new thermocouple cut from the same spools of wire was used each run to avoid errors attending contamination of the thermocouple on a previous run. Calibration of the annealed thermocouples at the synthetic diopside point was carried out at intervals by Dr. J. F. Schairer and found to be + 1 to 2°C, well within the reported accuracy.

In the solid-media apparatus the pressure on the sample is measured indirectly by means of the back pressure on the driving ram. No correction was made for piston friction in the essentially piston-out type procedure employed. The pressure was maintained to ± 0.1 kb. There

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[2] Experience in the diopside-water system (Yoder, unpub. data, 1952) has indicated that considerable hydrogen may be lost as a result of diffusion through the platinum tube wall at the high temperatures employed in the present system. No control or correction for this loss of effective H_2O was made herein. It is evident that consideration of this problem must be given in systems requiring runs over 2 hours in duration at temperatures above 1200°C.

may be as much as a 1 to 3 kb difference between the pressure calculated for the solid-media apparatus and the hydrostatic pressure measured in the gas-media apparatus (Richardson, Bell, and Gilbert, 1967, p. 394). This difference is not attributed solely to piston friction but to differences in shear strength and compressibility of the various parts surrounding the sample. The nature of the curves determined herein was relatively insensitive to errors of such magnitude, and therefore pressure differences between the two types of apparatus could not be evaluated. The temperature was measured by means of a new, annealed Pt:Pt 90 Rh 10 thermocouple in contact with one end of the platinum sample capsule. Recorded fluctuations during the runs indicate that the temperature is known only to $\pm$ 10°C. No corrections were made for the effect of pressure on the thermocouple. The sealed sample capsule was surrounded with a powder of crushable alumina to avoid excessive deformation of the capsule. The alumina was removed by hand-picking after the run; however, complete removal was not attempted if the weight was sufficiently close to the prerun weight. Water containment was checked primarily by visual observation on opening the capsule and by the nature of the phase assemblage.


A   Weight per cent   B
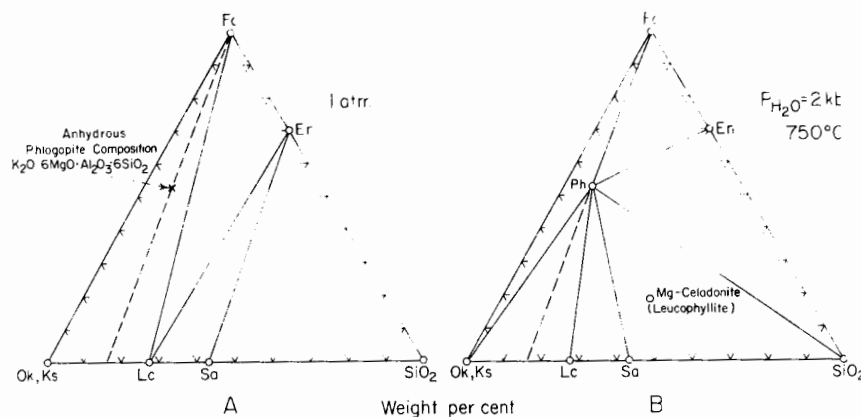
Fig. 1A. Plot of the anhydrous composition of phlogopite, $K_2O \cdot 6MgO \cdot Al_2O_3 \cdot 6SiO_2$, in the Fo–Ks–$SiO_2$ system. Abbreviations are defined in text except for Sa = sanidine. The joins are those determined at 1 atm by Schairer (1954). The same joins are probably valid at high pressures in the gas-absent region prior to melting with the exception of Lc-En, which is replaced by Fo-Sa at a pressure below 10 kb (Yoder and Tilley, 1962, p. 499, table 52). Luth (1967b p. 393, fig. 4, curve 30) schematically represented Fo + Sa → Lc + En at about 1000°C, essentially independent of pressure up to 3.5 kb. Although he did not specially study the reaction, none of his products include Lc + En, and Fo + Sa was obtained only below 960°C. The dashed line is the base of the projection presented in figure 5.

B. Plot of the phlogopite composition on the base plane Fo–Ks–SiO_2 projected from H_2O. The joins are those believed to be stable in the presence of a gas phase prior to melting in the system. The composition of Mg–celadonite is also projected into the anhydrous plane to indicate the direction of change of composition of a possible solid solution in phlogopite. Based on data of Luth (1967b) and Wones and Dodge (1968).

PLATE 1

$40\,\mu$
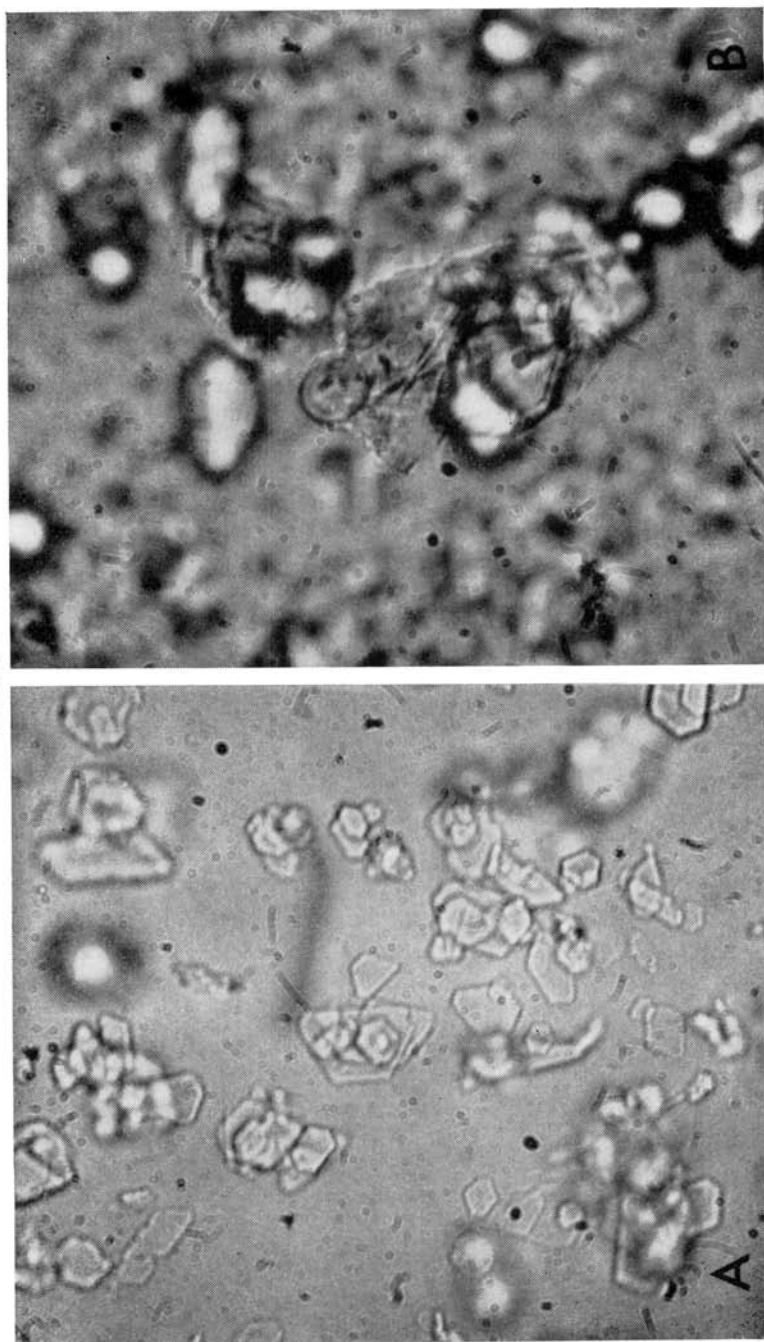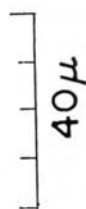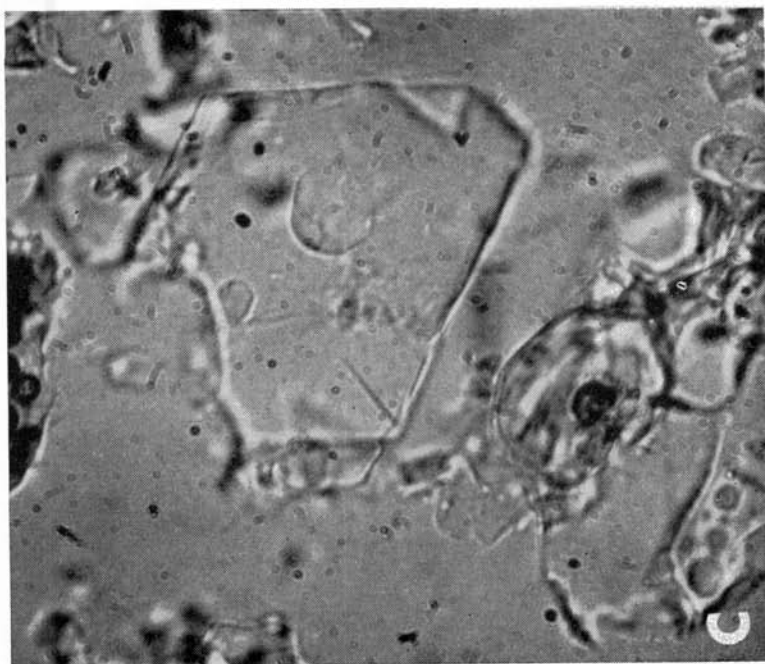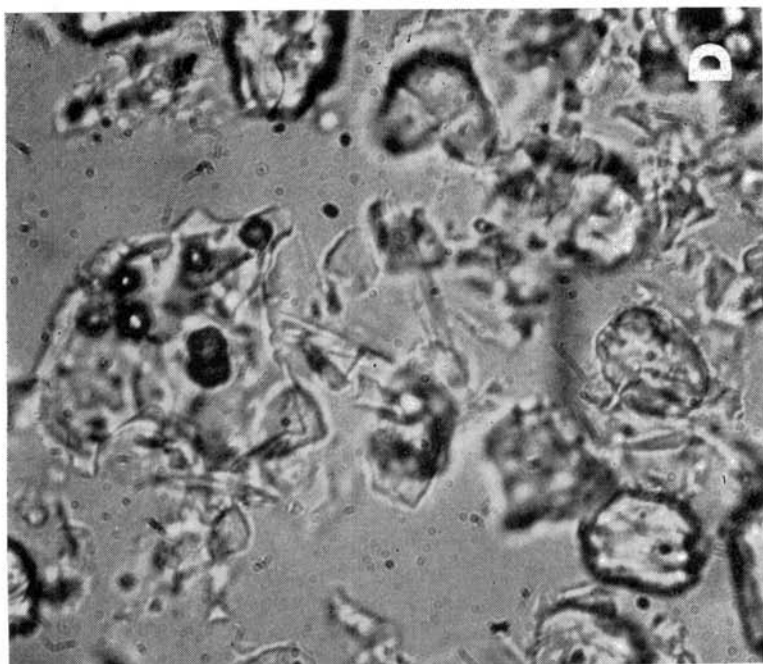
Phase identification.—Phases encountered were identified mainly with optical techniques and in some cases confirmed by powder X-ray diffraction. The platinum tubes were opened with considerable care so as not to disturb the contents, and the physical character of the charge was observed under a low-power binocular microscope (<80 X). Portions of the charge were then selected for detailed study under the petrographic microscope (<630 X). This procedure was necessitated by the common occurrence of quench products on the main charge and in the volume ocupied by the gas phase when present. The crystalline phases encountered include phlogopite (Ph), forsterite (Fo), leucite (Lc), kalsilite (Ks), and orthorhombic kalsilite (Ok). The compositional relationships of these phases to each other are displayed in figures 1A and 1B. In addition, the liquid phase (L) quenched to a glass but on some occasions was represented in part by quench crystalline products. The gas phase (G) quenched to a glass, some quench crystals, and water.

Phlogopite appeared as hexagonal plates, usually in thick books, when stable (pl. 1-A) and as minute acicular crystals, not uncommonly spherulitic, when formed during the quench (pl. 2-C and D). The judgment as to the presence of stable or quench crystals was usually easy to make except when the extremely thin and large diameter plates formed in the gas quench were present. The chemical composition of the phlogopite produced in the runs was not determined directly, and it was not possible to deduce from the assemblages whether that phase was stoichiometric or whether solid solution had taken place. Solid solution toward Mg–celadonite (Kardymowicz, 1960; Seifert, 1968), $KMgAlSi_4O_{10}(OH)_2$ (see fig. 1B) and toward $KMg_{2.5}Si_4O_{10}(OH)_2$ (Seifert and Schreyer, 1965, p. 1115) is possible as well as partial replacement of K^+ by H_3O^+, leading to a hydronium mica. Forsterite grows within synthetic phlogopite at high temperatures under hydrothermal conditions in the subsolidus region, presumably because of gas leaching, described in detail below.

PLATE 1

A. Faceted phlogopite grown from synthetic crystals + 20.0 wt percent H_2O at 1150°C, 10 kb, for 2 hours. Rare forsterite (lower left-hand corner, rounded high relief crystals out of focus) and glass balls (middle left side), representing part of the quenched gas, are also present. Interpretation: Ph + Fo + G.

B. Large grain in center of photomicrograph consists of a faceted forsterite crystal of high relief surrounded by glass containing needles of quench phlogopite. Grown at 1325°C, 10 kb, for 2 hours from synthetic phlogopite without additional H_2O. Interpretation: Fo + L (incongruent melting of phlogopite).

C. Large faceted crystal of phlogopite with attached glass at center. Lower left, high relief forsterite with phlogopite and glass with vesicles. Quench phlogopite also present but not readily discernible. Grown from "glass" at 1225°C, 10 kb, for 4 hours in the presence of 9.3 wt. percent H_2O. Interpretation: Ph + Fo + L (bubbles in glass presumed to have formed during quench).

D. Products of run at 1275°C, 10 kb, for 1 hour using "glass" starting material with 11.9 wt percent water. High relief forsterite, large piece of glass with several bubbles (at top) and low relief needles of quench phlogopite (center). Interpretation: Fo + L.

On the other hand, liberation of forsterite may be the result of formation of a complex solution of phlogopite with the above-mentioned micas as well as eastonite.

Forsterite formed faceted crystals when grown in the liquid (pl. 1-B) and developed as rounded grains when appearing in phlogopite as the result of the presumed gas leach (pl. 2-A). Quench forsterite appeared as whiskers on faceted forsterite or as chains of somewhat rounded prismatic forms (pl. 2-B).

Kalsilite was best observed in glass with forsterite and occurred, when well formed, as relatively thin, colorless, hexagonal plates with low birefringence. No twinning was observed. Tuttle and Smith (1958, p. 581) gave the kalsilite $\rightleftarrows$ orthorhombic kalsilite inversion at 500 kg/cm³ as 840°C, and Luth (1967b, p. 376) believed the inversion took place at about 875° ± 25°C and 3090 bars. On the assumption that solid solution is minimal, one or both of these sets of data may be in error, judging from the presence of these polymorphs in the runs to be presented. The inversion was found to take place between 2 and 5 kb at 1200°C.

The form of leucite could not be ascertained because it was observed only with large amounts of forsterite and orthorhombic kalsilite or kalsilite. However, its low index of refraction, low birefringence, and powder X-ray diffraction pattern made it readily identifiable. The isotropic form of $KAlSi_2O_6$, occasionally preserved metasably in other systems (for example, diopside-sanidine), was not seen, nor was twinning, suggestive of its inversion from the isometric phase, evident in the orthorhombic form.

The liquid phase was usually represented by glass, the index of refraction of which was variable mainly because of the wide range of water content as well as other compositional, pressure, and temperature variables. The glass often contained quench phlogopite (pl. 1-B, 2-C and D) or quench forsterite (pl. 2-B), making index-of-refraction measurements unreliable as a measure of change of composition. Water may be expelled as quench crystals are formed. The H_2O content of the liquids obviously could not be determined by direct analysis of the quench glass. An estimate of the H_2O content of the liquid was made by the phase-assemblage method (Yoder, Stewart, and Smith, 1957, p. 209) to be outlined below.

The quenched gas phase may be represented in bulk by several portions. The first observation made on opening the sample capsule was emission of water bubbles. The presence of water under room comditions, however, does not always indicate that free gas existed during the run. The water diffuses out of the glass at such high rates that it can be seen to accumulate in the cracks of the glass. For the same reason, the appearance of vesicles in the glass of the quenched liquid does not always mean that free gas existed during the run (pl. 1-C and D). Such vesicles could have formed during the quench while the quenched liquid, now glass, was still plastic. Some of the gas phase is also represented by minute balls of glass of very low index of refraction (pl. 2-A),

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PLATE 2

40 μ
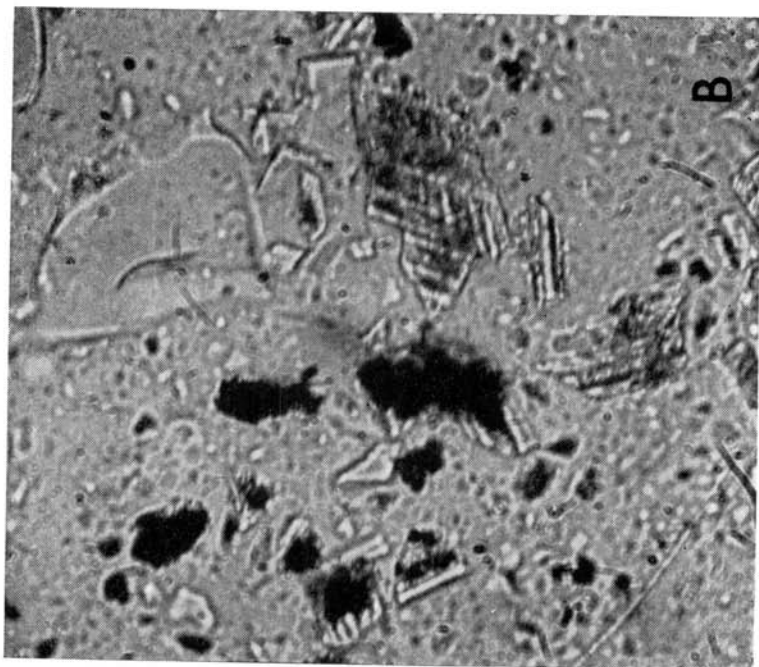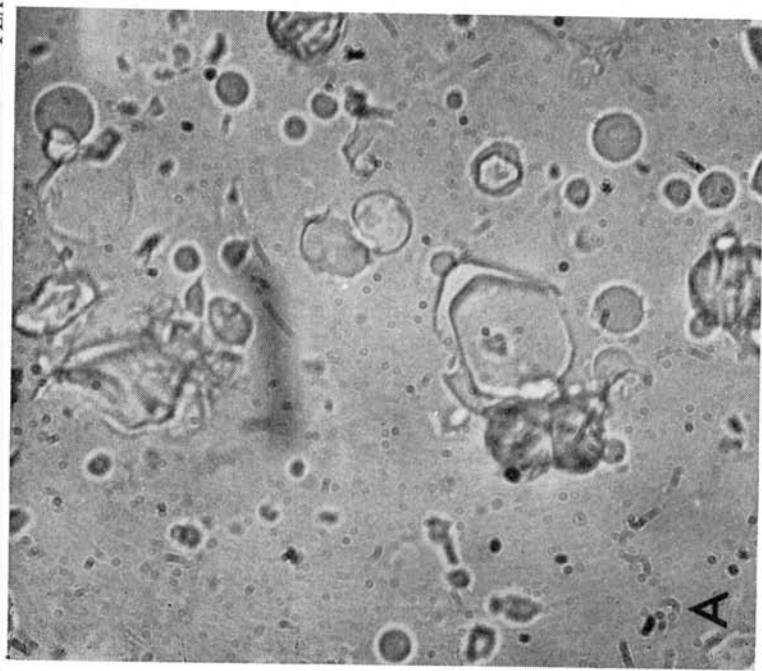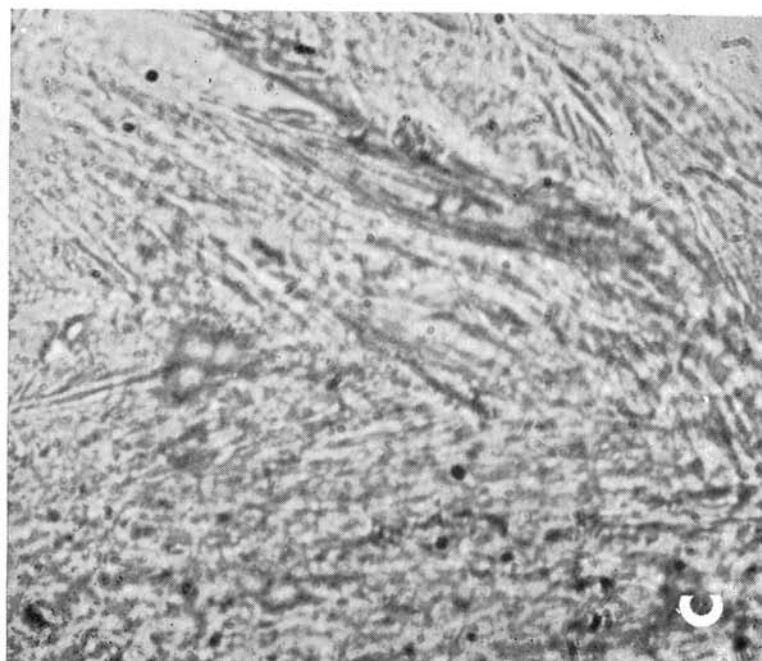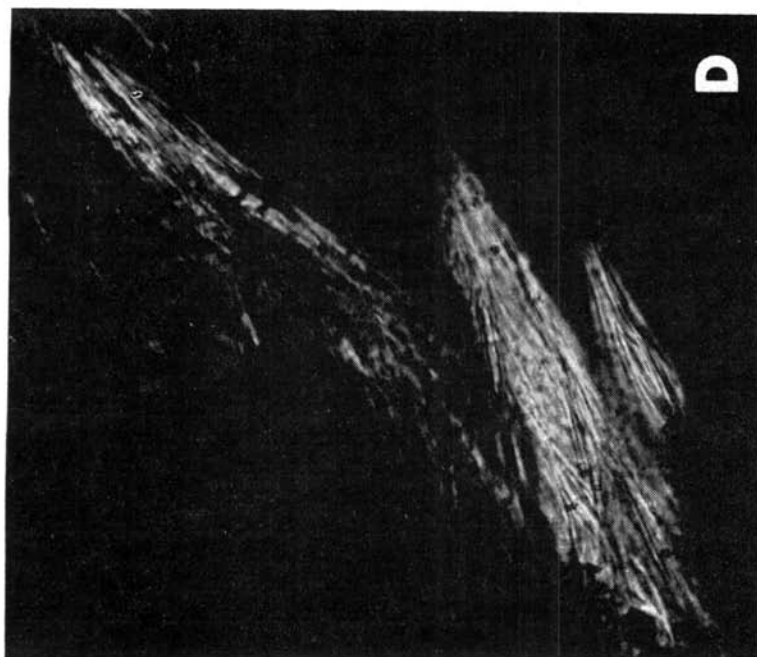
usually stuck to the wall of the tube or in piles in the free space at one end of the main part of the charge. Similar glass also may coat the crystals (pl. 2-A) and usually has a pink tinge when viewed in relatively high index of refraction media, compared to the glass formed from the liquid phase. Still another portion of the gas phase is represented in the inclusions in the crystals. Two-phase inclusions often appeared in for-sterite when grown in the appropriate region where a free gas phase existed. In one case, when an excessive amount of free H_2O was present in a liquid $+$ gas region, the glass of the quench liquid contained pink balls of glass from the quench gas phase. In some runs, another portion of the gas phase precipitated as large, very thin, hexagonal-shaped plates of quench phlogopite. These plates were mainly on the surface of the charge and especially at the free end of the charge, where most of the gas phase accumulated. These quench crystals, not uncommonly coated with pink glass themselves, were a source of much trouble in ascertain-ing the phases stable during the run. It appeared as though the quench mica was first to quench out of the gas phase, then the glass formed from the liquid phase, followed by the formation of the glass of the gas phase, and finally the remaining portion of gas condensed to a saturated solution. The presence of a meniscus on the glass of the quenched liquid was considered prime evidence that a free gas phase existed during the run. At the highest pressures studied, evidence of critical phenomena was looked for in those runs in the L $+$ G region but not found, although it is realized that special techniques may be required to ascer-tain those unique relationships.

EXPERIMENTAL RESULTS

The products obtained from the two starting materials, "glass" and synthetic phlogopite, in the presence of different amounts of water are presented in table 1. The listing of the products as having grown during the run or during the quench obviously involves a judgment by the experimenters. The discrepancies between previous work, discussed below,

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PLATE 2

A. Synthetic phlogopite, especially center and top center, with coating of glass (part of quench gas), the same glass (very low index of refraction) forming numerous free balls as well. Rare, rounded forsterite in high relief. Grown from "Xtl" at 1175°C, 10 kb, for 6 hours in presence of 28.6 wt percent H_2O. Interpretation: Ph + Fo + G.

B. Right of center: glass with herringbone texture of quench forsterite. Center: glass made opaque by numerous bubbles. Top center: clear glass with some needles of quench phlogopite. Grown from synthetic phlogopite crystals in presence of 15.6 wt percent H_2O at 1350°C, 20 kb, for 1 hour. Intepretation: L + G.

C. Quench phlogopite with interstitial glass containing a myriad of bubbles, grown from synthetic phlogopite with 23.2 wt percent H_2O at 1350°C, 30 kb, for 1 hour. Note radiating crystals. Interpretation: L + G.

D. Same material as C in slightly different position under crossed nicols. Note sprays of fibrous crystals.

TABLE 1

Results of hydrothermal treatment of materials of phlogopite

composition or its anhydrous equivalent

T, °C	Starting material*	Weight percent added H$_2$O	Time, hours	Observed products
			Total P = 1 kb	
1200	Xtl	0.0	2	Fo + Gl + q-Ph
1200	Gl	5.6	2	Fo + Ok + Gl + q(?)-Lc
1200	Gl	7.2	2	Fo + Ok + Gl + q-Ph + q(?)-Lc
1200	Gl	9.0	2	Fo + Ok + Gl (meniscus) + q-Ph + q-G** +q(?)-Lc
			Total P = 2 kb	
1200	Xtl	13.8	4	Fo + Gl + q-Ph
1200	Xtl	0.0	4	Ph + Fo + Gl
1200	Gl	16.1	4	Fo + Gl + q-Ph + q-G
1200	Gl	0.0	4	Fo + Lc + Ok
1200	Gl	5.2	4	Ph + Fo + Gl + q-Ph
1200	Gl	8.7	4	Ph + Fo + Gl + q-Ph
1175	Xtl	21.3	6	Ph + Fo
1175	Gl	13.7	6	Ph + Fo
			Total P = 3.5 kb	
1200	Xtl	19.9	4	Fo + Gl + q-Ph + q-G
1200	Gl	11.4	4	Fo + Gl + q-Ph + q-G
			Total P = 5 kb	
1300	Xtl	0.0	2	Fo + Gl + q-Ph (rare)
1300	Xtl	31.2	2	Fo + Gl (bubbles) + q-Ph (rare) + q-G
1275	Xtl	0.0	2	Fo + Gl + q-Ph (trace)
1275	Xtl	27.3	2	Fo + Gl + q-Ph (small amount) + q-G
1275	Gl	14.3	2	Fo + Gl + q-Ph (rare)
1275	Gl	4.3	4	Fo + Gl + q-Ph (small amount)
1275	Gl	3.8	4	Fo + Gl + q-Ph (rare)
1250	Xtl	19.2	2	Fo + Gl + q-Ph + q-G
1250	Xtl	0.0	4	Ph + Fo + Gl + q-Ph
1250	Gl	11.6	2	Fo + Gl + q-Ph (trace)
1225	Xtl	17.8	2	Fo + Gl + q-Ph + q-G
1225	Gl	11.0	2	Fo + Gl (bubbles) + q-Ph
1200	Xtl	0.0	4	Ph + Fo + Gl
1200	Gl	0.0	4	Fo + Ks + Lc
1200	Gl	1.7	4	Fo + Ks + Lc + Ph
1200	Gl	14.1	4	Ph + Fo + Gl + q-Ph
1200	Gl	9.2	2	Ph + Fo + Gl
1200	Xtl	22.8	4	Fo + Gl + q-Ph + q-G
1200	Xtl	12.2	2	Ph + Fo + Gl
1175	Xtl	26.4	5	Ph + Fo + q-G
1175	Gl	12.1	5	Ph + Fo + q-G
1100	Xtl	29.4	4	Ph + Fo (rare)
1100	Gl	16.0	4	Ph + Fo (rare)
1050	Gl	14.0	20	Ph + Fo (rare)
			Total P = 6 kb	
1350	Gl	15.3	2	Fo + Gl (bubbles) + q-Ph
			Total P = 6.25 kb	
1210	Xtl	29.6	4	Fo + Ph + Gl + q-G
1210	Gl	15.1	4	Fo + Ph + Gl (bubbles) + q-Ph + q-G (rare)
			Total P = 7 kb	
1270	Xtl	0.0	6	Ph + Fo + Gl

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TABLE 1 (continued)

T, °C	Starting material	Weight percent added H₂O	Time, hours	Observed products

T, °C	Starting material	Weight percent added H_2O	Time, hours	Observed products
			Total P = 7.5 kb	
.1200	Xtl	25.5	6	Fo + Gl (bubbles) + q-G
1200	Gl	10.3	6	Fo + Ph + Gl (bubbles) + q-Ph
			Total P = 8 kb	
1350	Gl	10.7	2	Fo + Gl + q-Ph
			Total P = 10 kb	
1440	Xtl	17.6	40 min	Gl + q-Fo + q-Ph
1350	Xtl	7.9	1	Fo + Gl (bubbles) + q-Ph
1350	Gl	7.5	1	Fo + Gl (bubbles) + q-Ph
1325	Xtl	0.0	2	Fo + Gl + q-Ph
1325	Gl	3.1	2	Fo + Gl
1325	Gl	2.0	2	Fo + Gl
1325	Gl	1.1	2	Fo + Ks + Gl
1300	Xtl	15.2	1	Fo + Gl (bubbles) + q-Ph + q-G
1300	Xtl	0.0	1	Fo + Ph (rare) + Gl + q-Ph
1300	Gl	0.0	1	Fo + Lc + Ks
1300	Gl	1.8	1	Fo + Gl
1300	Gl	14.8	1	Fo + Gl (bubbles) + q-Ph (small amount)
1300	Gl	9.1	1	Fo + Gl + q-Ph
1300	Gl	5.8	1	Fo + Ph + Gl + q-Ph
1275	Xtl	0.0	4	Ph + Fo + Gl
1275	Gl	2.5	4	Fo + Gl + q-Ph
1275	Gl	1.0	4	Fo + Lc + Ks + Gl
1275	Gl	3.7	4	Fo + Ph + Gl + q-Ph
1275	Gl	1.8	1	Fo + Ks + L
1275	Gl	8.2	1	Fo + Ph + Gl + q-Ph
1275	Gl	11.9	1	Fo + Gl + q-Ph
1250	Xtl	16.6	1	Fo + Gl + q-Ph + q-G
1250	Gl	10.6	1	Fo + Ph + Gl (bubbles)
1250	Gl	0.8	4	Fo + Lc + Ks + Gl + q-Ph (rare)
1250	Gl	2.3	4	Fo + Lc + Ks + Gl + q-Ph (rare)
1250	Gl	3.1	4	Ph + Fo + Gl
1250	Gl	6.5	4	Ph + Fo + Gl
1225	Xtl	0.0	4	Fo + Ph + Gl + q-Ph
1225	Xtl	19.7	1	Fo + Gl + q-Ph + q-G
1225	Gl	13.4	1	Fo + Ph + Gl (bubbles)
1225	Gl	2.9	4	Fo + Ph + Gl
1225	Gl	0.0	5	Fo + Lc + Ks
1225	Gl	6.8	5	Ph + Fo + Gl + q-Ph
1225	Gl	29.3	4	Fo + Gl + q-Ph + q-G
1225	Gl	20.6	4	Fo + Gl + q-Ph + q-G
1225	Gl	9.3	4	Fo + Ph + Gl + q-Ph
1225	Gl	15.2	4	Fo + Gl (bubbles) + q-Ph
1225	Gl	18.5	4	Fo + Gl (bubbles) + q-Ph
1225	Gl	56.4	4	Fo + Gl + q-Ph + q-G
1200	Xtl	25.1	1	Fo + Gl + q-Ph + q-G
1200	Xtl	35.1	6	Fo + Gl + q-Ph + q-G
1200	Gl	0.9	4	Fo + Lc + Ks + Ph
1200	Gl	2.6	4	Ph + Fo + Lc + Ks
1200	Gl	6.3	4	Ph + Fo + Gl
1200	Gl	15.2	4	Ph + Fo + Gl (bubbles) + q-G
1200	Gl	18.6	6	Ph + Fo + Gl + q-Ph + q-G
1200	Gl	12.2	1	Ph + Fo + Gl
1175	Xtl	28.6	6	Ph + Fo + q-G
1175	Gl	18.9	6	Ph + Fo + q-G
1150	Xtl	20.0	2	Ph + Fo + q-G
1150	Gl	10.9	2	Ph + Fo + q-G
			Total P = 10.5 kb	
1400	Gl	17.5	1	Gl + q-Fo + q-Ph

TABLE 1 (continued)

T, °C	Starting material	Weight percent added H_2O	Time, hours	Observed products
			Total P = 15 kb	
1350	Xtl	13.1	1/2	Gl + q-Fo + q-Ph
1300	Xtl	17.1	1/2	Ph + Fo
1300	Gl	10.2	1-1/2	Ph + Fo + Gl
1200	Xtl	16.2	2-1/4	Fo + Gl + q-Ph + q-G
1175	Xtl	16.3	2	Ph + Fo + q-G
			Total P = 20 kb	
1400	Xtl	14.0	1	Gl + q-Ph + q-G
1350	Xtl	15.6	1	Gl + q-Fo + q-Ph
1350	Xtl	0.0	1	Fo + Gl + q-Ph
1325	Xtl	0.0	1	Ph + Fo
1300	Xtl	20.4	1	Fo + Gl + q-Fo + q-Ph
1250	Xtl	21.9	1	Fo + Gl + q-Ph
1200	Xtl	19.3	2	Fo + Gl + q-Ph + q-G
1175	Xtl	22.8	2	Ph + Fo + q-G
1175	Xtl	0.0	2	Ph + Fo
1150	Xtl	25.0	2	Ph + Fo + q-G
			Total P = 30 kb	
1400	Xtl	0.0	1/2	Fo + Ph (small amount) + Gl + q-Ph
1400	Xtl	0.0	1	Fo + Gl + q-Ph
1375	Xtl	0.0	1	Ph + Fo + Gl (small amount) + q-Ph
1350	Xtl	0.0	1/2	Ph
1350	Xtl	23.2	1	q-Ph
1325	Gl	19.5	1	Fo + Gl + q-Ph
1300	Gl	18.2	1	Fo + q-Ph
1225	Xtl	19.2	1	Fo + q-Ph
1200	Xtl	17.5	1	Ph + Fo + Gl
1200	Xtl	26.4	2	Fo + Gl + q-Ph
1175	Xtl	20.3	1	Ph + Fo + q-G
			Total P = 37.5 kb	
1200	Xtl	16.1	1	Ph + Fo

*Gl = sintered mixture quenched from 1500°C and containing Fo + q-Fo + Gl; Xtl = synthetic phlogopite prepared from Gl at 700°C and 5 kb.

**q-G = glass portion of quench gas when present as balls or coatings on other phases.

and the present study are probably directly attributable to this judgment. It was not possible to demonstrate equilibrium by the customary reversal of reactions involving *stable* reactants and products because of the formation of quench products and the rapid growth of phases on run-up. A region of composition hitherto not knowingly investigated (compare Luth, 1967, p. 391-392) for a hydrous mineral involves H_2O contents insufficient to saturate the liquid or to convert all the crystalline materials of the requisite composition to the hydrous mineral. This region, referred to as the water-deficient or gas-absent region (Yoder, 1952, 1955), is vital to an understanding of the melting relations, and its recognition aids greatly in the interpretation of the products. The results are presented in a series of projections: P-T, T-X at P = 10 kb, and

X at P = 10 kb and T = 1225°C. Each projection contributes to the understanding of the previous projection.

P-T projection.—Some of the results are plotted in figure 2 to show primarily the limits of stability of phlogopite under two principal conditions. Curve C is the maximum stability curve of phlogopite in the gas-absent region where incongruent melting takes place: Ph → Fo + L. It terminates at the low-pressure end at a singular point, II. The curve C is based mainly on experiments using synthetic phlogopite to which no additional H_2O was added. The critical supporting experiments in the gas-absent region depend mainly on the interpretation of the observed phlogopite as stable, metastable, residual, or quench product. The faceted nature of the books of mica in glass from liquid (pl. 1-C) eliminates the possibility of their interpretation as residuals of crystals formed on the run-up or quench products but does not exclude the possibility of their being metastable products. Formation of phlogopite in a region generated by the metastable extension of the curves to be described below is considered most unlikely under the high temperatures and pressures involved. The curvature of curve C is no doubt due, for the most part, to the change in volume with pressure of the hydrous liquid.

Curve A expresses the reaction Ph + G → Fo + L and may be considered the maximum stability of phlogopite in the presence of an excess of gas, that is, H_2O sufficient to saturate its coexisting liquid and produce a free gas phase. Curve A is terminated at the low-pressure end by a singular point, III, where the liquid lies on an extension of the plane Fo–Ph–G. An additional curve, not shown in figure 2, rises from the singular point III in very close proximity to curve A. The reaction, Ph + Ok + G → Fo + L, has not been investigated directly but was identified by Luth (1967b, p. 382, table 3, i, 5). At pressures below singular point III the curve becomes Ph + G → Fo + Ok + L, which terminates at the invariant point I, involving the phases Ph, Fo, Lc, Ok, L, and G.

The complete sequence of curves generated by the phases in equilibrium at the invariant point I are outlined in figure 3 with the use of Schreinemaker's (1916) principles and the Morey and Williamson (1918) coincidence theorem. Each univariant curve is designated by the absent phase in parentheses. The sequence of univariant curves is similar to that illustrated by Luth (1967b, p. 393) except that (G) and (Lc) are reversed in position. His sequence was based on the assumption that Ph = Fo + Ok + L + G, which requires that the H_2O content of the liquid be *less* than that of those possible liquids lying on a plane passing through the compositions of Fo–Ok–Ph. The data presented in table 1 for total pressure = 1 kb indicate that the water content of the liquids (min of 7.2 wt percent) is *greater* than that of those possible liquids lying on a plane passing through the compositions of Fo–Ok–Ph. Therefore, the volume Fo–Ok–Lc–L contains the phlogopite composition, and the reaction becomes Ph = Fo + Ok + Lc + L, no free gas being involved.
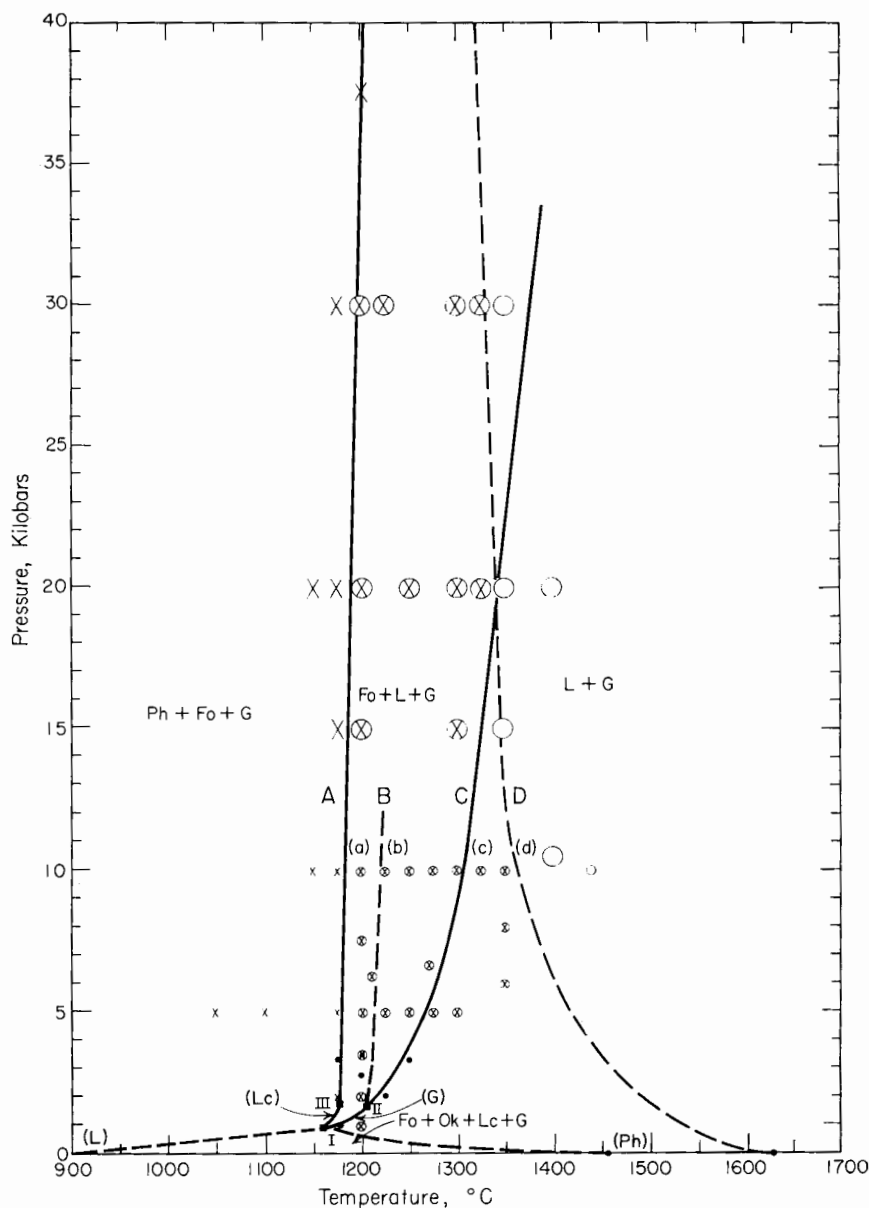
Fig. 2. Pressure-temperature diagram for compositions on the join $K_2O \cdot 6MgO \cdot Al_2O_3 \cdot 6SiO-H_2O$. The solid squares mark an invariant point I and two singular points II and III. X = crystals + gas; circle with an X = crystals + liquid + gas; circle = liquid + gas. The symbols are only relevant to the equilibria represented by curves A and D. Curve A is the maximum stability of phlogopite in the presence of a gas phase. Curve D is very close to the minimum liquidus in the presence of a gas phase. Curve B marks the beginning of melting of the gas-absent assemblage Ph + Fo + Ks (or Ok) + L, and curve C is the maximum stability of phlogopite in the absence of a gas phase. Black dots are the data points of Luth (1967b) bearing on the melting of phlogopite. The lettered points at 10 kb appear in figure 4. The curves (L), (Ph), (G), (Lc) are designated by the absent phase in the relevant reactions which appear in greater detail in figure 3.
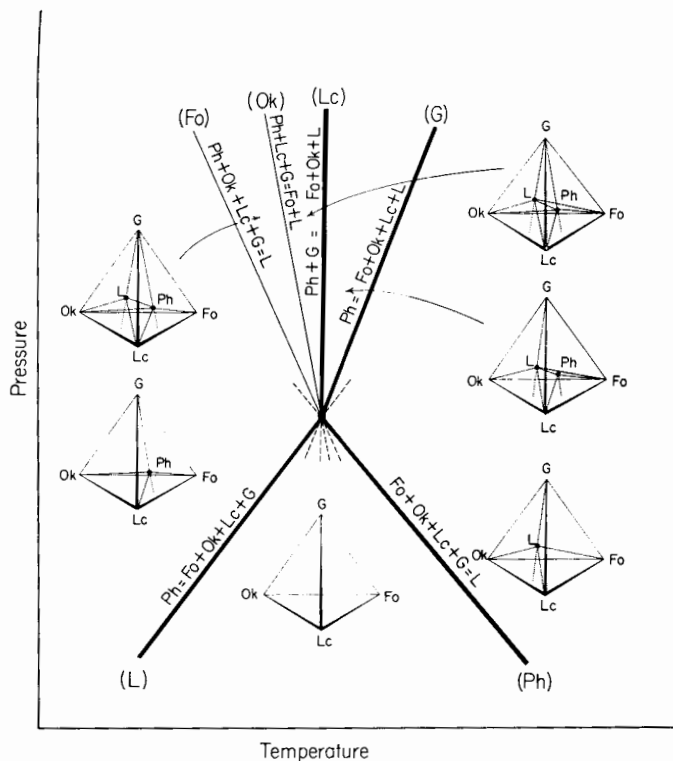
Fig. 3. Sequence of invariant curves immediately about the invariant point I involving phlogopite (Ph), forsterite (Fo), leucite (Lc), orthorhombic kalsilite (Ok), liquid (L), and gas (G). Each curve is indicated by the absent phase. Beginning of melting in the presence of gas is given by curves (Fo) and (Ph). Heavy lines are those reactions exhibited by compositions on the join $K_2O \cdot 6MgO \cdot Al_2O_3 \cdot 6SiO_2–H_2O$, which includes phlogopite composition.

As will become evident, the issue of singular import is the H_2O content of the liquid involved in the melting of phlogopite.

The data for curve (L) exhibited in figures 2 and 3 are taken from Wones (1967) and Luth (1967b), and curve (Ph) is estimated from the beginning of melting of the Fo–Ok–Lc system at 1 atm, $1465° \pm 10°C$ (Luth, 1967a, p. 175), and the invariant point I, believed to be about $1160°C$ and 1 kb (Luth, 1967b).

The reaction for curve (G) is Ph → Fo + Lc + Ks + L; however, no direct observations have been made on curve (G). Curves B and C evolve from curve (G) through the singular point II generated by the colinear arrangement of Ph–Fo–L resulting from the expansion of the liquid field across the extension of the Ph–Fo join. An additional singular point may exist on curve (G), depending on the geometric configuration of the liquid field. The reaction for curve B is Ph + Lc + Ok → Fo + L.

Curve D is one of a family of curves, dependent on the H_2O content, very close to the lowest temperature liquidus in the presence of a gas

phase on the phlogopite–H_2O join. It originates at the 1 atm liquidus for the anhydrous phlogopite composition which is near (?) 1628°C (to be corrected for alkali loss). Curve D and curve C do not intersect in P-T-X space in the region studied, as would appear in the projection: they record phenomena in different regions of composition.

T-X projection at P = 10 kb.—An appreciation of the significance of the two principal curves A and C in figure 2 may be gained from an examination of a partial T-X projection at 10 kb (fig. 4). The significant changes of phase are marked with small letters in parentheses on both figures 2 and 4. For example, the point marked (a) on the P-T projection of figure 2 is expressed as a horizontal line in figure 4 at 1185°C, marking the beginning of melting for the assemblage Ph + Fo + G. The horizontal line marked (b) in figure 4 is the beginning of melting of the assemblage Ph + Fo + Lc + Ks. Point (c) is the maximum stability of phlogopite itself in the absence of a gas phase, phlogopite melting incongruently to Fo + L. The curve extending initially in a horizontal direction from (d) is the liquidus for those compositions in which a gas phase is present. The liquidus rises with increasing water content because of the change of the liquid-gas tie line to be described in connection with figure 5.

Attention is called to the fact that the system is at least quarternary and may even be quinary, and only those fields cut by part of the join $K_2O \cdot 6MgO \cdot Al_2O_3 \cdot 6SiO_2$–$H_2O$ are illustrated. The critical observation is that phlogopite is stable in the absence of a gas phase at a temperature well above the beginning of melting in the silicate-rich part of the join, (a) in figure 4. Furthermore, the initiation of melting in the gas-free assemblage, Ph + Fo + Lc + Ks, is at a somewhat higher temperature (b) than that for the gas-present region (a). It is the former region that is of great import in the partial melting process of the mantle and lower crust. The H_2O contents of the liquids *cannot* be read from figure 4; however, estimates are suggested in the following figure 5.

X projection at T = 1225°C and P = 10 kb.—As a further explanation of the events taking place at 10 kb, a compositional projection in the broad view of the Fo–H_2O–Lc:Ks (1:1 mole) plane is given for 1225°C in figure 5. The data points are indicated by a small x. The region marked Fo + L + G is based on those run products that appeared after quenching as euhedral or subhedral forsterite crystals (= Fo); clear glass (= L in part), usually highly vesiculated; balls or coatings of a pinkish glass (= G in part); a milky fluid (= G in part), usually exuded when the container wall was punctuated; and needles of mica, considered to have formed during the quenching process, not being stable during the run. The Ph + Fo + L regions exhibited faceted crystals of phlogopite, often in books about 10 microns thick, subhedral forsterite, and clear glass but did not have any of the above-named products attributed to the gas phase, nor was the glass highly vesiculated (compare pl. 1-C and D with pl. 2-B). The anhydrous composition yielded
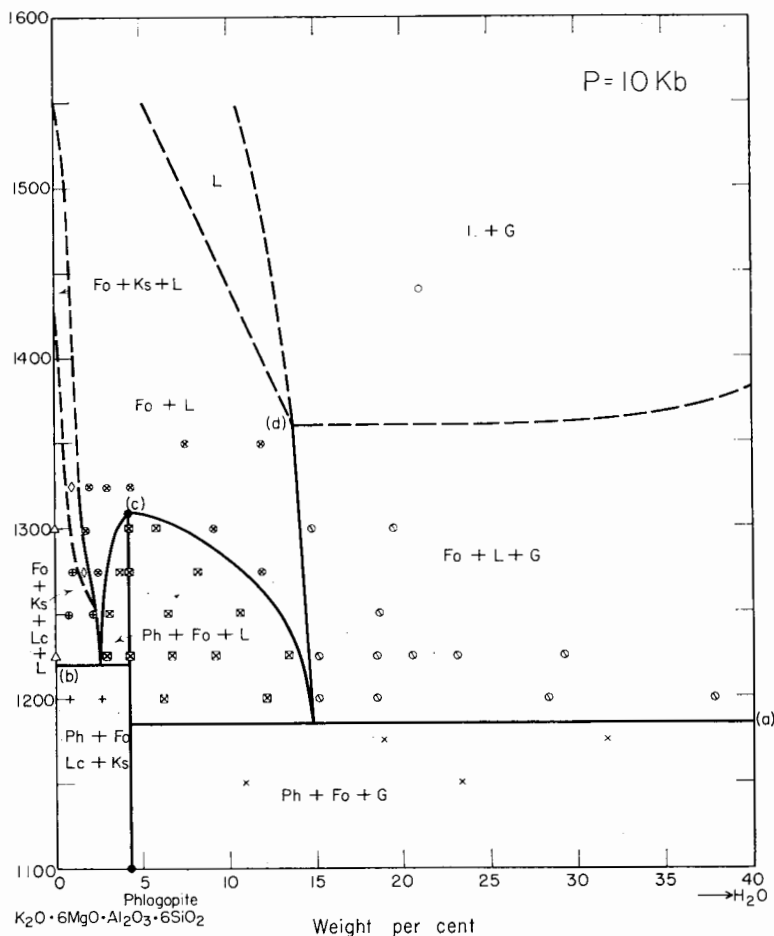
Fig. 4. The temperature-composition projection at 10 kb for the silicate-rich portion of the $K_2O \cdot 6MgO \cdot Al_2O_3 \cdot 6SiO_2$-$H_2O$ join. The lettered points and lines are also indicated in figure 2, and the data at 1225°C are exhibited in figure 5. The H_2O contents of the liquids cannot be read from this figure; estimates are suggested in figure 5.

Fo + Lc[3] + Ks in accord with that produced at 1 atm, taking into account the polymorphic change is $KAlSiO_4$.

The H_2O content of the liquid in equilibrium with Fo and G is seen to be of the order of 22 wt percent, whereas the H_2O content of liquid in equilibrium with the two identical assemblages containing Fo and Ph is of the order of 20 and 4 wt percent.[4] These estimates are determined

[3] Note should be made of the probable breakdown of Lc → Ks + sanidine at higher pressures and lower temperatures as outlined by Scarfe, Luth, and Tuttle (1966, p. 728) below 10 kb.

[4] These estimates are maximum values in light of the possible hydrogen loss by diffusion mentioned in footnote 2.
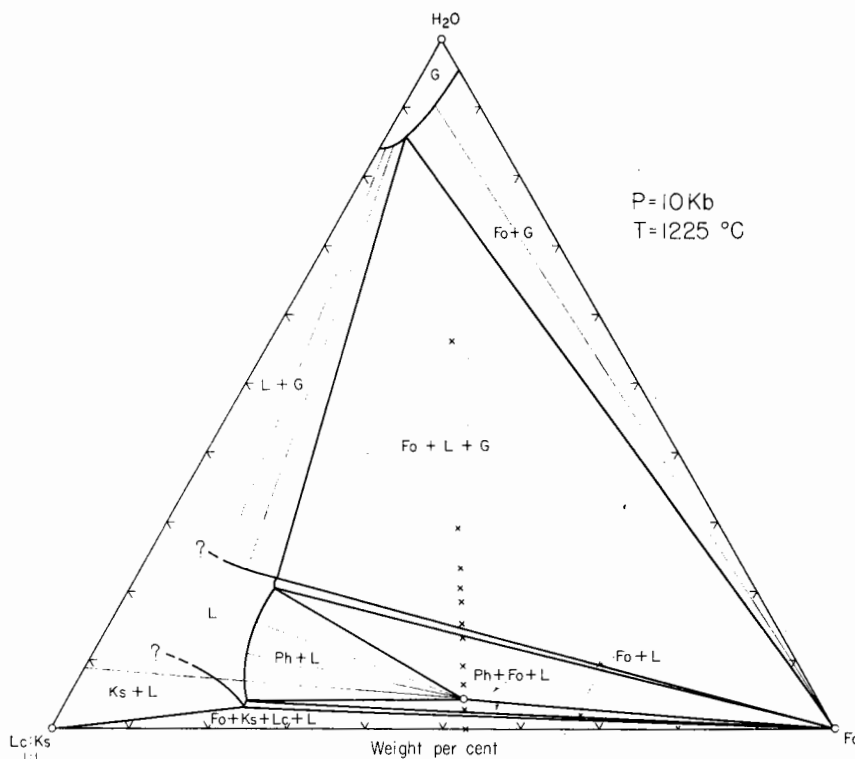
Fig. 5. Pseudoternary section at $P_T = 10$ kb and 1225°C for the system Fo–H_2O–Lc:Ks (1:1 mole). Compositions investigated, marked with an X, lie on the join $K_2O \cdot 6MgO \cdot Al_2O_3 \cdot 6SiO_2$–$H_2O$ and are the basis of this schematic construction. The dashed line extending the line from Fo through Ph indicates the locus of possible liquid compositions at the singular point III.

solely on the basis of the intercepts on the $K_2O \cdot 6MgO \cdot Al_2O_3 \cdot 6SiO_2$–$H_2O$ join and on estimates[5] of the forsterite content in the partial melt regions.

The dashed line in figure 5 is a construction line to show that the liquid field has expanded below the projection of Fo–Ph, a condition that arises at the singular point II shown in figure 2.

The choice of the composition of gas phase in equilibrium with Fo and L was made on the basis of the observation that phlogopite itself develops forsterite inclusions with increasing temperature prior to melting. Provided no solid solution was involved or errors made in preparing the phlogopite composition, the gas composition could not lie on the $K_2O \cdot 6MgO \cdot Al_2O_3 \cdot 6SiO_2$–$H_2O$ join if forsterite appeared in the phlogo-

[5] Accurate measure of the proportions of phases would have been most helpful in outlining the stable phase assemblages; however, this powerful method could not be applied precisely in the present study because of the variety and distribution of quench products.

pite crystals in the presence of a gas phase. For this reason and because of the nature of the observed assemblages, a highly alkaline composition of the gas phase is indicated. Experiments by Morey and Chen (1955) in the K_2O–Al_2O_3–SiO_2–H_2O system support this view. Luth (1967b, p. 378 and 389) attributed his failure to produce 100 percent phlogopite from the requisite composition also as a consequence of the abstraction of alkaline constituents by the gas phase.

DISCUSSION OF PREVIOUS RESULTS

Previous work in the same region of pressure and temperature includes Yoder and Eugster (1954), Crowley and Roy (1964), and Luth (1967b). None of the studies include runs in the gas-absent region. Studies at lower pressures include Wones and Dodge (1968) and Wones (1967), and those at higher pressures include Markov, Petrov, Delitsin, and Ryabinin (1966) and Kushiro, Syono, and Akimoto (1967).

The products of the critical runs at 2 and 5 kb by Yoder and Eugster (1954, table 2b) were reexamined. The melting of phlogopite in the presence of an excess of gas at 5 kb was not recognized as such by Yoder and Eugster. The run at 1140°C and 5 kb with a total H_2O content of 49.3 wt percent consisted of small faceted books and a few very large plates of phlogopite and forsterite, both rimmed with a pink glass, now believed to have formed as a quench product from part of the large amount of gas. Another critical run at 1200°C and 5 kb with a total water content of 44.7 wt percent consisted of faceted forsterite, glass, and a few very large plates of phlogopite. The very large faceted crystals of phlogopite observed by them at the highest temperatures at 5 kb, now believed to be formed as a quench product from the gas phase, were then intercepted as a stable product. These runs, as now interpreted, are consistent with the present study. The appearance of forsterite was considered then as evidence of incomplete breakdown which would have been complete if sufficient time were provided. The forsterite is now considered to be a by-product of the reaction of the initially pure water with the phlogopite composition in achieving the requisite gas composition. Two of their four sealed-tube runs at 2 kb are consistent, using the present interpretation of the presence of forsterite. An examination of the tube weight recorded after the 1160°C run clearly indicates that all the water was lost during the run, and the run should have been discarded. The results, however, are in accord with those to be expected in the anhydrous region at that temperature. The presence of Lc in the run at 1100°C cannot be accounted for, except possibly on the basis of excessive gas leaching, and their conclusion of incomplete breakdown appears to be justified. The excessively large amounts of water present relative to the amount of starting material in the sealed platinum tubes appear to have led to the difficulties in interpretation experienced by them.

Crowley and Roy (1964) were well aware of the difficulties of interpretation and, with the belief that their own data on gels and crystalline

mixtures were not "unequivocal", indicated that the breakdown curve of phlogopite in the present of an excess of H_2O was about 100°C higher than that of Yoder and Eugster. They searched for possible melting but did not encounter melting in their runs up to 1160°C and 2 kb.

Luth (1967b) examined phlogopite in the broader scope of the $K_2O–MgO–Al_2O_3–SiO_2–H_2O$ system. The invariant point marking the beginning of melting for phlogopite was studied in particular by Luth. His six runs on the Ph–H_2O join (Gel composition no. 38 + water) above 1 kb, all of which bear on the melting curve in the presence of an excess of H_2O, are plotted in figure 2. Four are consistent with the present results; however, the two runs at 1200°C suggest that the beginning of melting in the presence of an excess of H_2O should be 25° higher than illustrated in figure 2. In the event that some or all of the excess H_2O was lost during these two runs, the products are in accord with phlogopite stable in the gas-absent region.

No garnet was encountered in the run at 37.5 kb, the highest pressure studied, even though Kushiro, Syono, and Akimoto (1967) indicate that it and other undefined phases may be stable at about that pressure.

APPLICATION OF RESULTS

Melting of a hydrous phase.—The melting behavior of phlogopite has been outlined under the two unique conditions where a gas phase is present and absent. The results appear to be applicable, in general, to other hydrous minerals. For example, the melting of glaucophane (Gp), which lies in the system forsterite (Fo)–enstatite (En)–albite (Ab)–H_2O, was presented by Ernst (1961). His sequence of curves about the invariant point is based on a composition of liquid containing less than 3.4 wt percent H_2O. The high H_2O content of liquid reported by him, 5 ± 2 wt percent, is not in accord with the sequence of curves (Ernst, 1961, p. 755, fig. 6). The curve purported to be Gp = Fo + En + L + G, designated by (Ab) in his figure 6, implies that the water content of the liquid was *less* than those whose compositions lie on the projection of the plane Fo–En–Gp (<3.4 wt percent, assuming the glaucophane contains the ideal H_2O content of 2.30 wt percent, or <4.4 wt percent, using the H_2O content of synthetic glaucophane of 3 ± 1 wt percent measured by Ernst). Although the errors involved do not warrant a definitive conclusion, it is likely that the reaction actually observed by him was Gp + G = Fo + En + L. The sequence of curves, designated by the absent phase in parentheses, then becomes (L) (Fo) (En) (Ab) (G) (Gp) instead of (L) (Fo) (G) (En) (Ab) (Gp). There is little doubt that glaucophane under these circumstances is stable to higher temperatures in the gas-absent region than indicated by his "breakdown" curve. The final breakdown of glaucophane, curve (G), which was not investigated by Ernst, is achieved by Gp = Fo + En + Ab + L, the liquid containing *more* H_2O than those whose compositions lie on the projection of the plane En–Fo–Gp, no gas phase being involved.

The apparent trifling change of sequence of curves about the invariant point demonstrated in the case of phlogopite, and perhaps also glaucophane, has great theoretical significance in connection with the melting of hydrous minerals in general. As now viewed, there is involved (1) a large increase in the stability field of hydrous minerals, (2) a hitherto unrecognized melt region, and (3) new degrees of freedom in the behavior of liquids generated on partial melting. The first point is obvious from an inspection of figure 2, where the curve A represents the upper stability limit of phlogopite in the *presence* of a gas phase and curve C is the maximum stability of phlogopite in the *absence* of a gas phase. Both curves involve the production of liquid. The latter two points are amplified in the next section.

Melting of a hydrous assemblage.—The melting of an *anhydrous* assemblage in the presence and absence of a gas was outlined by Yoder (1965). He indicated the high probability that H_2O was stored in the mantle not as a free gas but in a variety of hydrous minerals stable to very high pressures. The cases he described involved the breakdown of the hydrous mineral prior to melting. It is now possible to outline the events that take place where the hydrous phase remains stable into the melt region. The projection in figure 4 may be used to illustrate the melting of the assemblage Fo + Lc + Ks + Ph. If it is assumed that the amount of Ph is very small, melting would begin at 10 kb at about 1220°C with all the phlogopite being consumed. The H_2O content of the initial liquid would be small, about 3 wt percent (see fig. 5). With further temperature rise the H_2O content of the liquid would *decrease* until complete melting was achieved. In other words, the melting behavior after initial melting would be similar to that of an anhydrous assemblage in the absence of a gas phase. Consider the same assemblage wherein phlogopite is the predominant phase. Such an assemblage would be analogous to the amphibolite layer proposed by Wagner (1928) and Gisolf (1929). On initial melting at the same pressure and temperature, some of the anhydrous phases are consumed in the liquid, and the liquid has the same low H_2O content. On further rise in temperature, the H_2O content of the liquid *increases* until the hydrous phase is consumed. This behavior suggests that in the region of generation the H_2O content of magma is limited, in the case of phlogopite, to the proportion of hydrous phase initially present, in contrast to the excessively H_2O-rich magmas possible where a gas phase is present (see fig. 5). The H_2O contents of those hydrous minerals now believed to exist in the mantle are restricted to a few percent, and their proportion of the mantle assemblage is probably small. Herein lies the apparent discrepancy between laboratory investigations performed in the presence of a gas phase, where the H_2O contents of the liquids were large, and the low-H_2O contents believed, on the basis of field deductions, to exist in natural magmas. Melting in the absence of a free gas phase appears to generate liquids having H_2O contents more in accord with those predicted by

field workers.[6] *Initial* low-H_2O content of magma does not preclude the possibility of explosive eruption. The mechanism outlined by Yoder (1965) in which a free gas phase appears on saturation through pressure release is still applicable.

Kimberlite.—The principal groundmass phases of kimberlite are forsterite, phlogopite, and calcite. Some consider a portion of the olivine, as well as the many foreign fragments usually present in the rock, as inherited. The fragmental character of the rock, predominantly pipe-like occurrence, containment and incorporation of accessory "high-pressure" minerals, and highly variable mode suggest formation under conditions involving a gas at very high pressures and possibly a highly reactive liquid. The present data on one of the principal minerals of kimberlite bear on the origin of this rare and unique rock type.

The observation that natural phlogopite is stable to high pressures is documented, although limitations may be imposed at depths equivalent to about 125 km (Kushiro, Syono, and Akimoto, 1967). The rock would similarly be restricted to these and shallower depths. The highly alkaline nature of the liquids coexisting with phlogopite implies a very reactive environment. In addition, it implies that derivative liquids of *kimberlite composition*, if indeed they exist, result from a high degree of partial melting of the parental material under hydrous conditions. The close association of forsterite with phlogopite, especially its incongruent melting relationship, is relevant to the production of kimberlite. The ease of formation of phlogopite as a quench product invites a reevaluation of the textures displayed in the groundmass of kimberlite. Although experimental study of kimberlite requires inclusion of calcite and some control of the H_2O–CO_2 ratio in the gas and liquid phases, it is clear that the behavior of phlogopite places many constraints on the mode of formation of kimberlite.

[6] It is necessary to recall that melting in the absence of a gas phase is *not* equivalent to melting under conditions where the H_2O pressure is less than the total pressure by virtue, for example, of the presence of a large amount of another gaseous component (for example, CO_2). On the other hand, the presence of a very small amount of another gaseous component—that is, an amount limited to its solubility in the liquid—gives rise to the same gas-absent equilibria. Such amounts of additional gaseous components would not alter the above conclusions. In brief, the presence of another *free* gaseous component restricts the assemblages to those that may exist with gas at the effective partial pressure of H_2O. Those assemblages that are prohibited from coexisting with an H_2O gas phase would, therefore, not be realized in a multicomponent *free* gas.

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