Water-undersaturated melting experiments bearing upon the origin of potassium-rich magmas

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ABSTRACT. The water-undersaturated melting relationships of an orendite (with 1.23% H₂O as shown by chemical analysis) from the Leucite Hills, Wyoming, have been determined at pressures up to 30 kbar. The dominant liquidus and near-liquidus phases are leucite, olivine, orthopyroxene, clinopyroxene, and garnet. Leucite is stable only at pressures below 5 kbar, but at 27 kbar, minor olivine, orthopyroxene, clinopyroxene, and garnet crystallize simultaneously at or near the liquidus. The following reaction relationships occur with falling temperature in the orendite magma: (a) a reaction between olivine and melt to yield orthopyroxene at pressures above 12 kbar; (b) a reaction between olivine and melt to yield phlogopite at pressures below 12 kbar; (c) a reaction between olivine, orthopyroxene and melt to yield phlogopite and probably clinopyroxene at pressures above 12 kbar; (d) a reaction between leucite and melt to yield sanidine at pressures below 5 kbar. Electron microprobe analyses demonstrate that the ortho- and clinopyroxenes crystallized from orendite are aluminiumpoor; the clinopyroxenes contain insufficient aluminium to balance sodium and titanium (Al < Na+2Ti) and these elements must either be partly balanced by (undetermined) chromium or ferric iron or be involved in substitutions which do not require trivalent ions for charge balance. The experimental results indicate that relatively silica-rich potassic magmas such as orendite form under water-undersaturated (essentially carbon dioxide free) conditions at pressures of about 27 kbar by small degrees of melting of phlogopite-garnet-lherzolite or by larger degrees of melting of peridotite which has been enriched in potassium and incompatible elements. The peralkalinity of some potassic magmas (such as orendite and wyomingite) could reflect a primary geochemical characteristic of the source rock, but could also result from the melting of phlogopite in the presence of residual pyroxenes. The association of silica-poor, mafic madupites and relatively silica-rich orendites and wyomingites in the Leucite Hills can be explained in terms of the relative effects of water and carbon dioxide on melting processes within the upper mantle.

POTASSIUM-RICH volcanic and hypabyssal rocks are characterized by high $K_2O:Na_2O$ ratios (> 2:1) and high contents of incompatible elements. The abundacne of other elements varies considerably (Sahama, 1974), and even in a single area both ultrabasic and phonolitic lavas can occur (e.g. the Leucite Hills, Wyoming). The rocks are alkaline and are characterized by the presence of feldspathoids (usually leucite and, or, kalsilite), alkali amphiboles and, or, alkali pyroxenes. Other commonly occurring minerals are diopsidic augite, phlogopite, sanidine, plagioclase, olivine and melilite.

The unusual chemical and mineralogical characteristics of K-rich alkaline rocks have led to many hypotheses for their origin (e.g. Sahama, 1974). These can be broadly divided into three groups: (a) those including various processes of assimilation of crustal material with or without selective enrichment of potassium and associated elements by gaseous transfer (Rittmann, 1933; Holmes, 1950; Marinelli and Mittempergher, 1966); (b) those involving the high-pressure fractionation of picritic or alkali-ultrabasic magmas (Wade and Prider, 1940; Borley, 1967; O'Hara and Yoder, 1967); (c) those whereby potassic melts are considered to originate as primary magmas in the upper mantle (Kay and Gast, 1973; Carmichael et al., 1974; Ferguson and Cundari, 1975).

Recent geochemical and experimental studies have failed to discriminate satisfactorily between the various hypotheses. The limestone assimilation hypothesis seems to lack universal applicability on geological grounds (Holmes, 1950; Prider, 1960; Borley, 1967) and is incompatible with experimental data (e.g. Wyllie, 1974) and with strontium and oxygen isotope data (e.g. Powell and Bell, 1974; Turi and Taylor, 1976). Isotope studies have been used to support assimilation hypotheses (e.g. assimilation of sialic rocks by nephelinite or carbonatite) for the rocks of some localities (Barbieri et al., 1975; Turi and Taylor, 1976) but it appears that assimilation alone cannot account for all of the geochemical characteristics of K-rich lavas, such as their high K, Rb and, in some cases, Ni and Cr contents. Evidence that K-rich alkaline magmas are derived by the high-pressure fractional crystallization of picritic or alkali ultrabasic magmas (i.e. cognate xenoliths or xenocrysts of high-pressure origin) is lacking in most localities (e.g. Prider, 1960). Finally, high-pressure melting experiments on a madupite (Barton and Hamilton, 1979), a biotite-mafurite (Edgar et al., 1976) and a clinopyroxene-leucitite (Thompson, 1977) indicate that mafic K-rich magmas are not the melting products of anhydrous or hydrous lherzolite, but the possibility that CO₂ is of major importance in the genesis of these magmas (e.g. Edgar and Condliffe, 1978; Ryabchikov and Green, 1978; Wendlandt, 1977) or that they are derived from mantle of abnormal composition (e.g. Lloyd and Bailey, 1975; Hawkesworth and Vollmer, 1979) cannot be ruled out.

In this paper the results of water-undersaturated melting experiments on an orendite from the Leucite Hills, Wyoming, are presented. These results have an important bearing upon the origin of relatively silica-rich, potassic alkaline rocks.

Rock chosen for study

An orendite from the Leucite Hills was chosen for study for the following reasons:

(a) The lavas are highly magnesian, most having 100Mg/(Mg + ΣFe^{2+})* ratios between 72 and 82. Judging from the petrography of the lavas, the high Mg-Fe ratios do not result from the presence of cumulate ferromagnesian phases, and it seems unlikely that such highly magnesian magmas are the fractionation products of more mafic picritic or ultramafic lavas.

(b) The modal ferromagnesian minerals are also highly magnesian; clinopyroxene is almost pure diopside and olivine is in the range Fo_{94-90} (Carmichael, 1967). This is within the range of olivine composition believed to occur in the upper mantle (e.g. Ringwood, 1975; O'Hara *et al.*, 1975) suggesting that the Leucite Hills orendites could represent primary magmas.

(c) Carmichael *et al.* (1974) and Barton and Wood (1976) have calculated that orendite could have been in equilibrium with a lherzolite mineral assemblage at pressures > 25 kbar.

*Total iron calculated as Fe²⁺.

A sample of orendite from North Table Mountain, previously studied by Carmichael (1967) and Barton (1979), was selected for experimental study. This lava contains phenocrysts and microphenocrysts of phlogopite (up to 2-3 mm but often < 1 mm) set in a dark-coloured, fine-grained groundmass of leucite, sanidine, diopside, potassic richterite, apatite, and accessory phases (priderite, wadeite). A chemical analysis of this lava (from Carmichael, 1967, Table 12) is given in Table I together with a CIPW norm. The orendite is characterized by high K₂O, SrO, BaO, ZrO₂, and $100Mg/(Mg + \Sigma Fe^{2^{-1}})$, moderately high SiO₂ and relatively low Al₂O₃ and Na₂O. The CIPW norm contains acmite, potassium metasilicate and quartz.

Quartz-normative K-rich lavas are not common, though they do occur in other localities besides the Leucite Hills (e.g. West Kimberley, Australia; Wade and Prider, 1940; Prider, 1960). The appearance of quartz in the norm is not due to secondary silicification or the high Fe_2O_3/FeO ratio of orendite. In the Leucite Hills there appears to be complete chemical gradation between the quartznormative orendites and olivine-normative orendites and wyomingites (Carmichael, 1967) and thus the orendite used in this study may be considered to be representative of silica-rich, potassic magmas.

 TABLE I. Chemical analysis and CIPW norm of orendite A 1770
 1770

Chemio	al analysis*	CIPW norm
SiO ₂	55.14	Q 2.28
TiO ₂	2.58	Z 0.41
ZrO_2	0.27	or 57.54
Al_2O_3	10.35	lc —
Cr_2O_3	0.04	ne —
Fe_2O_3	3.27	th 0.72
FeO	0.62	ac 6.83
MnO	0.06	ns —
MgO	6.41	ks 3.68
CaO	3.45	di 1.23
SrO	0.26	hy 15.69
BaO	0.52	ol —
Na ₂ O	1.21	cm 0.06
K₂Ō	11.77	hm 0.97
P_2O_5	1.40	il 1.42
H_2O^+	1.23	tn 4.61
H_2O^-	0.61	ap 3.29
CO ₂	0.20	
SO3	0.40	
Fotal	99.79	98.73

 $100 \text{ Mg/(Mg + }\Sigma Fe^{2+}) \quad 76.23$

* Carmichael, 1967, Table 12.

Experimental procedures

Starting materials (dried, fine rock powders) were reacted in sealed platinum capsules. In the high-pressure experiments the only water present was that bound structurally in hydrous minerals (1.23 wt. %), and this amount of water was insufficient to saturate liquidus charges even at 1 kbar. Some CO_2 and SO_3 were also present in the experiments (Table I).

The experiments were carried out in a one atmosphere furnace, in an argon-filled, internally-heated pressure vessel (up to 5 kbar) and in a solid-media, piston-cylinder device using a furnace assembly containing both tale and boron nitride; piston-out technique was used exclusively. Temperatures, which were measured with Pt-Pt 13% Rh thermocouples calibrated periodically at the melting point of pure gold, are uncorrected for the effects of pressure on the *emf* and are considered to be precise to ± 5 °C for runs at 5 kbar and below and ± 10 °C for piston-cylinder runs. Pressures of runs at 10 kbar and above are uncorrected for possible friction effects, but calibration of the piston-cylinder apparatus with respect to other laboratories yielded close agreement with published results (Hensen and Barton, 1976).

Unfortunately, most of the experiments reported in this paper were completed before the results of Merrill and Wyllie (1973) and Stern and Wyllie (1975) on the loss of iron to platinum capsules were available, and thus no special precautions (e.g. the use of Ag-Pd capsules) were taken to reduce Fe loss. In any case, Pt is the only suitable capsule material for water-bearing experiments at high temperatures. Chemical analyses indicate that 50-80% of the initial Fe was lost during high-pressure, near-liquidus experiments of 0.75-2 h duration on orendite. These Fe losses are comparable with those found by Merrill and Wyllie (1973) and Stern and Wyllie (1975) for runs of similar duration. We consider that the loss of 50-80% of the initial Fe from an orendite containing 3.6% total FeO will have less effect on the phase relationships than the loss of similar proportions of the initial Fe from basaltic or andesitic melts containing 6-14% total FeO. Experiments in which Fe was added to the orendite to compensate for Fe loss suggest that the loss of these amounts of iron shifts near-liquidus phase boundaries to higher temperatures by as much as 30°C, but does not alter the relative order of appearance of the phases. In addition, several near-liquidus experiments on orendite at 20 and 30 kbar were duplicated using run times of 0.25, 0.5, and 1 h. No change in the phase assemblage produced in the runs of different duration was observed, though undoubtedly the Mg/(Mg + ΣFe^{2+}) ratios of the minerals and melt varied as a function of run duration.

Several phase boundaries were reversed by holding charges at some temperature above a previously determined phase boundary and then cooling to a temperature below that of the boundary. Reversals introduce additional problems such as increased iron-loss due to longer run durations, which may cause phase boundaries to shift as a function of time (e.g. see Stern and Wyllie, 1975), and, particularly in reversals of the liquidus, nucleation failure (e.g. Gibb, 1974; Donaldson, 1979). In spite of these problems, however, the phase assemblages produced in the reversal runs were in all cases identical with those in the non-reversed runs, though the relative proportions of the phases differed in the two types of runs. In the reversals of the liquidus, for example, there was an overall reduction in the amount of crystals, with garnet being relatively less abundant and clinopyroxene more abundant than in single-stage runs.

Charges were examined optically and by X-ray diffraction. Particular care was taken to distinguish optically between primary and quench phases. In the case of phlogopite the textural criteria given by Yoder and Kushiro (1969) proved useful. In addition, quench phlogopite was always more strongly pleochroic than primary phlogopite. Quench clinopyroxene tended to form smaller, less euhedral crystals than primary clinopyroxene. Analyses of primary crystalline phases were obtained with a Cambridge Geoscan microanalyser using an accelerating voltage of 15 kV and a specimen current of around 15 na. A variety of synthetic minerals, glasses, and pure metal standards was used. Where possible, more than six grains of each phase in any charge were analysed and the analyses averaged.

Experimental results and phase relationships

The results of the melting experiments are listed in Table II and have been used to construct the phase diagram in fig. 1. Many of the difficulties involved in the identification of the phases and in the determination of the phase boundaries are similar to those discussed by Barton and Hamilton (1979). The tabulated results and the phase diagram refer to the Fe-depleted orendite but, as noted previously, the phase relationships of natural orendite magma can be discussed on the basis of these data.

At low pressures the melting interval is dominated by olivine, leucite, clinopyroxene, and phlogopite, with olivine and leucite as primary liquidus phases. The results at 1 atmosphere differ slightly from those reported by Carmichael (1967) for the same rock: we locate the liquidus about 35 °C higher at ~ 1250 °C and find that leucite is the primary liquidus phase and that olivine crystallizes a few degrees below the liquidus. Leucite is eliminated from the phase assemblage at some pressure between 1 atmosphere and 5 kbar and olivine is the sole primary liquidus phase until it is joined by orthopyroxene at 12 kbar (~ 1250 °C). There is a decrease in the amount of olivine when orthopyroxene begins to crystallize indicating the existence of a reaction relationship between olivine and melt at pressures of about 12 kbar with orthopyroxene as the product. Olivine appears to continue to crystallize at higher pressures, however, but it forms small crystals and occurs in small amounts which makes positive identification difficult. Clinopyroxene joins orthopyroxene and minor olivine on the liquidus at ~ 25 kbar

i		(trours)	
Total Pre	Pressure = 1	Atmosphere	
A5 1255	55 6	G1	
AB 1243	13 24	G1 + (Ic)	
A16 1230	9	G1 + Lc + 01	
A18 1175	5 24	G1 + Lc + 01	
		G1 + Lc + O1 + (Cpx)	
A21 1125	5 24	G1 + Ic + 01 + Cpx	
A24 1075	5 12	G1 + Lc + 01 + Cpx	
A24R 1075	5 15	G1 + Lc + O1 + Cpx	Reversed from 1300 [°] C
A27 1050	0 24	G1 + Lc + (01) + Cpx	
A30 1025	5 24	GI + Ic + (01) + Cpx + San	Leucite decreased in amount
A33 1000	0 48	(G1) + Lc + (O1) + Cpx + San	Glass very rare - may be absent
A36 975	5 48	Lc + (OI) + Cpx + San + Ph	Residual phlogopite
A36R 975	5 58	Lc + (01) + Cpx + San	Reversed from 1300 ⁰ C. Leucite de-
			creased
A39 925	5 120	Lc + (01) + Cpx + San + Ph + Amph.	Residual
A39R 925	5 130	Lc + (01) + Cpx + San	Reversed from 1300°C. Leucite de-
Total Pre	Pressure = 5	5 kbar	creased
285 1200	4	61	Abundant guench phlogopite
289 1175	4	61 + 01	Abundant guench phlogonite
~		+	
		;	abundant than at 1175°C. Abundant
273 1150	4	G1 + 01	Ouench phlogopite present
		x:0 + 4a + 60 + 60	Colourises subsdral which not
269 1100	e C	61 + Ph + Cnv	abundant
			Class there wave
		- (FDC)	Class voly tale
		GW: + URS + 300 + UA + (TS)	LUSSOR ATOROCOL SETA
Total Pre-	Pressure = 10 kbar) kbar	
1062 12	1250 1	G1 81	Rare guench phlogopite
1056 12:	1225 0.75	GI + 01	Large, euhedral olivine crystals
1057 12	1200 1	G1 + 01 + (Cpx) + 75p 0.	Olivine decreased slightly in abundance
1061 11	1150 2	G1 + (01) + Cpx + 7Sp + Ph 34	Rare olivine probably present
1059 11	1100 7.75	GI + Cpx + Ph + 7Sp + San + 3Ap	
Total Pre	Pressure = 1	~3	
		G1 + 01 + 0mx	Charge first held at 1300 ⁰ C for 15 minutes
	2	51	:
1073 11	-	61 8	Raze quench phiogopite
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1100 9.25 $c1$ cyx ct Pressure 27 kbar ct tt 1330 1 ct ct tt tt 13130 1 ct tt tt tt tt 13130 2 ct tt tt tt tt 13130 2 ct tt tt tt tt 1310 1.55 ct tt tt tt tt 1310 1.55 ct tt tt tt tt 1200 2.5 ct tt tt tt tt 1200 1.5 ct tt tt tt tt 1200 2.5 ct tt tt tt tt tt 1300 0.5 ct tt tt tt tt tt 1200 1.5 ct tt tt tt tt tt tt	Revei
Pressure 271 kbar 1380 1 c1 cpx e01 1350 1 c1 cpx e01 1350 1.3 c1 cpx e01 1350 1.3 c1 cpx e01 1350 1.5 c1 cpx e01 1310 1.55 c1 cpx e01 1310 1.55 c1 cpx e01 1290 2 c1 cpx e01 1200 3.5 c1 cpx e0 1200 2.5 c1 cpx e0 1300 16.75 c1 cpx e0 1400 0.75 c1 cpx e0 1300 0.75 c1 cpx e0 1320 0.75 c1 cpx e0 1320 0.75 c1 cpx e0 1200 1 c1 cpx ct <td></td>	
1380 1 c1 1350 1 c1 $0px$ o1 1350 1.3 c1 $0px$ o1 1330 1.3 c1 $0px$ o1 1330 2 c1 $0px$ o1 1310 1.5 c1 $0px$ o1 1310 1.55 c1 $0px$ o1 1290 2 c1 $0px$ o1 1200 3.5 c1 $0px$ o2 1300 16.75 c1 $0px$ etc 1400 0.75 c1 $0px$ etc 1300 0.55 c1 $0px$ etc 1300 0.75 c1 $0px$ etc 1320 1.75 <td>present</td>	present
1130 1 $c1$ $c1$ $c1$ $c2$ $c1$ $c2$ $c1$ 1130 2 $c1$ $c2$ $c1$ $c2$ $c1$ 11310 1.5 $c1$ $c2$ $c1$ $c2$ $c1$ 11310 1.55 $c1$ $c2$ $c2$ $c1$ $c2$ $c1$ 11310 1.55 $c1$ $c2$ $c2$ $c2$ $c2$ $c2$ 1200 2.5 $c1$ $c2$ $c2$ $c2$ $c2$ $c2$ 1200 2.5 $c1$ $c2$ $c2$ $c2$ $c2$ $c2$ 1200 2.5 $c1$ $c2$ $c2$ $c2$ $c2$ $c2$ 1200 16.75 $c1$ $c2$ $c2$ $c2$ $c2$ $c2$ 1300 0.75 $c1$ $c2$ $c2$ $c2$ $c2$ $c2$ 1320 0.75 $c1$ $c2$ $c2$ $c2$ $c2$ $c2$ 1320 0.75 $c1$ $c2$ <	Rare quench phlogopite
1350 1.3 1330 2 1310 1.5 1310 1.25 1200 2.5 1100 16.75 1100 16.75 1100 0.5 1200 0.75 1300 0.75 1300 0.75 1360 0.75 1360 0.75 1320 1.75 1320 1.75 1220 1.75	
1330 2 1310 1.5 1310 1.25 1290 2 1200 2.5 1109 16.75 1400 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 1.75 1380 1.75	t Reversed from 1380 ^o C. Orthopyroxene very
1130 2 1130 1.5 1310 1.5 1290 2.5 1200 6.75 1200 6.75 1400 0.75 1360 0.75 1360 0.75 1360 1.75 1360 1.75 1360 1.75	abundant
1330 1.5 1310 1.25 1290 2.5 1200 2.5 1100 16.75 1400 0.75 1360 0.75 1360 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 1.75 1380 1.75	
1310 1.25 1290 2 1200 2.5 1100 16.75 1400 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 0.75 1380 1.75 1380 1.75 1380 0.75	
1290 2 1200 2.5 1109 1675 1400 05 1380 075 1380 05 1380 05 1380 1.75 1320 1.75 1320 1.75 1320 1.75	
1200 2.5 1109 16.75 1109 16.75 11400 0.75 11400 0.75 11380 0.55 11380 0.55 11380 1.5 11320 1.75 11200 1.75 11200 1.75	settling Gt Diivine decreased in abundance
1109 16.75 Pressure = 30 kg 1400 0.75 1380 0.75 1380 0.75 1320 1 1320 1 1200 1.75 11200 1.75	
1109 16.75 <u>Pressure = 30</u> 1400 0.75 1380 0.75 1380 0.75 1350 1 1350 1.75 1250 1.75 1100 16	
Pressure a) (Mar. 1400 0.75 c1 cpx + (6t) 1380 0.5 c1 cpx + (6t) 1380 0.5 c1 cpx + (6t) 1380 0.5 c1 cpx + (6t) 1380 0.55 c1 cpx + 6t 1320 0.75 c1 cpx + 6t 1320 1.75 c1 cpx + 6t 1220 1.75 c1 cpx + 6t 1100 16 c1 cpx + 6t	Apatite possibly present. Phlogopite
1400 0.75 c1 + Cpx + (ct 1380 0.5 c1 + Cpx + ct 1360 0.75 c1 + Cpx + ct 1350 1.75 c1 + Cpx + ct 1350 1.75 c1 + Cpx + ct 1350 1.75 c1 + Cpx + ct 1361 1.75 c1 + Cpx + ct	pleochroic
1380 05 c1 + Cpx + dt 1360 075 c1 + Cpx + dt 1350 1.75 c1 + Cpx + dt 1100 16 c1 + Cpx + dt	Quench phlogopite present
1560 0.755 G1 + Cpx + Gt 1350 1 G1 + Cpx + Gt 1320 0.75 G1 + Cpx + Gt 1320 0.75 G1 + Cpx + Gt 1100 1.75 G1 + Cpx + Gt	Quench phlogopite present
1350 1 G1 + Cpx + Gt 1320 0.75 G1 + Cpx + Gt 1250 1.75 G1 + Cpx + Gt 1100 16 G1 + Cpx + Gt	
1320 0.75 G1 + CPX + Gt 1250 1.75 G1 + CPX + Gt 1100 16 G1 + CPX + Gt	Garnet relatively abundant
1250 1.75 GL + Cpx + Gt 1100 16 GL + Cpx + Gt	
1100 15 GL + Cpx + GC	
	<pre>cutingytheme very available. Apartice Dossibly breacht</pre>
<u>Abbieviations</u> : Glagiass; Olaolivine; Opwaorthopyroxene; Cpwaclinopyroxene; Gtmg 	<pre>Gl=glass; Ol=olivine; Opx=orthopyroxene; Cpx=clinopyroxene; Gt=garnet; http://doi.org/or.com/encod/enco.html/argarnet/ice;</pre>
?=presence uncertain; ()=present in trace amounts. R denotes a two-stage run; unless	amounts. R denotes a two-stage run; unless
therwise stated, the length of time that t	otherwise stated, the length of time that the charge was held at the higher temperature

Table II. Selected Results of Experiments with Orendite + 1.23% ${
m H_2}^{
m O}$

(~1350 °C) and at ~ 27 kbar, these three phases precipitate together with garnet at or within a very small temperature interval of the liquidus $(\sim 1375 \,^{\circ}\text{C})$. At higher pressures, clinopyroxene and minor garnet are the primary liquidus phases.

Because of the difficulty in identifying olivine in the high-pressure experiments, a few experiments were carried out on an 'olivine-orendite' composition (95% orendite A1770+5% natural, forsteritic olivine [Fo90]). Olivine was easily identified after runs of 0.6-0.75 h duration at 1380 and 1360 °C and 27 kbar using this starting material.

At pressures below about 0.5 kbar the amount of water in the charge would be sufficient to saturate any melt phase formed, but at higher pressures the amount of water is insufficient to saturate liquidus charges. Thus, the liquidus must change slope from negative to positive at pressures ≤ 0.5 kbar.

+ Cpx+Gt+San+L

Cpx + Opx

+Gt + L

Cpx+Gt

+ L

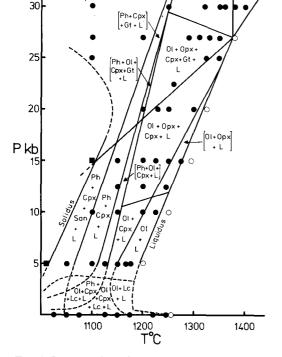


FIG. 1. Interpretation of water-undersaturated melting experiments on orendite. Symbols: open circles: above liquidus; solid circles: melt + crystals; solid squares: subsolidus. Abbreviations: Ol: olivine; Lc: leucite; Cpx: clinopyroxene; Ph: phlogopite; Opx: orthopyroxene; Gt: garnet; San: sanidine; L: melt; The less-well-determined boundaries are shown as dashed lines. For clarity, some

of the smaller phase fields have not been labelled.

In the orendite, the onset of phlogopite crystallization at pressures below about 12 kbar is marked by a decrease in the amount of olivine and melt. At temperatures just below the onset of phlogopite crystallization, olivine is absent and the phase assemblage is dominated by phlogopite, clinopyroxene and liquid. These data indicate the presence of a reaction relationship with falling temperature between olivine and melt to yield phlogopite. This reaction may be similar to that found by Yoder and Kushiro (1969) in their study of the stability of phlogopite under water-undersaturated conditions:

Forsterite + Liquid ⇒ Phlogopite

In the orendite magma, clinopyroxene may also participate in this reaction (cf. Barton and Hamilton, 1979), but this cannot be unambiguously decided on the basis of our results.

At pressures between ~ 12 kbar and ~ 30 kbar the phlogopite-producing reaction is more complex because both olivine and orthopyroxene, which are present in near-liquidus runs, cease to crystallize at temperatures just below the beginning of phlogopite crystallization. Furthermore, there appears to be an increase in the relative proportion of clinopyroxene when phlogopite begins to crystallize suggesting that the reaction occurring at these pressures is

 $Olivine_{ss} + Orthopyroxene_{ss} + Liquid \rightleftharpoons$ $Phlogopite_{ss} + Clinopyroxene_{ss}$

At still higher pressures (> 30 kbar), olivine is no longer stable and phlogopite (? and clinopyroxene) result from a reaction between orthopyroxene and melt.

From our data (Table II, fig. 1) it is evident that the phlogopite-producing reactions occur over a restricted temperature interval-less than 50 °C at pressures between 5 and 30 kbar. The width of the temperature interval appears to decrease with increasing pressure—at least at pressures up to 30 kbar.

The stability of phlogopite in orendite is compared with the stability of this mineral in another Leucite Hills lava, madupite, and with the stabilities of various synthetic phlogopites in fig. 2. Phlogopite is stable to higher temperatures in madupite than in orendite which could reflect the different water contents in the experiments on orendite and madupite. Recasting the chemical composition of orendite into a 'phlogopite-norm' (Carmichael, 1967; see also Beswick, 1976) suggests that the amount of water in the experiments on orendite (1.23%) was less than the amount required to satisfy all of the potential phlogopite in this rock. Comparison with the experimental results of

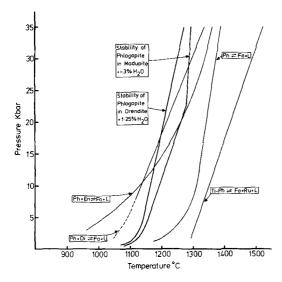


FIG. 2. The stability of phlogopite in water-undersaturated orendite magma compared with the stability of phlogopite in madupite +2.9% H₂O (Barton and Hamilton, 1979), the vapour-absent melting of titan-phlogopite (Forbes and Flower, 1974), the vapour-absent melting of pure magnesian-phlogopite (Yoder and Kushiro, 1969), the vapour-absent melting of phlogopite + enstatite (Modreski and Boettcher, 1972), and the vapour-absent melting of phlogopite + diopside (Modreski and Boettcher, 1973).

Yoder and Kushiro (1969), Eggler (1972) and Holloway (1973) indicates that under these conditions phlogopite will break down at lower temperatures than would be the case if sufficient water were present to satisfy all of the potential phlogopite. A similar calculation for madupite suggests that the water content in experiments on this rock (2.9%)was sufficient to satisfy all of the potential phlogopite. Thus, it appears likely that the decreased thermal stability of phlogopite in orendite compared with madupite reflects the lower water contents in experiments on the orendite, though it should be borne in mind that other factors, such as the lower SiO₂ and higher MgO contents of madupite, could also be important. In both madupite and orendite, the stability of phlogopite is 75-150 °C lower than the stability of pure magnesian phlogopite (Yoder and Kushiro, 1969) and therefore the stabilizing effect of Ti on the thermal stability of phlogopite described by Forbes and Flower (1974) does not seem to operate in the Leucite Hills magmas.

Sanidine is stable within the melting interval to at least 30 kbar but, because of the difficulty of identifying small amounts of this mineral (it forms very small crystals and was identified almost entirely by X-ray diffraction techniques), there is some uncertainty in the location of the sanidine stability curve. The true stability curve for sanidine probably lies at slightly higher temperatures than shown in fig. 1. The results at 1 atmosphere indicate that sanidine is the product of a reaction relationship between leucite and melt. This reaction is restricted to low pressures, however, as leucite was not encountered in the run products at 5 kbar.

The identification of spinel and apatite is also difficult because these phases occur in minor amounts and form small crystals. The results imply the existence of a stability field of spinel at 10 kb (Table II) but because spinel could not be positively identified in all charges this field has been omitted from fig. 1. Similarly, apatite is thought to occur in low-temperature, suprasolidus runs to 30 kbar, but the difficulty of distinguishing apatite and clinopyroxene in the fine-grained, near-solidus charges prohibits the precise location of its stability field. On the other hand, garnet crystallized in sufficient size and quantity to enable its uppertemperature stability to be determined with more certainty.

The slope of the solidus appears to change from positive to negative at a pressure of about 20 kbar. This may reflect the conversion of a low-pressure, amphibole-bearing sub-solidus assemblage to a high-pressure assemblage containing denser phases (e.g. Barton and Hamilton, 1979) but amphibole was not positively identified amongst the run products of orendite. Richteritic amphibole was, however, identified in sub-solidus runs at 5 kbar ($P_{H_2O} < P_{total}$) on a similar lava, wyomingite, from the Leucite Hills.

Electron microprobe analyses of crystalline phases

Electron microprobe analyses of olivines, orthopyroxenes, and clinopyroxenes produced in the experiments are listed in Tables III and IV.

Olivine. The olivine crystallized from orendite at 5 kbar are highly forsteritic (Fo₉₄). No analyses of olivines crystallized at higher pressures from orendite were obtained because of the small size of the crystals, but the compositions of these olivines may be estimated from the compositions of the coexisting orthopyroxenes (see below) using the experimental results of Medaris (1969) and Mori and Green (1978) for the distribution of Mg and Fe between orthopyroxene and olivine in synthetic and natural Mg-rich systems. The calculated olivine compositions fall in the range Fo_{88-91} . The olivine crystallized from the 'olivine-orendite' composition at 1380 °C and 27 kbar (Table III) is also forsterite-rich (Fo_{92}) . It is noteworthy that the 100 $Mg/(Mg + \Sigma Fe^{2+})$ ratios of olivine and ortho-

									Run No.	1040	1051	1068	1063
Start. Comp	1770	01-0r ^a	A1770	A1770	A1770	A1770	A1770	A1770	P (kb)	20	20	22.5	27
Run No.	289	1065	1012	1040	1068	1063	1047	1054	т (°с)	1300	1200	1260	1350
P (kb)	5	27	15	20	22.5	27	27	30					
T(°C)	1175	1380	1250	1300	1260	1350	1310	1350					
Phase	01	01	Орх	Орх	Орх	Орж	Орх	Орж	sio2	54.9	54.3	54.9	55.0
			-	-					TiO2	0.72	0.82	0.85	0.46
	41.4	41.7	56.8	57.4	57.4	57.2	57.7	57.5	AL 203	1.25	0,68	1.75	1,52
SiO2	41.4	41.7 0.07				0.26		0.49	Fe0 ^H	4.62	3.67	3.11	2.10
Tio2		-	0.46 0.58	0.33	0.26	1.07	0.27	1.93	MnO	0.18	0.19	0.17	0.17
A12 ⁰ 3 Fe0 [#]	-			1.14					MgO	21.0	19.6	20.3	22.0
	5.75	7.29	5.64	6.04	6.14	3.24	5.88	5.47	CaO	16.7	19.8	16.6	16.0
MnO		0.11	0.15	0.15	0.07	0.10	0.10	0,10	Na20	0.72	0.43	0.84	0.81
MgO	52.2	50.1	32.7	32.5	32.3	33.8	32.2	31.8					
CaO	-	0.01	2.32	2.64	2,52	2,53	2.24	2.56	·				
Na20	_	-	0.04	0.06	0.15	0.13	0.18	0.25	Total	100.1	99.5	98.5	98.1
Total	99.4	99.3	98.7	100.3	99.9	98.3	99.6	100.1					
Mg									Mg	- 0.89	0.91	0.92	0.95
$(Mg + \xi Fe^{2+})$	0.94	0.92	0.91	0.91	0.90	0,95	0.91	0.91	(Mg+{Fe	2*)			
Ca									<u>Ca</u> (Ca+Mg+ {Fe	2+,0.34	0.40	0.35	0.33
(Ca + Mg + ξ E	re ²⁺⁾ -	-	0.04	0.05	0.05	0.05	0.04	0.05					
									Chemi ca	l Formula	e (0≖6)		
Chemical Form	nulae (O=	4 or 6)							Si	1.972	1.973	2,001	1.98
Si	1.001	1.015	1.98	7 1.981	1.99	5 1.992	1.995	1.982	ALIV	0.028	0.027	-	0.01
Aliv	-	~	0.01	3 0.019	0.00	5 0.008	0.005	0.018	Al ^{VI}	0.025	0.002	0.050	0.05
Al ^{VI}	· _	-	0.01	1 0.027	0.02	4 0.037	0.038	0.061	Ti	0.019	0.022	0.023	0.01
Ti.	-	0.001	0.01	2 0.008	3 0.00	7 0.007	0.007	0.012	*Fe ²⁺	0.138	0.111	0.094	0.06
* 2+ Fe	0.116	0.148	0.16	5 0.174	0.17	8 0.094	0.171	0.158	Mn	0.005	0.005	0.005	0.00
Mn	-	0.002	0.00	5 0.004	4 0.00	2 0.003	0.003	0.003	Mg	1.123	1.062	1.100	1.18
Mg	1.882	1.817	1.70	6 1.672	1.67	4 1.755	1.675	1.643	Ca	0.645	0.770	0.647	0.61
Ca	-		0.08	7 0.098	B 0.09	4 0.094	0.084	0.095	Na	0.050	0.030	0.059	0.05
Na	. –	-	0.00	3 0.004	0.01	0.009	0.012	0.016					
٤z	1.001	1.015	2,00	0 2,000	2.00	0 2.000	2.000	2.000	ξ Z ≰X+Y	2.000			
E X + Y	1.998	1.968	1.98	9 1.987	7 1.98	9 1.999	1.990	1.988					
* Total iron		* Fa ⁺²							* Total	iron as	FeO or	Fe ²⁺	

Table II. Electron microprobe analyses of olivines and orthopyroxenes

Table N. Electron microprobe analyses of clinopyroxenes

1047 1043

27 27 30

т (°с)		20	22.5				30
- , -,	1300	1200	1260	1350	1310	1100	1350
sio ₂	54.9	54.3	54.9	55.0	56.2	53.9	55.9
TiO2	0.72	0.82	0.85	0.46	0.47	0.65	0.43
A1,0,	1.25	0,68	1.75	1,52	1.42	0.76	2.05
FeO	4.62	3.67	3.11	2.10	3.44	3.90	2.51
MnO	0.18	0.19	0.17	0.17	0.15	0.26	0.10
MgO	21.0	19.6	20.3	22.0	21.0	15.8	22.5
CaO	16.7	19.8	16.6	16.0	17.0	22.3	14.6
Na20	0.72	0.43	0.84	0.81	1.03	0.78	0.95
Total	100.1	99.5	98.5	98.1	100.7	98.4	99.0
Mg (Mg+{Fe	2+, 0.89	0.91	0.92	0.95	0.92	0.88	0.94
Ca Ca+Mg+ {Fe	2+,0.34	0.40	0.35	0.33	0.35	0.47	0.31
Chemica]	L Formula	∍ (0=6)					
Si	L Formula 1.972	e (0=6) 1.973	2,001	1.987	1.993	1.994	1.990
si Al ^{iv}			2,001	1.987 0.013		1.994 0.006	1.990 0.010
si Al ^{iv}	1.972	1.973			0.007		
Si	1.972 0.028	1.973 0.027	-	0.013	0.007	0.006	0.010
Si Al ^{iv} Al ^{vi}	1.972 0.028 0.025	1.973 0.027 0.002	- 0.050	0.013 0.051	0.007 0.052 0.012	0.006 0.027	0.010 0.076
Si Al ^{iv} Al ^{vi} Ti	1.972 0.028 0.025 0.019	1.973 0.027 0.002 0.022	- 0.050 0.023	0.013 0.051 0.012	0.007 0.052 0.012 0.103	0.006 0.027 0.017	0.010 0.076 0.011
Si Al ^{iv} Al ^{vi} Ti Fe ²⁺	1.972 0.028 0.025 0.019 0.138	1.973 0.027 0.002 0.022 0.111	- 0.050 0.023 0.094	0.013 0.051 0.012 0.063	0.007 0.052 0.012 0.103 0.004	0.006 0.027 0.017 0.120	0.010 0.076 0.011 0.075
Si Al ^{iv} Al ^{vi} Ti ⁽ Fe ²⁺ Mn	1.972 0.028 0.025 0.019 0.138 0.005	1.973 0.027 0.002 0.022 0.111 0.005	- 0.050 0.023 0.094 0.005	0.013 0.051 0.012 0.063 0.005	0.007 0.052 0.012 0.103 0.004 1.109	0.006 0.027 0.017 0.120 0.008	0.010 0.076 0.011 0.075 0.003
Si Al ^{iv} Al ^{vi} Ti Fe ²⁺ Mn Mg	1.972 0.028 0.025 0.019 0.138 0.005 1.123	1.973 0.027 0.002 0.022 0.111 0.005 1.062	- 0.050 0.023 0.094 0.005 1.100	0.013 0.051 0.012 0.063 0.005 1.188	0.007 0.052 0.012 0.103 0.004 1.109 0.648	0.006 0.027 0.017 0.120 0.008 0.880	0.010 0.076 0.011 0.075 0.003 1.197

* Total iron as FeO or Fe⁺²

^a Ol-Or is an "olivine-crendite" made by mixing 95% orendite A1770 with 5% olivine (Fo

pyroxene (En₉₃) crystallized from the 'olivineorendite' at 1380 °C and 27 kbar are similar, which provides justification for estimating the compositions of olivines in high-pressure runs on orendite from the compositions of coexisting orthopyroxenes.

The higher forsterite contents of the olivines crystallized from orendite at 5 kbar compared with the calculated compositions of olivines in the higher pressure runs and with the composition of olivine crystallized from the 'olivine-orendite' (which has a higher $100Mg/(Mg + \Sigma Fe^{2+})$ ratio than orendite) at 27 kbar could reflect either the effect of pressure on the distribution of Mg and Fe between olivine and melt (e.g. Longhi et al., 1978; Bender et al., 1978) or increased Fe loss in the runs at 5 kbar. In view of the longer duration of the near-liquidus experiments at 5 kbar compared with the near-liquidus experiments at higher pressures

(Table II), it is likely that Fe loss is mainly responsible for the higher forsterite contents of olivines crystallized at 5 kbar.

Orthopyroxene. The orthopyroxenes precipitated from orendite are > 90% En+Fs and contain 4-5% Wo (Table III). All of the analysed orthopyroxenes are from runs less than 80 °C below the liquidus and, with one exception, have remarkably uniform Mg/(Mg+ Σ Fe²⁺) ratios (0.90–0.91), reflecting the tendency for the crystal: liquid ratio to remain fairly constant prior to the onset of phlogopite crystallization. The exception, a highly magnesian orthopyroxene (En₉₅), is from a reversed run which was presumably affected by Fe loss. A partial analysis of orthopyroxene from a onestage run at the same P-T conditions (run 1049) gave Eng1.

All of the orthopyroxenes have low Al contents, even those from runs in which garnet or spinel

1054

were absent. The Al contents are much lower than those of orthopyroxenes crystallized experimentally at high pressures and similar temperatures from basic and ultrabasic compositions (e.g. Green and Ringwood, 1967; Mori and Green, 1978). However, Modreski and Boettcher (1972, 1973) also found that orthopyroxenes crystallized from highly potassic melts with potash: alumina ratios close to unity were Al-poor, whereas those precipitated from potassic, metaluminous melts had high Al contents. Evidently the alkalis: alumina ratio of melts has a great influence on the Al content of coexisting orthopyroxene.

Clinopyroxene. The analyses of clinopyroxenes crystallized from orendite are given in Table IV. The clinopyroxenes have En + Fs + Wo > 92% but have variable Mg/(Mg + ΣFe^{2+}) ratios (0.88-0.95) and it is belived that clinopyroxene is sensitive to Fe loss (see also Stern and Wyllie, 1975; Barton and Hamilton, 1979). In contrast, the Ca/(Ca + $Mg + \Sigma Fe^{2+}$ ratios of the clinopyroxenes decrease systematically with increasing temperature. The Al contents also increase with increasing temperature but, as with the orthopyroxenes, the Al contents of the orendite clinopyroxenes are low in comparison with those precipitated from basaltic and some alkaline magmas at high pressures (Green, 1973a; Thompson, 1974a). However, the Al contents are similar to those of clinopyroxenes crystallized from madupite (Barton and Hamilton, 1979) and biotitemafurite (Edgar et al., 1976) under waterundersaturated conditions at similar pressures, and because all three rocks are peralkaline it is apparent that the low Al contents of the clinopyroxenes reflect the low alkalis: alumina ratios of the coexisting melts.

The behaviour of Al, Na and Ti with pressure in the near-liquidus orendite clinopyroxenes is similar to the behaviour of these elements in clinopyroxenes crystallized from madupite (Barton and Hamilton, 1979) and from a variety of basic magmas (Thompson, 1974a) at high pressures; Al and Na both increase with increasing pressure whereas Ti varies inversely with pressure. A notable feature of the orendite clinopyroxenes, however, is that Al is insufficient to balance Na and Ti (Al < Na + 2Ti) and in some cases is insufficient to balance Na alone (Al < Na). This indicates either the presence of (undetermined) Cr or Fe^{3+} in octahedral and tetrahedral coordination or. alternatively, that Na and Ti are involved in substitutions which do not require the presence of trivalent ions (e.g. Ferguson, 1977).

The coexisting ortho- and clinopyroxenes in orendite show a similar degree of mutual solid solubility to magnesian pyroxenes crystallized experimentally at similar pressures and temperatures from ultrabasic (e.g. Mori and Green, 1978) and basanitic (Green, 1973a) compositions.

Discussion

One of the major problems in the present study concerned the identification of olivine in the highpressure experiments. If, as we suggest, olivine was present in these experiments, then at a pressure of about 27 kbar the orendite precipitates olivine, orthopyroxene, clinopyroxene, and garnet simultaneously at or near the liquidus and therefore at this pressure the orendite could have been in equilibrium with the mineral assemblage of garnetlherzolite; that is, it could be a primary magma. The wide melting interval of orendite at high pressures does not mitigate against a primary magma origin; a narrow melting interval at the pressure of magma generation is unlikely in situations where solid solutions and reaction relationships are important. However, the proposal that quartz-normative potassic magmas such as the orendite are primary magmas is in conflict with the results of experimental studies using synthetic and natural basaltic and ultramafic compositions which indicate that the melts produced in the upper mantle under anhydrous (volatile-absent) or waterundersaturated conditions at 25-30 kbar are very rich in normative olivine ($\sim 25\%$) and range in composition from picrite to olivine-basanite or olivine-nephelinite (O'Hara, 1968; Green, 1973a). In addition, the results of Modreski and Boettcher (1973) show that the melting of phlogopite in model mantle assemblages in the absence of a vapour phase produces guartz-normative liquids at pressures up to 15 kbar and silica-undersaturated liquids (olivine- and, or, leucite-normative) at higher pressures (above about 20 kbar). These data thus imply that silica-saturated magmas, such as the orendite, cannot be derived by the melting of lherzolite or garnet-lherzolite at pressures above 15-20 kbar.

Although there is some doubt about the presence of olivine in the high-pressure experiments on orendite, the experiments on the 'olivine-orendite' composition demonstrate that magmas more magnesia-rich and less silica-rich than the orendite can be in equilibrium with olivine (together with orthopyroxene and minor clinopyroxene and garnet). We suggest, therefore, that the olivinenormative orendites (and wyomingites) from the Leucite Hills are primary magmas derived by partial melting in the upper mantle under waterundersaturated conditions at pressures of about 27 kbar. These magmas contain up to about 10% olivine in the norm (Carmichael, 1967; Barton, unpubl. data), which is also less than that con-

sidered appropriate for primary magmas formed at 25-30 kbar (see above). However, it is worth emphasizing that the high level of enrichment of K and incompatible elements in the Leucite Hills magmas compared with garnet-lherzolite (probably $\leq 0.1 \% K_2 O$ requires that these magmas are produced by very small degrees of fusion (< 1 %) or that the mantle is heterogenous with some parts enriched in K and other LIL elements. At very low degrees of fusion, the residual phases exercise only limited control over the major element composition of the melt (O'Hara, 1968) and, furthermore, the work of Kushiro (1975) has shown that addition of small amounts of K can shift melts in equilibrium with forsterite and enstatite to more silica-rich compositions. Thus, the proposal that olivinenormative orendites and wyomingites are primary magmas is not necessarily in confilict with other models in which higher degrees of fusion are usually considered.

The origin of silica-saturated orendites remains problematical. It is probable that olivine would be more abundant in orendite magma containing more water than was present in the experiments. This follows from the work of Kushiro (1972), who demonstrated that the primary liquidus volume of olivine expands relative to that of ortho- and clinopyroxene with increasing water content, and that melting of hydrous lherzolite would produce silica-saturated magmas at pressures up to at least 20 kbar. Increasing the water content in experiments on orendite would depress the liquidus temperatures, increase the thermal stability of phlogopite and increase the amount of nearliquidus olivine at high pressures. Consequently, it is possible that silica-saturated potassic magmas could also be primary magmas, generated by melting of hydrous lherzolite or garnet-lherzolite. Unfortunately, there is no general agreement about the upper pressure limit for the formation of silica-saturated magmas in the upper mantle. Estimates range from 17-20 kbar (Nicholls and Ringwood, 1973) to 25 kbar (Mysen and Boettcher, 1975) or even > 25 kbar (Modreski and Boettcher, 1973). Using the same arguments that were used above concerning the origin of olivine-normative orendites, it is clear that these estimates do not necessarily apply to strongly potassic magmas produced by small degrees of melting (1% or less).

O'Hara (1968), Harris (1974), and Arndt (1977) have pointed out that extraction of < 1-2% melt from the upper mantle under static conditions is difficult to envisage. It is possible that the rarity of potassic magmas indicates that special tectonic conditions, rarely attained, are necessary to bring about segregation of the melt and allow its passage to the surface. Alternatively, if the mantle is markedly heterogenous, with some parts enriched in K and incompatible elements, larger degrees of melting could produce magmas with the chemical characteristics of the orendites and wyomingites of the Leucite Hills. Evidence that metasomatism in the upper mantle, leading to enrichment in K and other LIL elements, is concomitant with or precedes the formation of alkaline magmas by anatexis has been presented by Aoki (1975), Boettcher et al. (1977), Cox et al. (1976), Erlank and Rickard (1977), Hawkesworth and Vollmer (1979), and Lloyd and Bailey (1975). Possible source rocks include the phlogopite- and potassic-richterite-bearing peridotites described by Aoki (1975) and Erlank and Rickard (1977), some of which are peralkaline (note that the Leucite Hills lavas are also peralkaline). The pyroxenes in these nodules tend to have low Al contents and it may therefore be significant that the pyroxenes crystallized from orendite magma at high pressures have low Al contents in comparison with pyroxenes crystallized from phlogopiteand potassic-richterite-free peridotites. However, it is not possible on the basis of the experimental results for orendite to decide unambiguously whether relatively silica-rich potassic magmas are derived from pristine mantle peridotite or from parts of the mantle that are enriched in potassium and other incompatible elements.

It is now widely accepted that many of the geochemical characteristics of potassium-rich volcanic rocks can be explained by the presence of phlogopite in the upper mantle (e.g. Carmichael et al., 1974; Powell and Bell, 1974; Beswick, 1976), and petrographic evidence for the presence of primary phlogopite in garnet-lherzolite has been presented by Dawson et al. (1970), Aoki (1975) and Carswell (1975). Eggler (1978) and Eggler and Holloway (1977) have reviewed the general principles of the melting of hydrous phases, including phlogopite, in the upper mantle, and Holloway and Eggler (1976) have modelled the fluid-absent melting of peridotite containing phlogopite and dolomite. Because these authors were not specifically concerned with the origin of potassium-rich magmas, it is appropriate to consider here the possible role of phlogopite in the genesis of these magmas. The following discussion is based mainly upon the experimental results for the melting of phlogopite in orendite and madupite (Barton and Hamilton, 1979) magmas, and applies to the melting of phlogopite in the absence of a vapour phase when the only volatile components initially present are bound in the hydrous phase.

The stability of phlogopite in madupite (with about 3% H₂O) is similar to that of phlogopite in biotite-mafurite with 5% H₂O (Edgar *et al.*, 1976) and is probably close to the maximum stability of

hydroxyl phlogopite in natural systems (both rocks are magnesia- and potash-rich and relatively silicapoor, and the experiments were performed under water-undersaturated conditions). At all pressures, phlogopite in the madupite melts at temperatures below the anhydrous garnet-lherzolite solidus (fig. 3) and, in the absence of other less refractory hydrous phases, the melting of phlogopite would define the water-undersaturated solidus of garnetlherzolite*. The amount of phlogopite in the pristine upper mantle is most probably small, about 1% according to Carswell (1975), and the amount of melting of phlogopite-garnet-lherzolite would also be small until the anhydrous solidus is approached. Phlogopite would melt over a small temperature interval (the results for orendite and madupite suggest that this would be about 50-75°C, but the results of Holloway and Eggler [1976] suggest that it is closer to 100 °C) and once it had melted, virtually all of the K₂O in the source rock would have entered the melt producing a strongly potassic magma; because of the incongruent melting behaviour of phlogopite (Yoder and Kushiro, 1969) the potash contents of the melt could exceed the amount of potash held in stoichiometric phlogopite (see also Beswick, 1976). The results for madupite and orendite indicate that during this initial stage of melting the alumina contents of the residual pyroxenes would increase, which may result in the earliest melts of phlogopite-garnet-lherzolite being peralkaline. The same effect is seen in the systems phlogopite-enstatite and phlogopite-diopside (Modreski and Boettcher, 1972, 1973) in which peralkaline melts are produced because the stable pyroxenes are peraluminous. At more advanced stages of fusion, the potash contents of the melts are diluted and metaluminous magmas are produced. The melting of peridotite which has been enriched in K and incompatible elements is more complex because of the probable presence in these rocks of hydrous phases which

* The presence of volatiles other than water could increase the thermal stability of phlogopite. Ryabchikov and Green (1978) show that addition of CO₂ to biotitemafurite +5% H₂O increases the stability of phlogopite by about 50 °C, but the maximum melting temperature phlogopite in biotite-mafurite of $+H_{2}O+CO_{2}$ $(\sim 1300 \,^{\circ}\text{C})$ at 30 kbar is still below the solidus temperature of anhydrous garnet-lherzolite (Ito and Kennedy, 1967) at this pressure. Fluorine increases the stability of hydrous minerals significantly (Kushiro et al., 1967; Holloway and Ford, 1975) and F-rich phlogopite could be stable to temperatures above those of the peridotite solidus, i.e. under these conditions phlogopite could behave as a refractory phase during the melting of mantle peridotite. However, Aoki and Kanisawa (1979) have shown that phlogopites in peridotites contain less than about 5000 ppm F.

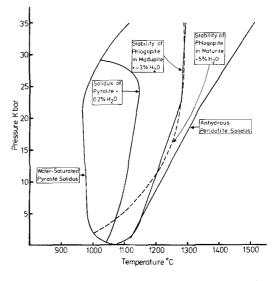


FIG. 3. The melting curves of phlogopite in madupite +2.9% H₂O (Barton and Hamilton, 1979) and biotitemafurite +5% H₂O (Edgar *et al.*, 1976) compared with the melting curves of anhydrous peridotite (Ito and Kennedy, 1967), water-saturated pyrolite (Green, 1973b), and pyrolite +0.2% H₂O (Green, 1973b).

are less refractory than phlogopite. Because some of these peridotites are peralkaline, and contain alkali-rich, alumina-free phases such as potassic richterite, it is likely that the initial melts would also be peralkaline. The melting of phlogopite in the presence of residual pyroxenes could then increase the peralkalinity of the melts, but until experimental data are available for the melting behaviour of such peridotites, the composition of the melts produced at any stage of fusion cannot be predicted with any certainty.

The conclusion that the earliest melts produced during the fusion of phlogopite-garnet-lherzolite are strongly potassic (see also Edgar *et al.*, 1976) and that phlogopite will break down at or close to the garnet-lherzolite solidus is at variance with suggestions that essentially anhydrous (volatilepoor) nepheline-normative basalts form in equilibrium with residual titan-phlogopite (e.g. Thompson, 1974b). Liquids which equilibrate with residual phlogopite must be saturated with this phase and, in the absence of a reaction relationship, must have phlogopite as a liquidus phase with some appropriate water content. It is extremely unlikely that alkali basalt with < 0.6 % K₂O could satisfy these conditions.

Finally, the production of primary potassic melts in the upper mantle can be considered in terms of the principles established by Eggler (1978) and Holloway and Eggler (1976) for the melting of peridotite in the presence of small amounts of H_2O and CO₂. These authors have concluded that melting will be essentially isobarically invariant for a relatively wide range of $CO_2/(CO_2 + H_2O)$ in the source peridotite, and that the invariant liquid will be strongly silica-undersaturated, probably ranging in composition from nephelinite at 15 kbar to melilitite at 30 kbar (Mysen and Boettcher, 1975; Brey and Green, 1977; Eggler, 1978). At extremely low values of $CO_2/(CO_2 + H_2O)$ in the source peridotite (essentially CO2-free) melts richer in silica will be produced; the precise compositions of these melts depend on the initial water content of the peridotite, but the liquids will always be silica-rich compared with melts produced from peridotite with a higher $CO_2/(CO_2 + H_2O)$. At extremely low degrees (< 2-5%) of fusion of natural peridotite, melting is unlikely to be isobarically invariant (Mysen and Kushiro, 1977; Wendlandt and Mysen, 1978) and a restricted range of liquid compositions can be produced for a given $CO_2/(CO_2 + H_2O)$ in the source peridotite. For reasons discussed previously, we believe that these melts will be strongly potassic and at pressures of 25-30 kbar will range in composition from relatively silica-rich, peralkaline magmas such as orendite and wyomingite, which form under H₂Oundersaturated essentially CO₂-free conditions, to silica-poor, mafic magmas such as biotite-mafurite, which Ryabchikov and Green (1978) have shown could form by melting of peridotite under waterundersaturated conditions in the presence of CO_2 .

Madupite is a mafic, potassic magma similar in some respects to biotite-mafurite, and although Barton and Hamilton (1979) concluded that the madupite they studied was not a primary magma derived by melting of lherzolite, its high 100 Mg/(Mg+ Σ Fe²⁺) ratio (77.03) suggests that it has not undergone large amounts of fractionation involving removal of ferromagnesian phases. It is reasonable to conclude, therefore, that the presence of mafic, silica-poor lavas (madupites) and relatively silica-rich lavas (wyomingites and orendites) in the Leucite Hills primarily reflects the effects of different volatiles (H₂O and CO₂) on melting processes within the upper mantle.

Conclusions

From the results of high-pressure, water-undersaturated melting experiments on an orendite we conclude that relatively silica-rich potassic magmas can be generated as primary liquids at depths of about 90 km in the upper mantle. The source peridotite contains some water but is essentially carbon dioxide free. The amount of water present influences the composition of the melt produced:

with low water contents, olivine-normative orendites and wyomingites are formed, but with higher water contents, orendites and wyomingites that are just saturated in silica may be formed. With increasing pressure, these melts become poorer in silica (richer in normative olivine). Melting of peridotite containing carbon dioxide in addition water yields mafic, silica-undersaturated to magmas similar in composition to biotite-mafurite and, possibly, some madupites. With increasing pressure, these magmas also become increasingly undersaturated in silica, and richer in normative olivine. The melting of phlogopite in the presence of residual ortho- and clinopyroxenes could explain the peralkalinity of potassic magmas such as orendite and wyomingite (and biotite-mafurite and madupite). Alternatively the peralkalinity of these magmas could reflect the unusual chemistry of the source rocks and it is not possible to decide on the basis of the experimental results whether K-rich alkaline magmas are the product of very small degrees of fusion of pristine mantle peridotite containing minor phlogopite (and probably also apatite and other minor phases) or of larger degrees of melting of heterogenous source rocks enriched in potassium and other LIL elements. The difficulty of extracting small quantities (≤ 1 %) of melt from the residual crystals together with geochemical evidence (Cox et al., 1976; Hawkesworth and Vollmer, 1979) that at least some K-rich magmas are derived from parts of the mantle that are anomalously enriched in incompatible elements suggests that the second alternative is most likely to be correct. In either case, it is probable that the occurrence of potassic volcanism is strongly influenced by the prevailing tectonic conditions, as it is necessary that relatively small volumes of magma of highly unusual composition rise to the surface from depths of ~ 90 km sufficiently rapidly that equilibration with the surrounding wall rocks and fractional crystallization do not occur.

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