

## Subsolidus and melting experiments of a K-rich basaltic composition to 27 GPa: Implication for the behavior of potassium in the mantle

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### ABSTRACT

Subsolidus and melting experiments of a K-rich basaltic composition have been performed to 27 GPa. Pyroxene and majoritic garnet contain significant amounts of K<sub>2</sub>O (1–2 wt%) at 6–12.5 GPa and above 22.5 GPa, respectively. Both pyroxene and garnet may act as main reservoirs for K in the mantle. Sanidine (KAlSi<sub>3</sub>O<sub>8</sub>) or its polymorph potassium hollandite is the first phase to be melted up to 20 GPa, but potassium hollandite becomes a liquidus phase at  $P \geq 22.5$  GPa. In contrast to its typical incompatible behavior at low pressures, potassium is a compatible element in the deep mantle, at least in basaltic systems. This compatible behavior implies that a K-rich melt like kimberlite is difficult to generate at lower mantle conditions.

### INTRODUCTION

The behavior of K in the deep mantle is of considerable interest from the viewpoint of geophysics and geochemistry, because <sup>40</sup>K is one of the important heat sources during the evolution of the Earth. However, the geochemical properties of K and even its host minerals in the deep mantle have not been clarified sufficiently. Recent experiments (Harlow 1997; Tsuruta and Takahashi 1998) have demonstrated that the solubility of K<sub>2</sub>O in pyroxene evidently increases at high pressures, showing that pyroxene is a potential host for K in the mantle. These studies thus raised questions about where K is hosted at higher pressures outside the stability region of pyroxene, and its relation to potassium hollandite, a polymorph of KAlSi<sub>3</sub>O<sub>8</sub> (Yagi et al. 1994).

The estimated K<sub>2</sub>O content of a pyrolite mantle is ~0.03 wt% (McDonough and Sun 1995), which is much lower than the 0.15 wt% in a chondritic silicate mantle (Ringwood 1979), and the reason for this difference is still controversial. Potassium is normally regarded as a geochemically incompatible element in the Earth's mantle, due to its large ionic radius. However, in melting experiments of an average continental crust composition, Irifune et al. (1994) found that the stability field of potassium hollandite extends toward the liquidus at pressures >16 GPa. This result strongly suggests that K may behave more compatibly in the deep mantle. Experimental investigations on the geochemical behavior of K in basaltic and peridotitic systems to lower mantle conditions, therefore, are of great importance for evaluating the K budget of the Earth. Moreover, large amounts of ba-

saltic oceanic crust have been recycled into the deep mantle of which ~10% are K-rich alkali basalts.

In the present investigation, subsolidus and melting experiments on an alkali basalt were conducted at ~2.5 to 27.0 GPa for studying geochemical properties of K in the deep mantle. Melting experiments on the same starting material (JB1) were performed to 12.5 GPa by Tsuruta and Takahashi (1998), but subsolidus phase relations and compositions were poorly determined in that study.

### EXPERIMENTAL METHODS

The starting material was a K-rich basalt, JB1, a reference rock distributed by the Geological Survey of Japan. Its composition is generally similar to that of the mid-ocean ridge basalt (MORB), but with much higher K<sub>2</sub>O (Table 1). A dry glass of JB1 was made by fusing sample powder at 1250 °C with  $f_{O_2}$  controlled close to Ni-NiO. High-pressure and high-temperature experiments were conducted using the multi-anvil press at the Tokyo Institute of Technology. Three cell assemblies, which are designated as 14/8, 10/5, and 7/2 (octahedron edge length of MgO pressure medium/truncated edge length of WC anvil), were developed in this study; these assemblies were used for experiments at pressures  $\leq 7.5$ ,  $10.0 \leq P \leq 20.0$ , and  $>20.0$  GPa, respectively. Sample temperatures were measured with a W5%Re-W26%Re thermocouple. A cylindrical LaCrO<sub>3</sub> heater was used for both the 14/8 and 10/5 cell assemblies. The heater employed in the 7/2 assembly is Re foil. For all experiments, a Re capsule was used. The temperature gradient across the sample capsule was ~50 °C/mm for the 14/8 assembly and ~70 °C/mm for the 10/5 assembly, based on enstatite-diopside thermometry. The temperature gradient in the 7/2 assembly was not determined for lack of proper thermometry, but it could be much larger.

Pressures at room temperature were calibrated using

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**TABLE 1.** Representative phase compositions synthesized at different pressures and temperatures from a K-rich basalt JB1

Phase	JB1	5.0 GPa, 1400 °C				20.0 GPa, 1700 °C			20.0 GPa, 2280 °C		
		melt	coe	gt	px	gt	K-hol	sti	melt	gt	sti
SiO <sub>2</sub>	53.53	61.67	99.84	40.85	54.98	47.05	65.03	90.76	54.28	46.33	96.76
TiO <sub>2</sub>	1.44	4.67	0.05	0.85	0.77	1.41	0.25	0.22	0.66	0.52	0.22
Al <sub>2</sub> O <sub>3</sub>	14.85	11.72	0.14	21.85	13.29	16.69	19.00	3.55	15.89	19.22	0.68
Cr <sub>2</sub> O <sub>3</sub>	0.05	0.02	0.03	0.10	0.06	0.07	0.03	0.00	0.13	0.09	0.03
FeO*	7.92	5.57	0.36	14.94	5.19	9.93	0.55	0.89	7.30	8.76	0.29
MnO	0.16	0.07	0.00	0.32	0.08	0.20	0.00	0.01	0.19	0.21	0.00
MgO	7.64	1.17	0.07	11.57	8.25	10.10	0.17	1.23	9.45	12.44	0.02
CaO	9.12	3.35	0.14	9.23	11.44	10.84	0.47	1.10	8.92	10.71	0.13
Na <sub>2</sub> O	2.64	1.06	0.03	0.33	4.77	3.18	0.86	0.56	2.20	2.17	0.00
K <sub>2</sub> O	1.31	6.64	0.02	0.02	0.29	0.02	13.55	0.01	1.90	0.05	0.04
Total	98.7	95.9	100.7	100.1	99.1	99.5	99.9	98.3	100.9	100.5	98.2

Note: coe = coesite; gt = garnet; px = pyroxene; K-hol = K-hollandite; sti = stishovite; CAS = Ca, Al-rich phase; CaPv = CaSiO<sub>3</sub> perovskite.  
\* Total iron as FeO.

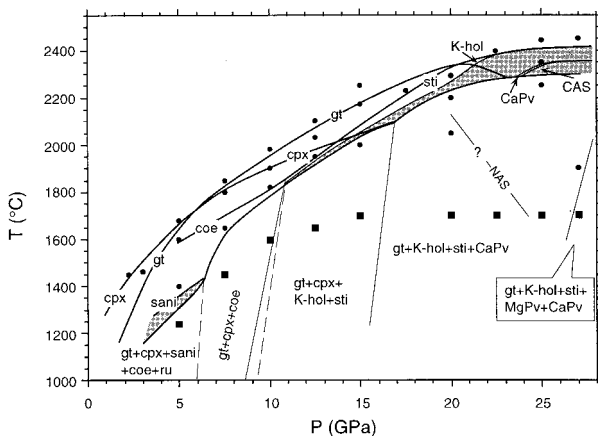
resistance changes associated with Bi (I-II and III-V), Pb (I-II), ZnS, GaAs, and GaP. Pressure calibrations at high temperatures (1000 °C, 1500 °C, and 1800 °C) were performed using the quartz-coesite transition, and the  $\alpha$ - $\beta$  and  $\beta$ - $\gamma$  transitions in Mg<sub>2</sub>SiO<sub>4</sub> ( $\gamma$  = MgSiO<sub>3</sub>+MgO). Extrapolating the calibration curve of the 7/2 assembly, 27.0 GPa can be generated with a press load of 980 tons. Other aspects of the experimental procedure are similar to those described by Takahashi et al. (1993).

Both subsolidus and melting experiments were performed on JB1. Heating durations for subsolidus runs were 6 to 10 h. For melting experiments, durations ranged from ~30 to 60 min at low pressures to ~5 to 10 min at

high pressures. Well-crystallized textures with chemically homogeneous grains and consistency of results among groups of runs led to the conclusion that a close approach to equilibrium was achieved.

## RESULTS

Experiments were performed with a pressure interval of 2.5 GPa, and the results are summarized in a *P-T* diagram (Fig. 1). In melting experiments, especially those at higher pressures, the temperature gradient within the capsule helps to determine the crystallization sequence easily. However, liquid migration within the capsule causes some difficulties in determining equilibrium melt compositions precisely. Melt compositions may be biased toward the bulk composition to some extent, but it will not affect the general conclusions of this study. At 5.0 GPa and 1250 °C, the starting material crystallized into an assemblage of garnet, pyroxene, sanidine, coesite, and trace rutile. However, at ~6 to 10 GPa, subsolidus phases consisted of only garnet, pyroxene, and coesite with no K-phase. Sanidine is unstable at this pressure range (Yagi et al. 1994), decomposing into K-rich wadeite (K<sub>2</sub>Si<sub>4</sub>O<sub>9</sub>), kyanite, and coesite. Neither K-rich wadeite nor kyanite existed in the run products, however, based on extensive compositional mapping. In a multi-component system like basalt at high pressures, K-rich wadeite and kyanite will be selectively dissolved into pyroxene and/or garnet. High K<sub>2</sub>O contents in pyroxenes at this pressure range, as shown later, support this speculation. At pressures >10.0 GPa, a KAlSi<sub>3</sub>O<sub>8</sub> phase with the hollandite structure appears (potassium hollandite), and coesite transforms to stishovite. These two phases with garnet remained as the main subsolidus phases up to 27.0 GPa. Other subsolidus phase changes with increasing pressure are gradual dissolution of pyroxene into garnet and crystallization of CaSiO<sub>3</sub> perovskite and an Na,Al-rich phase (NAS) when the pressure is >20 GPa. Crystallization of Mg-rich perovskite was confirmed at 27.0 GPa and 1700 °C by both electron microprobe and X-ray diffraction. However, with a temperature increase of 200 °C at the same pressure, no Mg-rich perovskite was detected (Fig. 1). This result



**FIGURE 1.** Subsidiary and melting phase relations of a K-rich basalt JB1. K-phase KAlSi<sub>3</sub>O<sub>8</sub> in sanidine or hollandite structure is the first disappearing phase until 20 GPa. At 22.5 GPa and above, however, potassium hollandite becomes the liquidus phase together with stishovite. Shaded regions show the stability areas of K-phases. gt = garnet; cpx = pyroxene; sani = sanidine; coe = coesite; ru = rutile; K-hol = potassium hollandite; sti = stishovite; CaPv = Ca-rich perovskite; MgPv = Mg-rich perovskite; NAS = Na,Al-rich phase; CAS = Ca,Al-rich phase. Both solid circles and squares represent experimental runs, and those in solid squares are performed generally along the temperature variations in the Earth's mantle (Akaogi et al. 1989).

TABLE 1. *Extended.*

22.5 GPa, 1700 °C				22.5 GPa, 2400 °C			25.0 GPa, 2350 °C					
gt	K-hol	sti	melt	K-hol	sti	gt	melt	K-hol	sti	CAS	CaPv	
46.38	66.77	98.71	44.10	61.98	99.17	46.15	48.55	63.61	98.88	41.75	44.55	
1.06	0.44	0.05	2.31	0.12	0.05	0.49	1.09	0.14	0.02	0.17	2.28	
17.37	17.63	0.23	12.18	20.14	0.25	17.98	14.86	20.43	0.14	42.43	3.06	
0.07	0.07	0.04	1.79	0.62	0.04	0.73	0.18	0.08	0.00	0.16	0.05	
10.69	0.75	0.25	11.32	0.36	0.21	8.18	9.70	0.46	0.25	1.35	1.93	
0.21	0.03	0.00	0.16	0.01	0.01	0.20	0.19	0.01	0.00	0.03	0.06	
10.25	0.27	0.01	7.55	0.07	0.00	11.72	10.91	0.14	0.04	2.76	1.39	
10.25	1.61	0.05	9.28	2.28	0.05	11.40	10.81	2.81	0.10	11.08	37.98	
2.96	1.46	0.01	3.69	1.92	0.00	2.55	2.98	1.79	0.01	0.84	0.49	
0.05	10.98	0.00	0.74	11.63	0.03	0.07	0.17	10.53	0.03	1.38	0.07	
99.3	100.0	99.3	93.1	99.1	99.8	99.5	99.4	100.0	99.5	101.9	91.9	

shows that the transition from majoritic garnet to perovskite has a positive Clapeyron slope. The Ca,Al-rich silicate phase (CAS) reported by Irifune et al. (1994) was not observed under subsolidus conditions of this study. Some representative phase compositions are summarized in Table 1.

Figure 2 shows variations of  $K_2O$  contents in subsolidus pyroxenes and garnets as a function of pressure generally along the temperature variations in the Earth's mantle (Akaogi et al. 1989), as shown by the solid squares in Figure 1. At ~7.5 to 12.5 GPa, pyroxene contained substantial  $K_2O$  (~1.4 to 1.9 wt%), which decreased greatly outside this pressure range. No K-rich phase was stable at ~6 to 10 GPa with K entering entirely into pyroxene. Coexisting garnet and silica contained virtually no K. Two processes occurred when pressure was >10 GPa: Pyroxene strongly dissolved into garnet and potassium hollandite crystallized. At 12.5 GPa, only a few extremely small potassium hollandite grains (~1 to 2  $\mu\text{m}$ ) were observed from careful compositional mapping. Pyroxene

at these conditions is rich in  $K_2O$ . With further pressure increase, most of the K exists in the form of K-hollandite, and as a result its content in pyroxene decreases radically. The  $K_2O$  content in pyroxene at 15.0 GPa is only 0.15 wt%, which is consistent with abundant K-hollandite in the mode of the run products (Fig. 2).

Garnet contains virtually no  $K_2O$  until 22.5 GPa, but increases abruptly at higher pressures. The  $K_2O$  in garnets formed at 25.0 GPa and 27.0 GPa was 0.50 wt% and 1.37 wt%, respectively. To check whether the high  $K_2O$  in garnet was caused by metastable growth or K-rich inclusions, experiments at the same conditions were repeated with slightly moistened starting materials. Trace water in the starting material promotes chemical reaction, thus avoiding metastability problems. Very similar chemical compositions were obtained, which confirmed that equilibrium in dry experiments was closely approached; therefore, the high  $K_2O$  contents in majoritic garnets at high pressures are verified. Modal amounts of potassium hollandite in the experimental run products decreased

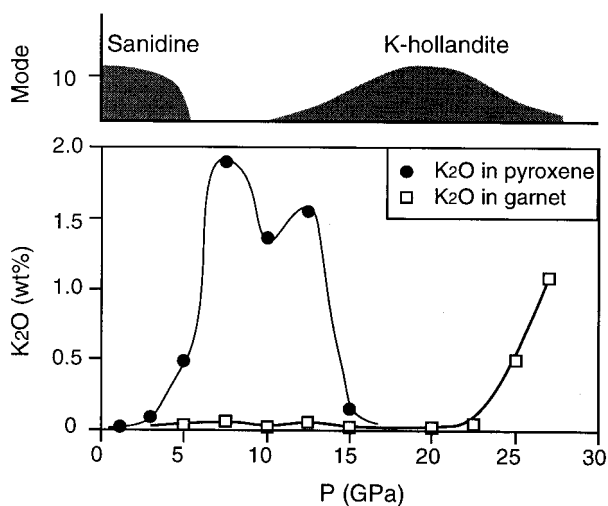


FIGURE 2. Contents of  $K_2O$  in subsolidus pyroxene and garnet as a function of pressure generally along the temperature variations in the Earth's mantle as shown by the solid squares in Figure 1; also shown are the modal variations sanidine or potassium hollandite.

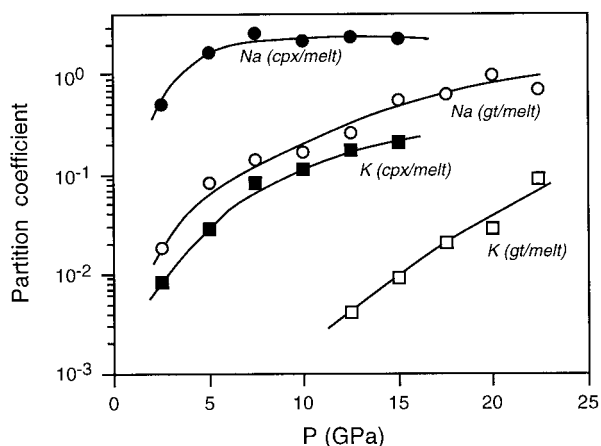


FIGURE 3. Variation of partition coefficients for Na and K between pyroxene, garnet, and melt as a function of pressure. Partition coefficients of K ( $X_{\text{crystal}}/X_{\text{melt}}$  in weight percentage) increase much more quickly than those of Na. Partition coefficients were measured at near liquidus conditions at each pressure. Pyroxene data are similar to those reported by Tsuruta and Takahashi (1998) to 12.5 GPa.

gradually from above 22.5 GPa, and the other subsolidus phases contained virtually no K. These results support crystallization of K-rich garnets at these conditions. Edgar and Mitchell (1997) reported that garnet may contain 1 to 2 wt% of  $K_2O$  at pressures as low as 12 GPa, but this was not observed in the present study.

Concerning melting relations (Fig. 1), sanidine is the first phase to be consumed with increasing pressure to 6 GPa followed by coesite, garnet, and pyroxene. Garnet replaces pyroxene as the liquidus phase at ~6 to 7 GPa and remains on the liquidus to ~20 GPa. Potassium hollandite is also the first phase to be melted out up to at least 20 GPa. However, at  $P \geq 22.5$  GPa, potassium hollandite becomes a liquidus phase together with stishovite. At ~25 to 27 GPa, two new phases, Ca-perovskite and CAS appear, formed by the incongruent melting of majoritic garnet. Variations in the melting sequence of the K-phase and formation of K-rich CAS (1.38 wt%) strongly affect the chemical compositions of partial melts generated at different pressures (Table 1). With sanidine and coesite being melted first, the partial melt formed at 5.0 GPa was silicic. It was rich in  $K_2O$  (6.64 wt%) and  $SiO_2$  (61.7 wt%) and poor in  $Na_2O$ , MgO, and FeO. In contrast, the interstitial partial melt coexisting with potassium hollandite and stishovite at 25.0 GPa and 2350 °C was very poor in  $K_2O$  (0.17 wt%) and  $SiO_2$  (48.6 wt%) but rich in MgO and FeO. Potassium strongly partitions into potassium hollandite, and the  $D_K(\text{hollandite/melt})$  was ~60.7. Such a refractory nature for potassium hollandite indicates that K is a geochemically compatible behavior at lower mantle conditions (at least in a basaltic composition) in contrast to its extremely incompatible property at low pressures. The partitioning of Na and K between pyroxene, garnet, and melt determined in a series of experiments near the liquidus of JB1 are shown in Figure 3. All of these partition coefficients increase gradually with pressure. The value of  $D_K(\text{cpx/melt})$  changes from 0.01 at 2.5 GPa to 0.21 at 15.0 GPa, and  $D_{Na}(\text{gt/melt})$  from 0.02 to ~1.0. Around 20 GPa, K is still strongly enriched in the partial melt, but Na was distributed almost equally between garnet and the partial melt.

## DISCUSSION

High pressure affects crystal chemistry in two possible ways. As commonly viewed in phase transformations, the coordination number of some elements increases with pressure. The sanidine to potassium hollandite transformation is a good example. A less well-studied relationship in high-pressure crystal chemistry, as emphasized by Harlow (1997), is differential ionic bond compressibility. Hazen and Finger (1982) pointed out that bond compressibility is proportional to the cube of the mean bond distance in a polyhedron, and inversely proportional to cation formal charge. Accordingly, larger and lower-charge ions like  $K^+$  have relatively greater ionic compressibility in comparison with smaller and higher-charge ions. Substitution of K in pyroxene and garnet, as well as the variation in partitioning can be easily explained by differ-

ential compressibility of cations with pressure. Because of the relatively larger compressibility of  $K^+$ , partition coefficients for K between pyroxene, garnet, and melt increase much more quickly than those of Na (Fig. 3).

Implications of this study extend to the behavior of other trace elements. For example,  $Rb^+$  (radius = 1.49 Å) is normally regraded as a much more incompatible element than  $Sr^{2+}$  (radius = 1.13 Å) in the Earth's crust and mantle, mainly due to its relatively large ionic radius. This property is widely used in explaining Rb-Sr isotopic data. However, fractionation of  $Rb^+$  from  $Sr^{2+}$  in the deep mantle may not be so pronounced, considering differential ionic compressibilities as previously discussed. This case could cause significant changes in understanding the Sr isotopic data. Systematic investigations on elemental geochemical properties (e.g., U, Pb, Sm, Nd) at various pressures are needed to construct a framework for chemical geodynamics (Hofmann 1997).

In contrast to pyroxene, much higher pressures are needed for K to substitute into garnet. The cubic site in garnet, which contains divalent cations like  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Fe^{2+}$  is the largest one in the garnet structure. Because it is even smaller than the M2 site in pyroxene, much higher pressures are needed to compress  $K^+$  so that it can enter the cubic site in garnet. Results of this study show that both pyroxene and garnet may act as the main K reservoir but at different depths of the mantle.

The behavior of Na and K in partial melts changes abruptly at ~20 to 22.5 GPa. Partial melts formed below this pressure are K-rich and Na-poor, but above this pressure the melts show strikingly different properties (Table 1), particularly in terms of  $K_2O$  content. The  $K_2O$  content in the interstitial melt (~0.17 wt%) at 25.0 GPa represents the upper solubility limit needed to saturate potassium hollandite in a basaltic system. This result shows that a very low  $K_2O$  content in a silicate melt at high pressure may, nevertheless, crystallize potassium hollandite. These results, furthermore, show that formation of a K-rich melt at  $P > 22.5$  GPa is unlikely and argue for genesis of kimberlitic and lamproitic magmas at shallower levels in the mantle, contrary to the model of Haggerty (1994).

Potassium hollandites formed below 20.0 GPa are close to stoichiometric  $KAlSi_3O_8$ , with the combined contents of albite and anorthite being ~8.3 to 11.2 mol%. At  $\geq 22.5$ , potassium hollandites are Na and Ca-rich with combined albite and anorthite contents of ~24.5 to 40.1 mol%. An abrupt compositional discontinuity is confirmed within a narrow pressure range (~20.0 to 22.5 GPa) at 1700 °C. At the same pressure range, potassium hollandite changes abruptly from being the first consumed phase to being the liquidus phase (Fig. 1), implying the existence of a break in the melting curve of  $KAlSi_3O_8$ . A phase transformation is the most likely reason for causing these variations.

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