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Experimental evidence at high pressure for potassic metasomatism in the mantle of the Earth[1]

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Abstract

To assess the concentration of potassium in aqueous fluids as a model for metasomatism of the mantle of the Earth, we experimentally determined the solubility of potassium in an aqueous vapor in equilibrium with phlogopite and other phases to pressures of 30 kbar at 1100°C. The concentration of potassium (in grams of K_2O per 100 g H_2O) is 4 at 11 kbar, 7 at 20 kbar, and 25 at 30 kbar. Such values are sufficient to transfer from the interior of the Earth all of the K_2O to the continental crust during formation of the hydrosphere by outgassing. However, it is likely that most of this transport was by silicate-rich liquids.

Introduction

A number of investigators have suggested that primary alkaline magmas and particularly highly potassic melts are formed by partial melting of mantle material that was previously enriched in potassium and other components by precursory metasomatic processes (Sobolev, 1977; Ryabchikov and Green, 1979; Lloyd and Bailey, 1975; Boettcher and O'Neil, 1980). The present work was designed to provide a quantitative check on the possibility of such processes by experimentally measuring K_2O concentrations in aqueous vapors in equilibrium with phlogopite-bearing mineral assemblages typical of the mantle at high pressures and temperatures.

Earlier studies (Wendlandt, 1977; Yoder and Kushiro, 1969) revealed that subsolidus experiments at 20 kbar for the composition joins phlogopite–H_2O and phlogopite–H_2O–CO_2 quenched to an assemblage containing phlogopite plus forsterite. This demonstrates that incongruent solubility of phlogopite in an aqueous vapor under these conditions is significant and that K_2O and Al_2O_3 dissolve in the vapor in excess of that in phlogopite composition. In this work we extended the investigation of phlogopite-containing joins to higher H_2O concentrations and determined the H_2O contents at various pressures where phlogopite became unstable, dissolving entirely in the vapor, enabling us to determine K_2O contents of fluids in equilibrium with phlogopite, olivine, and some other phases typical of mantle assemblages.

Experimental procedures

Starting materials

A mixture of oxides of anhydrous phlogopite composition was prepared by sintering and partial melting at about 1100°C. Fired gels of pyrope and forsterite compositions were added to anhydrous phlogopite powder for some of our experiments.

Experiments were performed in sealed platinum capsules on mixtures of known proportions of silicate components and water.

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Apparatus

All the experiments were in piston–cylinder apparatus similar to that described by Boyd and England (1960). The experimental method was described earlier (Allen and Boettcher, 1978).

Identification

After sealing, the capsules were folded in such a way that the starting mixtures were contained in one half of each of the capsules. During the run, however, the second half of each capsule was filled with vapor phase, which precipitated quench material during fast isobaric cooling at the end of an experiment (see Fig. 1). Comparison of the material from both halves of the capsules was very useful for the distinction of primary and quench phlogopite crystals.

The nature of quench material changed considerably with pressure. Between 10 and 14 kbar, it was mainly an amorphous, glass-like phase forming spheres, rods, and coatings on primary crystals (Fig. 2). At these pressures, quench phlogopite occurred in minor amounts as small (<5 μm), thin flakes.

At 20 kbar the proportion of quench phlogopite was noticeably greater, forming large (>20 μm), thin plates with uneven extinction and some skeletal morphology. The spheres of amorphous material were typically situated along the growth figures of quench phlogopite. At 30 kbar, large (700 μm), euhedral (but thin) phlogopite plates were part of the quench material and were overgrown by irregular aggregates of phlogopite and amorphous material (Fig. 2). Primary phlogopites at all pressures were euhedral, relatively thick crystals (Fig. 3).

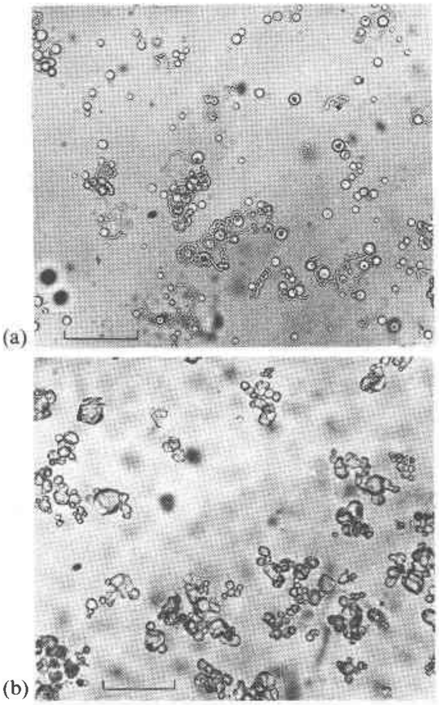

Fig. 1. Photomicrographs of products of run 33; (a) quench vapor in folded part of capsule, (b) forsterite + quench vapor in main part of capsule. Bars are 100 μm.

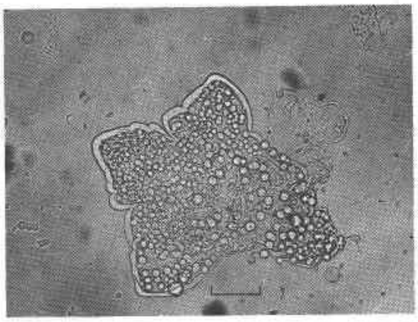

Fig. 2. Photomicrograph of quench vapor in products of run 26. Bar is 100 μm.

Olivines occurred in all our run products. They were typically euhedral, tabular grains whose average size increased with increasing pressure, ranging from 10 μm at 10 kbar to 500×150 μm at 30 kbar. Some olivines contained fluid inclusions.

The run products for the join phlogopite–pyrope–water contained orthopyroxene and spinel in addition to phlogopite and olivine.

Experimental results

The results of our experiments are summarized in Table 1. Their interpretation is based on the following reasoning. In the runs in which the products did not include primary phlogopite, all the K_2O was incorporated into the fluid phase, inasmuch as the co-

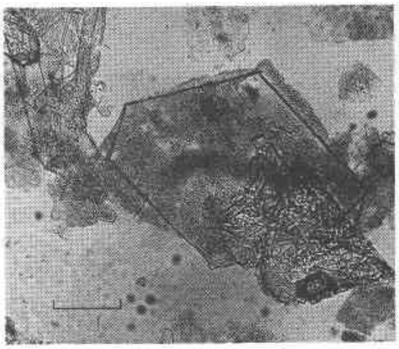

Fig. 3. Photomicrograph of thin plates of quench phlogopite and other quench products in run 24. Bar is 200 μm.

Table 1. Experimental data

Run	Pres (kbars)	Temp (°C)	Bulk composition	$\frac{g\ K_2O}{100\ g\ H_2O}$	Time (hrs)	Run products
32	10	1100	$Aph_{17}Fo_{35}W_{48}$	4.2	9	Fo+Ph+Q
33	12	1100	$Aph_{18}Fo_{36}W_{46}$	4.7	11.5	Fo+Q
30	14	1100	$Aph_{17}Fo_{35}W_{48}$	4.3	9	Fo+Q
23	20	1100	$Aph_{33}W_{67}$	5.8	13	Fo+Q
26	20	1100	$Aph_{37}W_{63}$	7.0	9	Fo+(Ph)+Q
3	20	1100	$Aph_{42}W_{58}$	8.7	8	Fo+Ph+Q
14	20	1100	$Aph_{42}W_{55}$	9.6	10	Fo+Ph+Q
11	20	1100	$Aph_{76}W_{24}$	36.6	8	Fo+Ph+Q
22	20	1050	$Aph_{10}Py_{40}W_{50}$	2.2	9	Opx+Sp+Q
25	20	1050	$Aph_{20}Py_{30}W_{50}$	4.8	11	Fo+Opx+Sp+Q
29	20	1050	$Aph_{24}Py_{24}W_{52}$	5.6	12	Fo+Opx+Sp+Q
27	20	1050	$Aph_{30}Py_{20}W_{50}$	7.2	12	Fo+(Opx)+Sp+Ph+Q
21	30	1100	$Aph_{47}W_{53}$	10.3	12	Fo+Q
19	30	1100	$Aph_{54}W_{46}$	13.8	8	Fo+Q
24	30	1100	$Aph_{57}W_{43}$	15.8	8.5	Fo+Q
31	30	1100	$Aph_{65}W_{35}$	21.9	10	Fo+Q
37	30	1100	$Aph_{71}W_{29}$	28	8.5	Fo+Ph+Q

Abbreviations: Aph is anhydrous phlogopite composition ($KMg_3AlSi_3O_{11}$); Fo is forsterite (Mg_2SiO_4); W is water (H_2O); Py is pyrope composition ($Mg_3Al_2Si_3O_{12}$); Ph is phlogopite; Opx is orthopyroxene; Sp is spinel; Q is quench material (amorphous substance and quench mica); parentheses indicate minor amount.

existing crystalline phases (olivine or olivine + orthopyroxene + spinel) contain only negligible amounts of this element. Interpolating between the compositions of two adjacent runs with and without primary phlogopite, we deduce the K_2O/H_2O ratio in the fluid coexisting with the traces of phlogopite in addition to forsterite or forsterite + orthopyroxene + spinel. In this manner, we estimated the values of K_2O concentrations (in grams of K_2O per 100 g of H_2O) in equilibrium with assemblages containing phlogopite and forsterite in 1100°C to be as follows: 4 at 11 kbar, 7 at 20 kbar, and 25 at 30 kbar.

The run products for the join phlogopite–pyrope–water at 20 kbar and 1100°C were buffered with respect to the chemical potential of SiO_2 (μ_{SiO_2}) by the presence of both forsterite and orthopyroxene and with respect to $\mu_{Al_2O_3}$ by olivine, orthopyroxene, and spinel. These compositions are more nearly representative of the chemistry of mantle material than are the joins phlogopite–water and phlogopite–forsterite–water. The concentration of K_2O in the vapor in equilibrium with phlogopite, forsterite, orthopyroxene, and spinel at 1050°C and 20 kbar was estimated from these experiments as 6 g K_2O per 100 g H_2O, only slightly lower than that for phlogopite + forsterite phase assemblages at the same pressure but at 1100°C.

Thus our experimental data permit us to evaluate K_2O/H_2O ratios in aqueous fluids. The same reasoning is also applicable to Al_2O_3 concentrations, inasmuch as this component also occurs in olivines only in trace amounts. It is also clear that the K_2O/Al_2O_3 ratios of our solutions were always close to unity (the same as in phlogopite). Unfortunately, it is not possible to estimate MgO and SiO_2 concentrations in aqueous solutions from our experimental data alone. However, from the results of Modreski and Boettcher (1973), who analyzed quenched vapor in equilibrium with forsterite, enstatite, and phlogopite at 1050°C and 10 kbar, we conclude that the MgO content of aqueous fluid at these conditions is negligible. Therefore, it is rather safe to assume that concentrations of magnesium in the fluid in our runs at 1100°C and 11 kbar are also very low, because the pressure–temperature conditions of these runs and those of Modreski and Boettcher (1973) are similar. From this we estimate the K_2O (3.4 wt%), Al_2O_3 (3.7 wt%), and SiO_2 (6.6 wt%) concentrations in the aqueous phase in equilibrium with forsterite and phlogopite at 1100°C and 11 kbar, with the total content of dissolved oxides being approximately 14 wt%. At higher pressures MgO concentrations in fluids coexisting with phlogopite-containing phase assemblages must be substantial, judging from the increasing amount of quench phlogopite.

Eggler and Rosenhauer (1978) determined the solubility of diopside in an aqueous fluid at 20 and 30 kbar and approximately 1200°C to be approximately 10 wt%, which corresponds to about 2.5 wt% of MgO in solution. We assume that in our experiments at the same pressures the MgO content of fluid was the same or higher because the chemical potential of MgO for a forsterite-containing phase assemblage must be higher than in the presence of diopside alone. Assuming 2.5 wt% as a minimum value, we estimate the concentrations of other components, and the results of these calculations show that the total

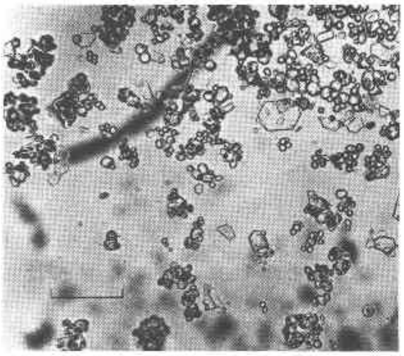

Fig. 4. Photomicrograph of primary phlogopite and forsterite in the products of run 32. Bar is 100 μm.

contents of dissolved silicate components in aqueous fluids in equilibrium with phlogopite and forsterite at 1100°C and pressures of 20 and 30 kbar are about 25 wt% and 50 wt%, respectively. It is clear that at 30 kbar fluids in equilibrium with phlogopite-containing phase assemblages are near critical conditions.

Table 2 illustrates that the proportion of solute in the vapor is a function of pressure, ranging from about 14 wt% at 11 kbar to about 55 wt% at 30 kbar. At 30 kbar, our vapors contain approximately 25 wt% dissolved solids. This is about twice the value for the solubility of diopside in a vapor containing 95 wt% H_2O and 5 wt% CO_2, determined by Eggler (1975). Experiments by Nakamura and Kushiro (1974) at 15 kbar reveal that aqueous vapor coexisting with forsterite and enstatite dissolves about 18 wt% SiO_2 at 1280°C and 22 wt% SiO_2 at 1310°C; the vapor coexisting with only enstatite contains up to 40 wt% SiO_2 at 1280°C and 15 kbar.

Petrological applications

Our experimental data were obtained for compositions with H_2O as the only volatile component. However, vapors in the mantle contain other volatile species, and experiments have shown that addition of components such as CO_2 and H_2 that lower the fugacity of H_2O will reduce the solubility of silicates in an aqueous vapor (for example, Shettel, 1973; Nakamura, 1974). Comparison of *P–T* coordinates for continental shield geotherms with the positions of vapor-phase isopleths for divariant assemblages corresponding to the following reactions (in the presence of H_2O and CO_2) shows that under these conditions H_2O/CO_2 values in vapors are high, particularly at depths below those of the stability of amphibole:

$$2\mathrm{Fo} + \mathrm{Di} + 2\mathrm{CO_2} = \mathrm{Do} + 4\mathrm{En};$$
$$\mathrm{Fo} + \mathrm{CO_2} = \mathrm{Mc} + \mathrm{En}$$

(Newton and Sharp, 1975; Eggler, 1977; Wyllie, 1979)

Our results show that under these conditions fluids may be very efficient agents for transporting K_2O. For example, temperatures of about 1050°C are reached under continental shields at depths of about 130 km corresponding to pressures of 40 kbar, from the geotherm of Clark and Ringwood (1964). Extrapolation of our results to 1050°C and 40 kbar clearly shows that the vapors in equilibrium with phlogopite would contain in excess of 30 g K_2O per 100 g of H_2O. If we accept 10 g K_2O/100 g H_2O as a conservative estimate, and if we assume that all the water in the present hydrosphere was transferred from the deep levels of the mantle of the Earth, then vapor could have transported $1.4 \cdot 10^{23}$ g of K_2O, which is approximately the amount in the continental crust. However, the shield geotherm intersects the peridotite–H_2O solidus at about 100 km, and it is more likely that much of the K_2O was transported in a silicate liquid.

It may be noted that the high mobility of K_2O-rich fluids under conditions of continental shield geotherms is consistent with the fact that only on continents do we find evidence for enrichment of mantle-derived magmatic rocks that commonly bring to the surface xenoliths of phlogopite-bearing ultramafic rocks. Under the higher temperature conditions of the deep oceanic lithosphere, vapor may have a higher value of CO_2/H_2O if carbonates are unstable (Eggler, 1978). Mysen *et al.* (1978) have experimentally investigated the mobility of H_2O in peridotite under mantle conditions. These preliminary results do suggest that the rate of migration of H_2O-rich fluids is sufficiently rapid to permit mobilization of K_2O and other components. However, high mobility of K_2O in aqueous fluids is necessary but not sufficient for intensive mantle metasomatism. There must also exist certain mechanisms for fixation of dissolved K_2O. One obvious method to precipitate K_2O is to decrease the pressure and temperature of the ascending vapor. The change in the CO_2/H_2O ratio of the vapor during ascent (Wyllie, 1979) would also affect the solubility of K_2O and other solutes. Crystallization of amphiboles at depths of about 60 km would certainly increase CO_2/H_2O, and the K_2O, Al_2O_3, and other components previously dissolved in the fluid would take part in metasomatic reactions.

Some K_2O is fixed in the upper levels of the mantle at depths of about 50 km, as evidenced by metasomatism of lherzolite xenoliths in alkali basalts (Boettcher and O'Neil, 1980; Stewart and Boettcher, 1977; Wilshire *et al.*, 1980). However, the abundance of phlogopite in kimberlites and in xenoliths in kimberlites suggests that considerable amounts of K_2O reside at depths greater than 50 km.

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