

# Conditions of phlogopite crystallization in ultrapotassic volcanic rocks

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**ABSTRACT.** Phlogopite occurs as an early crystallizing mineral in many ultrapotassic lavas of basaltic affinities. Based on high-pressure experiments in lavas of these compositions, the early crystallization of phlogopite is controlled in large part by the bulk compositions of the liquids from which it crystallizes but also by the total pressure and by the  $a_{\text{H}_2\text{O}}$ , with early phlogopite forming under a narrow range of  $a_{\text{H}_2\text{O}}$ , less than that represented by  $\text{H}_2\text{O}$ -saturated conditions. Variations in  $f_{\text{O}_2}$  do not appreciably affect phlogopite crystallization but high  $a_{\text{CO}_2}$  suppresses its crystallization. In ultrapotassic magmas, phlogopite will preferentially incorporate  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{MgO}$ , and  $\text{Al}_2\text{O}_3$  relative to the coexisting early silicate minerals, olivine and clinopyroxene, and thus, on fractionation of these minerals, phlogopite will be more effective in reducing these oxides in residual liquids. Phenocrysts and microphenocrysts of phlogopite in ultrapotassic lavas are directly related with respect to their  $\text{K}/\text{Ti}$ ,  $\text{K}/\text{Al}$ ,  $\text{K}/(\text{K} + \text{Na})$ , and  $\text{Mg}/(\text{Mg} + \text{Fe})$  ratios. Textural relations suggest phlogopite may form by reaction relationships involving liquid with olivine, and/or clinopyroxene. Such relationships are supported by the experimental studies on ultrapotassic rock compositions.

THE only common K-bearing minerals stable under upper-mantle conditions are phlogopite and K-richite; both occurring in mantle derived alkali basalts with  $\text{K}_2\text{O} \gtrsim \text{Na}_2\text{O}$  and as nodules in kimberlites. Phlogopite is the more important of these minerals as it has a wider stability field (Kushiro, 1970; Modreski and Boettcher, 1973) and contains more  $\text{K}_2\text{O}$ . Many authors have discussed variations in phlogopite compositions (particularly  $\text{TiO}_2$ ) and their relationship to mantle metasomatism (cf. Lloyd and Bailey, 1975; Harte *et al.*, 1975; Boettcher *et al.*, 1979; Boettcher and O'Neil, 1980; Farmer and Boettcher, 1981; Lloyd, 1981). The stability of phlogopites under mantle conditions has been determined by Kushiro *et al.* (1967), Yoder and Kushiro (1969), and Forbes and Flower (1974); and in synthetic systems, corresponding to simplified K-enriched mantle compositions, in the systems  $\text{K}_2\text{O}-\text{MgO}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  (Modreski and Boettcher, 1973),  $\text{KAlSiO}_4-\text{MgO}-\text{SiO}_2-\text{H}_2\text{O}-\text{CO}_2$  (Wendlandt and Egger, 1980).

High-pressure experiments on K-rich basaltic lavas with phlogopites as a suprasolidus phase are limited (Barton and Hamilton, 1979; Edgar *et al.*, 1976, 1980; Ryabchikov and Green, 1978; Arima and Edgar, in press).

Our purpose is to examine the physical and chemical conditions under which phlogopite crystallizes in alkali basaltic and ultramafic lavas with  $\text{K}_2\text{O} \gtrsim \text{Na}_2\text{O}$  (hereafter termed 'ultrapotassic rocks'). These conditions are important to any hypothesis for the genesis of these rocks by partial melting from mantle sources and may indicate the nature of such sources.

## *Experimental data on phlogopite crystallization*

Crystallization of phlogopite at or near the liquidus in experiments on ultrapotassic rocks naturally depends on the chemistry of the rock. Although it is theoretically possible to produce ultrapotassic rocks by very small degrees of partial melting of a model pyrolite mantle source (cf. Mitchell and Bell, 1976), phlogopite appearance at or near the liquidus in experiments on ultrapotassic rock compositions suggests that such rocks are derived by partial melting of a source more K-enriched than pyrolite.

To assess the proximity of phlogopite to the liquidus surfaces for various ultrapotassic rock compositions for which experimental data are available (Table I), the temperature interval between the liquidus and the first appearance of phlogopite ( $\Delta T$ ) has been plotted against the major oxides in the bulk rock compositions (fig. 1). All analyses used in fig. 1 have been recalculated to 100% eliminating  $\text{H}_2\text{O}^-$ . The  $\Delta T$  values have been determined from the  $P$ - $T$  diagrams listed in the sources quoted in Table I. All experiments were done on dried powder and glasses with 5 and 15 wt. %  $\text{H}_2\text{O}$  as an added component excepting Barton and Hamilton's (1979) experiments which were done with no additional  $\text{H}_2\text{O}$ , the  $\text{H}_2\text{O}$  content being entirely the  $\text{H}_2\text{O}^+$  content of the madupite,

Table I. Compositions of ultrapotassic rocks investigated experimentally. (All analyses recalculated to 100%).

	1	2	3	4
SiO <sub>2</sub>	43.98	40.61	42.6	44.71
TiO <sub>2</sub>	1.85	4.11	5.3	2.37
ZrO <sub>2</sub>	nd	nd	nd	0.28
Al <sub>2</sub> O <sub>3</sub>	9.91	8.06	8.3	8.06
Fe <sub>2</sub> O <sub>3</sub>	3.06	8.99	0.2	5.72
FeO	8.10	2.99	7.8	0.87
MgO	20.30	14.49	15.8	11.32
MnO	0.17	0.22	nd	0.15
CaO	8.75	14.87	10.7	12.20
Na <sub>2</sub> O	1.55	1.40	0.8	0.76
K <sub>2</sub> O	1.74	3.23	7.1	7.38
P <sub>2</sub> O <sub>5</sub>	0.37	1.02	nd	1.54
Cr <sub>2</sub> O <sub>3</sub>	0.16	nd	0.2	0.04
NiO	0.09	nd	nd	-
H <sub>2</sub> O <sup>+</sup>	-*	-*	-*	2.97
$\frac{100Mg}{Mg+Fe_T}$	77	70	78	77
$\frac{100K}{K+Na}$	41	60	85	87

Proximity of phlogopite to liquidus ( $\Delta T$ ) at different pressures and added H<sub>2</sub>O contents.

1		2		3	
P (Kb)	$\Delta T$ (°C)	%H <sub>2</sub> O	P (Kb)	$\Delta T$ (°C)	%H <sub>2</sub> O
20	138	15	30	96	5
10	159	15	30	74	15
			20	66	5
			20	74	15
			10	43	15
			10	107	5
			10	86	15

4		
P (Kb)	$\Delta T$ (°C)	%H <sub>2</sub> O
30	131	3
20	75	3
10	56	3

- Olivine ugandite (Edgar et al., 1980, Table 1, Fig. 1).
- Katungite (Edgar and Arima, 1981, Table 1) and Arima and Edgar (ms).
- Biotite mafurite (Edgar et al., 1976, Table 1, Fig. 1; Nyabchikov and Green, 1978, Fig. 1).
- Madupite (Barton and Hamilton, 1979, Table 1, Fig. 1) - includes SrO = 0.42, BaO = 0.68, SO<sub>3</sub> = 0.53.

\* For these starting compositions H<sub>2</sub>O<sup>+</sup> was removed by heating prior to the experiments. Composition 3 was prepared as anhydrous glass.

2.97 wt. % (recalculated—see Table I). All experiments represent H<sub>2</sub>O-undersaturated liquids at pressures above about 10 kb and therefore represent vapour-absent conditions. The exact amounts of H<sub>2</sub>O required to saturate these liquids at different pressures have not been determined.

**Bulk rock composition.** The relationship between the proximity of phlogopite crystallization to the liquidus in the experiments would seem intuitively to depend on the bulk compositions of the rocks from which the phlogopites crystallize. In relation to phlogopite formation, the main oxides in the bulk rock compositions (Table I) are K<sub>2</sub>O, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>. No other crystalline phases containing K<sub>2</sub>O appear prior to the crystallization of phlo-

pite in these experiments. TiO<sub>2</sub> is commonly high in phlogopites but also occurs in oxides (mainly spinels) and clinopyroxenes, whereas Al<sub>2</sub>O<sub>3</sub> occurs in clinopyroxenes and spinels in addition to phlogopite. CaO is invariably low in phlogopite but MgO is high, with 100Mg/(Mg + Fe<sub>T</sub>) ranging from 82 to 94. These oxides also occur in olivines and clinopyroxenes coexisting with phlogopite.

Fig. 1 shows that the assumption that the bulk rock chemistry controls the early crystallization of phlogopite is generally, but not invariably, true. For K<sub>2</sub>O the assumption is correct at 10 and 20 kb but the data for 30 kb are inconsistent (fig. 1a). Fig. 1b shows that high TiO<sub>2</sub> in the rock results in early crystallization of phlogopite at 20 and 30 kb but not necessarily at 10 kb. Decreasing Al<sub>2</sub>O<sub>3</sub> in the rock appears to increase the proximity to the liquidus of early phlogopite crystallization at 10 and 20 kb (fig. 1c). As phlogopite does not occur in the 30 kb experiments using olivine ugandite with high Al<sub>2</sub>O<sub>3</sub> (Table I), no conclusions can be made regarding the effects of Al<sub>2</sub>O<sub>3</sub> on phlogopite crystallization at this pressure. Increasing CaO in the rock promotes phlogopite crystallization at 10 and 20 kb but shows no correlation at 30 kb (fig. 1d). Decreasing MgO in the rock promotes early phlogopite crystallization at 10 and 20 kb whereas the opposite trend occurs at 30 kb (fig. 1e).

The relationships shown in fig. 1, while simplistic and based on the few available data, suggest that the proximity of phlogopite crystallization to liquidus temperatures is not entirely related to the bulk composition of the rocks from which it crystallized. In addition to pressure, the principal causes for lack of such relationships may be the variable amounts of H<sub>2</sub>O added in the experiments and the preferential incorporation of certain oxides into the coexisting crystalline phases and liquids relative to phlogopite. These possibilities are considered in later sections.

The significant parameter in terms of crystallization of phlogopite is the degree of K<sub>2</sub>O relative to Na<sub>2</sub>O enrichment (as 100K/(K + Na) mol., Table I) in the rock composition. This parameter is significant because the phlogopites crystallized in the experiments on these rocks show negligible substitution of Na for K and there are no other K- and Na-bearing minerals except clinopyroxene which crystallize prior to, or with phlogopite (Edgar et al., 1976; Barton and Hamilton, 1979; Edgar et al., 1980; Arima and Edgar, in press). Clinopyroxenes have low Na<sub>2</sub>O (< 0.7 wt. %) in runs at 30 kb and only very minor Na<sub>2</sub>O at 10 and 20 kb with 5 and 15 wt. % H<sub>2</sub>O added (Edgar et al., 1976, Table 4; Edgar et al., 1980, Table 6; Arima and Edgar, in press).

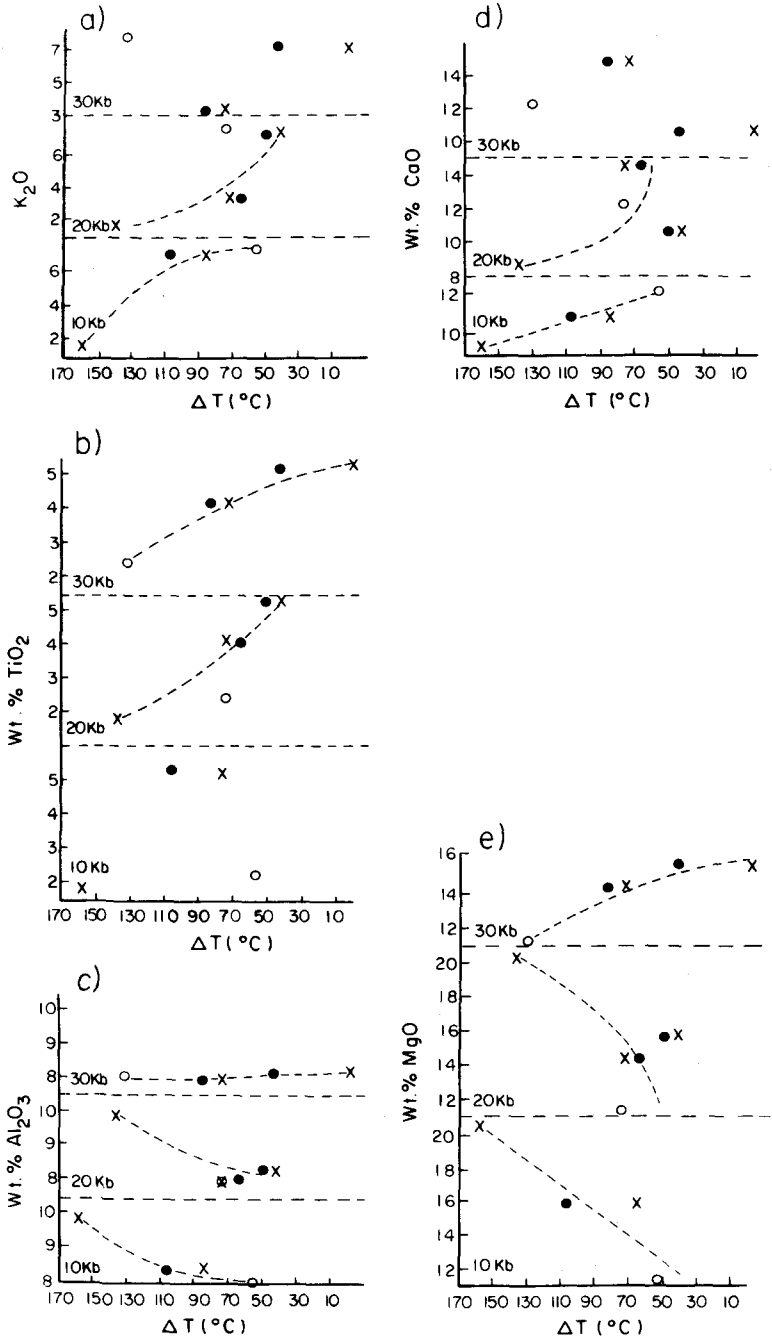


FIG. 1. Temperatures of initial crystallization of phlogopite relative to liquidus temperatures ( $\Delta T$ ) plotted against compositions of rocks used in experimental studies. Data for 10, 20, and 30 kb. Open circles, 2.97 wt. % H<sub>2</sub>O; filled circles, 5 wt. % H<sub>2</sub>O added; crosses, 15 wt. % H<sub>2</sub>O added. Trends indicated by dashed lines.

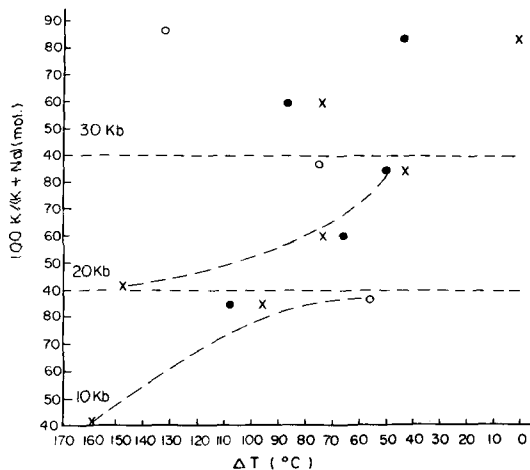


Fig. 2. Temperatures of initial crystallization of phlogopite relative to liquidus temperatures ( $\Delta T$ ) plotted against  $100K/(K + Na)$  for rocks used in experimental studies (see Table 1). Data for 10, 20, and 30 kb. Symbols as in fig. 1.

Fig. 2 shows  $100K/(K + Na)$  plotted against the temperature of crystallization of phlogopite relative to liquidus temperatures ( $\Delta T$ ) for the same compositions used in fig. 1. For the olivine ugandite, katungite and biotite mafurite, there is a progressive increase in  $\Delta T$  with increasing  $100K/(K + Na)$ . In contrast, the madupite, with  $100K/(K + Na)$  comparable to that of the biotite mafurite, shows a decrease in crystallization temperature with pressure. As the compositions of these rocks are otherwise comparable, the most likely explanation is the difference in the amounts of  $H_2O$  present in these experiments.

**Activity of  $H_2O$ .** The amount of  $H_2O$  in the bulk compositions of the rocks plotted in fig. 1, either as  $H_2O^+$  in the analyses or as the  $H_2O$  added in the experimental runs, is a rough approximation of the  $a_{H_2O}$  in the liquid from which phlogopite has crystallized as there are no vapour and hydroxyl-bearing phases which crystallize prior to phlogopite in any of the experiments. In fig. 1, the amount of  $H_2O$  in the experiments shows that at 30 kb relatively higher  $a_{H_2O}$  (15 wt. %  $H_2O$  added) favours early crystallization of phlogopite relative to lower  $a_{H_2O}$  (5 wt. % added). This effect is less pronounced at 10 and 20 kb and, in some cases the  $\Delta T$  values for both 5 and 15 wt. %  $H_2O$  added are within the limits of experimental error. The biotite mafurite is the only ultrapotassic rock in which phlogopite is observed on the liquidus at 30 kb with 15 wt. %  $H_2O$  added (Edgar *et al.*, 1976, Table 2). The same rock with 40 wt. %  $H_2O$  added at 30 kb (representing  $H_2O$ -saturated liquid) does not crystallize

phlogopite until about  $100^\circ C$  below the liquidus temperature and with 25 wt. %  $H_2O$  added at 20 kb (close to  $H_2O$ -saturated liquid) phlogopite first appears  $50^\circ C$  below the liquidus temperature (Edgar *et al.*, 1976, Table 2). For the olivine ugandite- $H_2O$  system (Edgar *et al.*, 1980, Table 2), phlogopite occurs  $50^\circ C$  below the liquidus in experiments with 25 wt. % added  $H_2O$  at 20 kb but does not appear in experiments with 40 wt. % added  $H_2O$  at least  $25^\circ C$  below the liquidus. These results, although by no means conclusive, suggest that at pressures ranging from 20 to 30 kb there is a critical range of  $a_{H_2O}$  which promotes early crystallization of phlogopite from ultrapotassic magmas.

**Fugacity of oxygen.** The majority of experiments (Barton and Hamilton, 1979; Edgar *et al.*, 1976, 1980; Arima and Edgar, in press) in which phlogopite crystallizes from ultrapotassic rock compositions have been done under  $f_{O_2} > NNO$  buffer as determined by the furnace buffering method (cf. Brey and Green, 1977). Ryabchikov and Green (1978) examined the same biotite mafurite composition studied by Edgar *et al.* (1976) using an HM buffer assemblage at 30 kb pressure and with the same added  $H_2O$  content. Comparison of these experiments indicates that variations in  $f_{O_2}$  have little effect on the proximity of phlogopite to liquidus temperatures at this pressure. However,  $f_{O_2}$  variations produce very marked changes in the compositions of the phlogopites, particularly with respect to  $TiO_2$  contents (see later).

**Activity of  $CO_2$ .** Although no extensive investigations have been made to determine the effects of  $a_{CO_2}$  on phlogopite crystallization from liquids of ultrapotassic compositions, it appears that crystallization of phlogopite is suppressed by high  $a_{CO_2}$ . In experiments on the same biotite mafurite composition used by Edgar *et al.* (1976), Ryabchikov and Green (1978, fig. 1) showed that at 30 kb phlogopite crystallization decreased rapidly from a liquidus phase at  $X_{CO_2} = 0-0.25$ , where  $X_{CO_2} = CO_2/(CO_2 + H_2O)$  mol., to a phase occurring almost  $100^\circ C$  below the liquidus at  $X_{CO_2} = 0.50$ . The amount of volatile component ( $CO_2 + H_2O$ ) added in Ryabchikov and Green's experiments was calculated molecularly equivalent to the 15 wt. %  $H_2O$  added. Neither the olivine ugandite nor the katungite compositions investigated with  $H_2O + CO_2$  produced any phlogopite at least  $130^\circ C$  below their liquidus although the conditions were limited to  $X_{CO_2} > 0.25$  (Edgar *et al.*, 1980; Arima and Edgar, in press). The main effect of added  $CO_2$  in terms of phlogopite crystallization may be to reduce the  $a_{H_2O}$  below that of the 5 to 15 wt. %  $H_2O$  level and hence reduce the stability of phlogopite close to the liquidus.

*Effect of rock composition on the compositions of early crystallizing phlogopites*

Comparison of the compositions of the ultrapotassic rocks for which high pressure experimental data are available with the compositions of the first phlogopites to crystallize (Barton and Hamilton, 1979; Edgar *et al.*, 1976, 1980; Ryabchikov and Green, 1978; Arima and Edgar, in press) indicates no correlation between bulk rock and phlogopite compositions. Excepting the 30 kb experiments (15 wt. % H<sub>2</sub>O added) on the biotite mafurite (Edgar *et al.*, 1976), where phlogopite occurs on the liquidus, the majority of phlogopites crystallize from liquids which have already crystallized one or more of the following: olivine, clinopyroxene, or spinels. Under the conditions where phlogopite crystallizes from the residual liquid, spinels are a very minor phase and their influence on the residual liquid composition is negligible, at least in terms of major elements. The main effect of crystallization of olivine and clinopyroxene, with respect to phlogopite crystallization from a residual liquid, will be the MgO and FeO.

Edgar *et al.* (1976) showed that the partitioning of Mg and Fe between phases coexisting with phlogopite in the biotite mafurite-H<sub>2</sub>O system at  $T > 1000^\circ\text{C}$  and with  $Mg/(Mg + Fe_T)$  of approximately 0.8–0.95 was such that\*:

$$M_{ilm} \ll M_{liq} < M_{ol} < M_{cpx} = M_{phl}$$

Similar calculations for the same composition with added H<sub>2</sub>O and CO<sub>2</sub> (Ryabchikov and Green, 1978) indicates the relationship:

$$M_{liq} \ll M_{cpx} < M_{phl} = M_{ol}$$

at  $X_{CO_2} \sim 0.25$  and  $T = 1300^\circ\text{C}$ . At  $X_{CO_2} \sim 0.50$  and  $T = 1200^\circ\text{C}$ , where orthopyroxene is present and olivine absent, the relationship is:

$$M_{liq} \ll M_{cpx} = M_{phl} < M_{opx}$$

Both relationships are for  $M$  of 0.8 to 0.9 approximately. For the madupite (Barton and Hamilton, 1979), limited analyses of coexisting phases indicate that at  $T > 1200^\circ\text{C}$  the relationship is:

$$M_{liq} \ll M_{cpx} \lesssim M_{phl}$$

for  $M$  in the same range as those of the biotite mafurite. For the olivine ugandite (Edgar *et al.*,

1980), with a comparable  $M$  value, the relationship at  $T \gtrsim 1000^\circ\text{C}$  is:

$$M_{cr} \ll M_{liq} \ll M_{phl} \lesssim M_{cpx} < M_{ol}$$

Experiments on the katungite (Arima and Edgar, in press), with a lower  $M$ , show the relationship at  $T > 1000^\circ\text{C}$  is:

$$M_{ti-mt} \ll M_{liq} \ll M_{cpx} < M_{phl}$$

for  $M$  of approximately 0.7 to 0.9.

These relationships indicate that phlogopite tends to have a higher relative  $M$  value than other coexisting phases. The order of appearance of  $M_{phl}$  can be approximately correlated with the degree of K enrichment, as  $100K/(K + Na)$ , in the rock from which it crystallized.  $M_{phl}$  is higher in the madupite, biotite mafurite, and katungite, with  $100K/(K + Na)$  values of 86, 85, and 60 respectively, than in the olivine ugandite with  $100K/(K + Na)$  of 41. If the magma contains sufficiently high  $100K/(K + Na)$  to crystallize phlogopite, and provided phlogopite and other phases can fractionate, phlogopite would be more effective in reducing the  $Mg/(Mg + Fe_T)$  in residual liquids than olivine, clinopyroxene, spinels, or oxide minerals.

The partitioning of TiO<sub>2</sub> for phases coexisting with phlogopite shows that for the biotite mafurite-H<sub>2</sub>O system at  $T > 1000^\circ\text{C}$  (Edgar *et al.*, 1976),  $TiO_{2(cpx)} < TiO_{2(phl)}$ . For the same composition with  $f_{O_2} = HM$  phlogopite coexists with olivine, orthopyroxene, and clinopyroxene (Ryabchikov and Green, 1978),  $TiO_{2(ol)} < TiO_{2(opx)} < TiO_{2(cpx)} < TiO_{2(phl)}$  at  $T = 1300^\circ\text{C}$ . High  $f_{O_2}$ , TiO<sub>2</sub> is preferentially incorporated into phlogopite, as suggested by Arima and Edgar (1981). For the madupite-H<sub>2</sub>O system (Barton and Hamilton, 1979), the relationship is  $TiO_{2(cpx)} < TiO_{2(phl)}$  at  $T > 1200^\circ\text{C}$ , and for the olivine ugandite-H<sub>2</sub>O system (Edgar *et al.*, 1980), the relationship is  $TiO_{2(ol)} \ll TiO_{2(cpx)} < TiO_{2(phl)}$ . In the katungite-H<sub>2</sub>O system, titanomagnetite and perovskite coexist with clinopyroxene and phlogopite (Arima and Edgar, in press). This results in the relationship

$$TiO_{2(cpx)} \lesssim TiO_{2(phl)} < TiO_{2(Ti-mt)} < TiO_{2(pv)}$$

These results indicate that, in the absence of a Ti-bearing oxide phase, TiO<sub>2</sub> may be preferentially incorporated into phlogopite rather than clinopyroxene; and that the order of preferential incorporation of TiO<sub>2</sub> in the coexisting phases is unrelated to the amount of TiO<sub>2</sub> in the bulk rock composition. Based on experimental data, Arima and Edgar (1981) have shown an apparent independence between Ti solubility in phlogopites and the bulk compositions from which the phlogopites crystallized. The solubility of Ti increases with

\* In the following equations the abbreviations used are:  $M$ — $Mg/(Mg + Fe_T)$ , liq—bulk liquid, cpx—clinopyroxene, phl—phlogopite, ol—olivine, opx—orthopyroxene, ilm—ilmenite, cr—chromite, Ti-mt—titanomagnetite, pv—perovskite.

increasing temperature and  $f_{O_2}$  and decreases with increasing pressure.

#### Formation of phlogopite by reaction relations

Phlogopite may result from various high-pressure reaction relationships. The reaction of olivine and liquid to produce phlogopite occurs in the katungite composition (Arima and Edgar, in press) in which olivine disappears under the same  $P$ ,  $T$  conditions as phlogopite crystallizes between approximately 12 and 22 kb with 15 wt. % added  $H_2O$ . At higher pressures, olivine is absent and phlogopite crystallizes directly from a residual liquid. The reaction  $\text{phlogopite} + L^1 \rightleftharpoons \text{olivine} + L^2$  has been suggested by Edgar *et al.* (1976) as a mechanism for generation of K-enriched liquids with  $K_2O/Na_2O > 1$  and is clearly implied by textural relations in the rocks of Leucite Hills (Carmichael, 1967; Kuehner *et al.*, 1981). In their study of madupite from Leucite Hills, Barton and Hamilton (1979) noted that crystallization of phlogopite was accompanied by a decrease in olivine and by a possible increase in clinopyroxene crystallization, suggesting a reaction  $\text{forsterite} + L \rightleftharpoons \text{phlogopite} + \text{diopside}$ ; a reaction originally proposed by Modreski and Boettcher (1973).

Katungite lavas contain melilite as an abundant constituent (Holmes, 1950). In the katungite- $H_2O$  system at  $P$  greater than about 8–12 kb and at 950–1050 °C, clinopyroxene + phlogopite are the major phases whereas at lower pressure olivine +

melilite are the major phases (Arima and Edgar, in press). This suggests the reaction  $\text{clinopyroxene} + \text{phlogopite} \rightleftharpoons \text{olivine} + \text{melilite} + \text{liquid}$ , similar to that proposed by El-Goresy and Yoder (1974).

#### Phlogopites in ultrapotassic lavas

Phlogopite occurs as both a phenocryst (or microphenocryst) and as a groundmass mineral in many ultrapotassic lavas. A survey of the literature produced twenty-one analyses of unequivocally phenocryst or microphenocryst phlogopites from such lavas for which whole-rock analyses are also available. Assuming these phlogopites represent early crystallization from liquids whose compositions are approximately represented by the rock analyses, comparisons can be made between the phlogopite compositions and the coexisting rocks and between the natural phlogopites and those crystallized in high-pressure experiments on these rocks. Inferences regarding the physical conditions of formation of natural phlogopites in ultrapotassic rocks, based on the limited experimental data on these rocks, must be made with caution. Many natural phlogopites have compositions comparable with those crystallized in the experimental studies. Lack of independent indicators of  $P$ ,  $T$ , etc. in the rocks from which the natural phlogopites crystallized makes assessment of physical conditions difficult.

Analyses of phlogopites and their host rocks from various localities are given in Table II.

Table II. Chemical parameters of phlogopite phenocrysts (or microphenocrysts) and their host rocks. Ratios as molecular proportions.

Locality	Phlogopite				Host rock				Reference
	$\frac{K}{Al}$	$\frac{100 K}{K + Na}$	$\frac{K}{Ti}$	$\frac{100 Mg}{Mg + Fe_T}$	$\frac{K}{Al}$	$\frac{100 K}{K + Na}$	$\frac{K}{Ti}$	$\frac{100 Mg}{Mg + Fe_T}$	
Leucite Hills, Wyoming	0.97	98	4.19	94	1.18	87	3.42	74	Carmichael (1967) Kuehner <i>et al.</i> (1981)
	0.99	-	4.27	94	1.12	85	4.19	80	
Eifel, West Germany	0.63	90	1.47	73	0.24	34	1.14	56	Duda and Schmincke (1978)
	0.61	90	1.42	79	0.25	35	1.37	45	
	0.64	89	1.54	81	0.29	31	1.64	50	
Central Sierra Nevada, California	0.76	91	2.89	87	0.71	74	3.87	62	Van Kooten (1980)
	0.79	91	4.00	90	0.72	71	4.35	70	
	0.73	92	3.43	91	0.65	70	3.89	70	
	0.70	91	2.29	82	0.31	46	2.30	65	
West Kimberley, W. Australia	1.05	98	1.00	86	1.06	89	1.67	61	Prider (1960) Mitchell (1981) Unpublished data
	1.35	97	0.86	86	1.43	93	1.22	56	
	1.14	98	1.31	86	1.28	94	1.00	74	
	1.22	99	1.53	92	2.67	85	0.83	77	
	1.12	100	1.11	89	1.31	95	1.51	66	
	1.14	100	1.91	91	1.22	99	2.50	61	
	1.07	99	1.25	88	1.40	87	1.02	72	
1.17	100	1.37	86	1.18	100	2.64	56		
Jumilla, Spain	1.06	94	1.40	83	0.73	77	3.30	83	Carmichael (1967)
S.W. Uganda	0.83	98	1.07	63	1.00	88	1.28	78	Edgar (1979)
Smokey Butte, Montana	0.74	97	0.74	80	0.48	72	1.25	75	Velde (1975)
Buell Park, Arizona									

Excepting the Eifel locality, in which phlogopite phenocrysts occur in tephrites with  $\text{Na}_2\text{O} > \text{K}_2\text{O}$ , all other localities contain rocks with  $\text{K}_2\text{O} > \text{Na}_2\text{O}$ . The only rock for which experimental data are available is the biotite mafurite from SW Uganda (Edgar *et al.*, 1976; Ryabchikov and Green, 1978).

There is a wide range of oxide compositions for lavas in which phlogopite occurs as a phenocryst or microphenocryst (41–55 wt. %  $\text{SiO}_2$ , 3–16 wt. %  $\text{Al}_2\text{O}_3$ , 1.3–7.3 wt. %  $\text{TiO}_2$ , trace–6.5 wt. %  $\text{Na}_2\text{O}$ , and 3.1–12.7 wt. %  $\text{K}_2\text{O}$ ). The  $100\text{Mg}/(\text{Mg} + \text{Fe})$  for these rocks ranges from 45 to 84, with the majority between 65 and 80, probably indicating these are 'primitive' lavas (Ringwood, 1975). Comparable, but less extreme, ranges of oxide compositions

occur in the phlogopites—33.9–42.8 wt. %  $\text{SiO}_2$ , 8.1–16.0 wt. %  $\text{Al}_2\text{O}_3$ , 2.1–11.3 wt. %  $\text{TiO}_2$ , 0.0–0.72 wt. %  $\text{Na}_2\text{O}$  and 8.2–11.1 wt. %  $\text{K}_2\text{O}$ . The  $100\text{Mg}/(\text{Mg} + \text{Fe})$  values range from 63 to 94 and in all analyses, excepting the phlogopite from the biotite mafurite of SW Uganda (Edgar, 1979), are higher than those of their host rocks.

Fig. 3a–d shows variations in molecular ratios between phlogopite phenocrysts and microphenocrysts, and their host rocks. Molecular ratios have been used to avoid possible errors caused by variations in the totals of the phlogopite and rock analyses.

In fig. 3a  $(\text{K}/\text{Al})_{\text{rock}}$  shows a positive correlation with  $(\text{K}/\text{Al})_{\text{phl}}$  with an approximate trend  $[(\text{K}/\text{Al})_{\text{phl}} \div (\text{K}/\text{Al})_{\text{rock}}]$  of  $\sim 0.5$ . This correlation

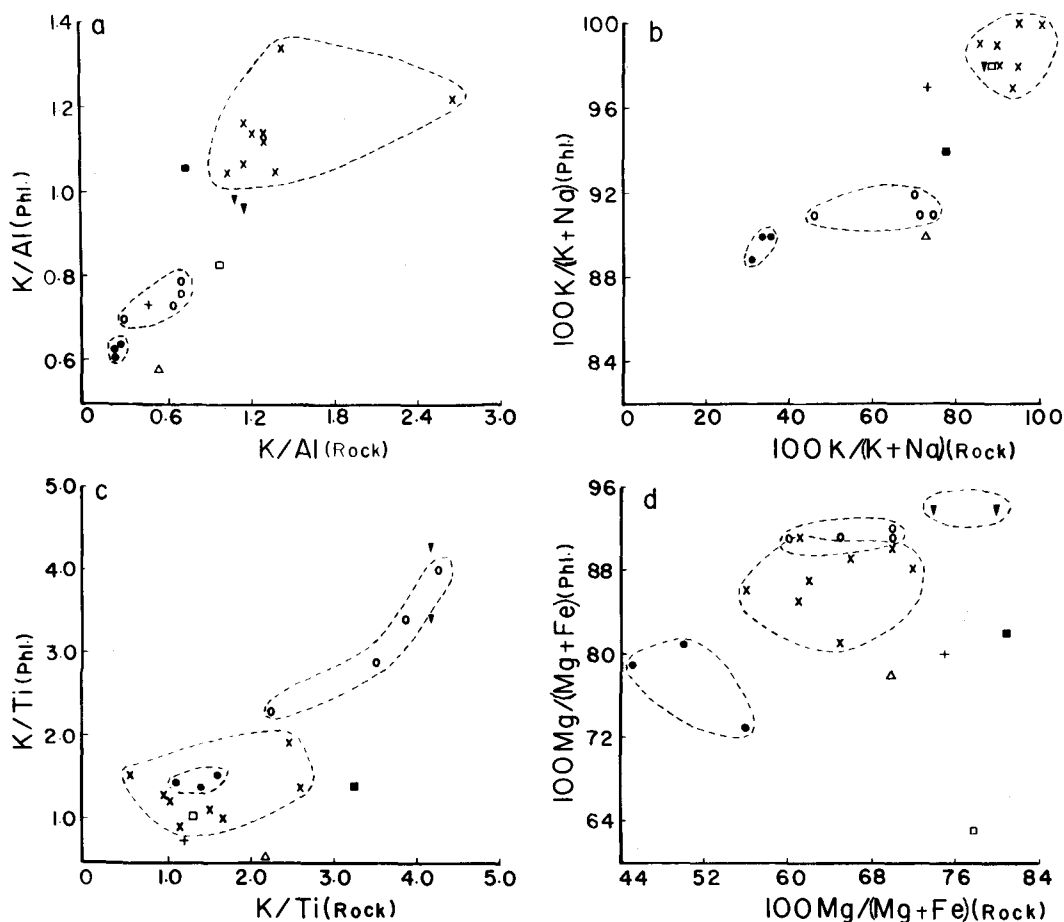


FIG. 3. Variations in chemical compositions of phlogopite phenocrysts and microphenocrysts relative to their host rocks. (a)  $(\text{K}/\text{Al})_{\text{phl}}$  vs.  $(\text{K}/\text{Al})_{\text{rock}}$ , (b)  $[100\text{K}/(\text{K} + \text{Na})]_{\text{phl}}$  vs.  $[100\text{K}/(\text{K} + \text{Na})]_{\text{rock}}$ , (c)  $(\text{K}/\text{Ti})_{\text{phl}}$  vs.  $(\text{K}/\text{Ti})_{\text{rock}}$ , (d)  $[100\text{Mg}/(\text{Mg} + \text{Fe})]_{\text{phl}}$  vs.  $[100\text{Mg}/(\text{Mg} + \text{Fe})]_{\text{rock}}$ . Symbols:  $\nabla$  = Leucite Hills, Wyoming;  $\circ$  = Central Sierra Nevada;  $\times$  = West Kimberley, W. Australia;  $\bullet$  = Eifel, Germany;  $\triangle$  = Buell Park, Arizona;  $\blacksquare$  = Jumilla, Spain;  $\square$  = SW Uganda;  $+$  = Smokey Butte, Montana. Dashed lines indicate ranges of analyses for major localities.

suggests that phlogopite compositions are closely controlled by the liquids from which they crystallize. The slope of the trend in fig. 3a as well as some of the scatter in the data may be explained by the effect of crystallization of clinopyroxene prior to phlogopite which, if abundant, may deplete the Al content in residual liquids from which the phlogopite crystallizes. This buffering effect of clinopyroxene will be more pronounced in rocks, such as those of Eifel and Sierra Nevada (cf. Duda and Schminke, 1978; Van Kooten, 1980) in which the  $\text{Al}_2\text{O}_3$  content of clinopyroxenes is higher than in those of the Leucite Hills and West Kimberley rocks (cf. Carmichael, 1967; Kuehner *et al.*, 1981). Fig. 3a shows that the rocks from the latter localities have  $(\text{K}/\text{Al})_{\text{rock}}$  values similar to those of their phlogopites whereas the former localities have  $(\text{K}/\text{Al})_{\text{phl}} > (\text{K}/\text{Al})_{\text{rock}}$ .

Fig. 3b shows the relationship of  $[100\text{K}/(\text{K} + \text{Na})]_{\text{phl}}$  vs.  $[100\text{K}/(\text{K} + \text{Na})]_{\text{rock}}$  and suggests that with increasing  $100\text{K}/(\text{K} + \text{Na})$  in the rock there is a progressive increase in the  $100\text{K}/(\text{K} + \text{Na})$  in the phlogopite; with the trend becoming asymptotic for some of the phlogopites from the West Kimberley rocks which contain no detectable  $\text{Na}_2\text{O}$ . Rocks with high  $\text{K}/(\text{K} + \text{Na})$  values will probably always crystallize phlogopites with relatively high  $\text{K}/(\text{K} + \text{Na})$  due to the K-Na substitution in phlogopites. Prior crystallization of clinopyroxene, a common phenocryst mineral in ultrapotassic lavas and the only other early crystallizing mineral likely to contain  $\text{Na}_2\text{O}$ , will not have a significant buffering effect on Na-K substitution in phlogopite as most clinopyroxenes in these lavas are very Na-poor (cf. Barton, 1979).

Plots of  $(\text{K}/\text{Ti})_{\text{rock}}$  vs.  $(\text{K}/\text{Ti})_{\text{phl}}$  (fig. 3c) show the same tendency as shown in fig. 3a but with a slope  $(\text{K}/\text{Ti})_{\text{phl}}/(\text{K}/\text{Ti})_{\text{rock}}$  of  $\sim 1$ . This suggests that even previously crystallized clinopyroxene, which in ultrapotassic rocks is moderately Ti-rich (cf. Barton, 1979), does not have a significant buffering effect on Ti content of phlogopites. In contrast to phlogopite, no correlation can be found between the  $\text{TiO}_2$  content of clinopyroxenes and their host rocks. If clinopyroxenes and phlogopites are in equilibrium in ultrapotassic rocks, as the common association of these minerals as phenocrysts would suggest, then the data in fig. 3c may imply that the  $\text{TiO}_2$  in phlogopite is controlled by the  $\text{TiO}_2$  content of the liquid whereas the  $\text{TiO}_2$  content of clinopyroxene is less affected by the liquid.

Phlogopites in ultrapotassic rocks often have very high  $\text{TiO}_2$  and low  $\text{Al}_2\text{O}_3$  contents. Distribution of these elements between octahedral and tetrahedral sites in the phlogopite structure is difficult to ascertain without knowledge of the  $\text{Fe}^{3+}$  contents which microprobe analyses do not pro-

vide. Based on optical absorption spectra, Farmer and Boettcher (1981) propose that the sequence of tetrahedral site preference in phlogopites from kimberlites and associated ultramafic xenoliths is  $\text{Si} > \text{Al} > \text{Ti} > \text{Fe}^{3+}$ . Mossbauer spectra of an Al-poor phlogopite from a wyomingite of Leucite Hills (Arima and Edgar, 1981) however suggests that  $\text{Fe}^{3+}$ , rather than Ti preferentially substitutes in the tetrahedral site.

The  $[100\text{Mg}/(\text{Mg} + \text{Fe}_T)]_{\text{phl}}$  vs.  $[100\text{Mg}/(\text{Mg} + \text{Fe}_T)]_{\text{rock}}$  plot (fig. 3d) suggests a positive relationship. The one phlogopite which clearly does not follow this relationship is that from the biotite mafurite (Edgar, 1979). Analysis of this phlogopite differs from the compositions of the phlogopites produced in the experimental studies on the same rock composition under low  $f_{\text{O}_2}$  conditions roughly corresponding to the NNO buffer (Edgar *et al.*, 1976, Table 5) but is closer to the phlogopite produced in the experiments at higher  $f_{\text{O}_2}$  corresponding to the HM buffer (Ryabchikov and Green, 1978, Table 3). As analysis of the natural phlogopites was done by microprobe, and hence  $\text{Fe}_2\text{O}_3$  was not determined, the  $100\text{Mg}/(\text{Mg} + \text{Fe}_T)$  value may actually be greater than that shown in fig. 3d, although it is unlikely that lack of  $\text{Fe}_2\text{O}_3$  analysis would be sufficient to raise the  $100\text{Mg}/(\text{Mg} + \text{Fe}_T)$  close to the trend. The possibility that the biotite mafurite composition does not represent the liquid from which the phlogopite crystallized is unlikely as this lava has a 'primitive' composition in terms of  $100\text{Mg}/(\text{Mg} + \text{Fe}_T)$  and the phlogopite is clearly an early crystallizing mineral. The trends shown by the biotite mafurite in fig. 3a-c also support this conclusion.

The relations in fig. 3d are highly sensitive to the amounts of olivine, clinopyroxene, and other ferromagnesian minerals which may crystallize prior to phlogopite.

Fig. 3a-d show that the compositions of phenocryst and microphenocryst phlogopites generally mimic the compositions of their host rocks. In contrast to phenocryst phlogopites, those occurring in the groundmass of ultrapotassic rocks, either together with phenocryst varieties or only in the groundmass, have quite different compositions notably in their lower  $\text{Al}_2\text{O}_3$  and higher  $\text{TiO}_2$  contents (cf. Edgar, 1979; Van Kooten, 1980).

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