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High Pressure Transitions in the System $KAlSi_3O_8$-$NaAlSi_3O_8$

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Abstract. Phase relations in the system $KAlSi_3O_8-NaAlSi_3O_8$ have been examined at pressures of 5–23 GPa and temperatures of 700–1200° C. $KAlSi_3O_8$ sanidine first dissociates into a mixture of wadeite-type $K_2Si_4O_9$, kyanite and coesite at 6–7 GPa, which further recombines into $KAlSi_3O_8$ hollandite at 9–10 GPa. In contrast, $NaAlSi_3O_8$ hollandite is not stable at 800–1200° C near 23 GPa, where the mixture of jadeite plus stishovite directly changes into the assemblage of calcium ferrite-type $NaAlSiO_4$ plus stishovite. Phase relations in the system $KAlSi_3O_8-NaAlSi_3O_8$ at 1000° C show that $NaAlSi_3O_8$ component gradually dissolves into hollandite with increasing pressure. The maximum solubility of $NaAlSi_3O_8$ in hollandite at 1000° C was about 40 mol% at 22.5 GPa, above which it decreases with pressure. Unit cell volume of the hollandite solid solution decreases with increasing $NaAlSi_3O_8$ component. The hollandite solid solution in this system may be an important candidate as a host mineral of K and Na in the uppermost lower mantle

Introduction

Alkali feldspar in the system $KAlSi_3O_8-NaAlSi_3O_8$ is one of the abundant minerals in the earth's crust. However, host minerals of K and Na in the deep mantle have not yet been sufficiently clarified. Behaviors of Na and K in the deep mantle are of considerable interest from geophysical and geochemical points of view, because ^{40}K is one of the important heat sources during the evolution of the earth.

High pressure transitions of synthetic $KAlSi_3O_8$ and $NaAlSi_3O_8$ as well as natural alkali feldspars have been examined by several investigators. Ringwood et al. (1967) first reported transformation of $KAlSi_3O_8$ feldspar into a new phase with the hollandite structure at about 12 GPa. Later Kinomura et al. (1975) found a field of three-phase assemblage of wadeite-type $K_2Si_4O_9$, Al_2SiO_5 kyanite, and SiO_2 coesite between those of hollandite and K-feldspar. They also determined roughly both of the transition boundaries under hydrous conditions. It is well known that $NaAlSi_3O_8$ albite breaks down into $NaAlSi_2O_6$ jadeite plus quartz at 2–3 GPa (Birch and LeComte 1960). Liu (1978a) found that jadeite dissociates into calcium ferrite-type $NaAlSiO_4$ plus stishovite at about 23 GPa. He also concluded that $NaAlSi_3O_8$ hollandite may be stable in a very limited pressure range near 20 GPa. Shock Hugoniots of alkali feldspars were also interpreted by transformation to the hollandite structure (Ahrens et al. 1969; Ahrens and Liu 1973; Sekine and Ahrens 1992). These results by the static and shock experiments suggest that hollandite may be stable as a solid solution in the system $KAlSi_3O_8-NaAlSi_3O_8$ at high pressures, and that it may be an important K- and Na-bearing mineral in the deep mantle.

In this study, firstly, the transition boundaries in $KAlSi_3O_8$ have been determined. Secondly, transitions in $NaAlSi_3O_8$ have been examined to clarify possible stability of $NaAlSi_3O_8$ hollandite. Thirdly, stability field of hollandite solid solution in the system $KAlSi_3O_8-NaAlSi_3O_8$ has been examined. Possible host minerals of K and Na in the lower mantle are also discussed.

Experimental Methods

Starting materials with the compositions of $(K_{1-x}, Na_x)AlSi_3O_8$ ($x=0.00$, 0.09, 0.17, 0.33, 0.50, 0.71, and 1.00) were prepared as follows. Reagent-grade K_2CO_3, Na_2CO_3, and Al-metal were dissolved in nitric acid, and mixed with alcoholic solution of $(C_2H_5O)_4Si$. From the mixed solutions, gels were precipitated, dried, and heated at 600–700° C. The heated gels were used as the starting materials. All of thee samples synthesized above were confirmed to be amorphous by powder x-ray diffraction method. Electron microprobe analysis showed that glasses prepared from the amorphous phases held the initial compositions within ±1.5 mol% of $NaAlSi_3O_8$. Polycrystalline albite synthesized from

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the $NaAlSi_3O_8$ glass at 2.5 GPa and 1000° C was also used as the starting material for $NaAlSi_3O_8$ composition. Powder x-ray diffraction showed that this material was a single phase of albite. All of the starting materials were dried at 120–150° C for 10–24 h just before the high pressure runs to remove any absorbed water.

High pressure experiments were performed using two kinds of high pressure apparatus, a pair of Bridgman anvils and a split-cylinder type multi-anvil apparatus. Phase relations of $KAlSi_3O_8$ were examined at pressures of 5–12 GPa and temperatures of 700–1200° C by means of the Bridgman anvils. This apparatus consists of cemented tungsten carbide with sintered diamond core, and is capable to generate up to about 20 GPa. The detailed design of this Bridgman anvil and the experimental techniques have already been given by Akaogi and Yamazaki (1991). Pressure was calibrated at room temperature using Bi I-II (2.55 GPa), Ba I-II (5.5 GPa), Bi III-V (7.7 GPa), Ba II-III (12.3 GPa), ZnS (15.5 GPa), and GaAs (18.3 GPa). Pressure at 1000° C was corrected by the transition boundaries of $\alpha-\gamma$ Fe_2SiO_4 (Yagi et al. 1987), the coesite-stishovite (Yagi and Akimoto 1976) and $ZnSiO_3$ pyroxene-ilmenite (Akaogi et al. 1990). The starting material of amorphous $KAlSi_3O_8$ was put into a sample chamber 0.9 mm in thickness and 2 mm in diameter between a pair of graphite discs 3.5 mm in diameter, which worked as a heater. The furnace was placed in a disc-shaped gasket 3.6 mm in thickness and 26 mm diameter made of pyrophyllite with a semisintered polycrystalline MgO core. The gasket was compressed by a pair of the Bridgman anvils, whose truncated faces were 26 mm in diameter. The recovered samples were examined by powder x-ray diffraction.

Phase relations for the $NaAlSi_3O_8$-containing compositions were examined at pressures of 13–23 GPa and temperatures of 800–1200° C, using the split-cylinder type cubic-octahedral anvil apparatus, which was newly installed in our laboratory (Akaogi et al. 1992). The apparatus is similar to a uniaxial split-sphere apparatus (Ito et al. 1984), except for that the shape of the first-stage anvils is not spherical but cylindrical. Tungsten carbide cubic anvils whose corners were truncated into triangular faces 1.5, 2.5 and 5.0 mm in edge were used, with the pressure medium of semisintered MgO octahedra 4.7, 6.8 and 9.9 mm in edge, respectively. Pressure was calibrated at room temperature using the same pressure-fixed points as those of the Bridgman anvils, in addition to GaP (23 GPa). Pressure at 1000–1200° C was corrected, using the boundaries of $\alpha-\beta$ and $\beta-\gamma$ transitions of Mg_2SiO_4 (Akaogi et al. 1989), and ilmenite-perovskite transition of $MgSiO_3$ (Ito and Takahashi 1989), in addition to the coesite-stishovite and $ZnSiO_3$ pyroxene-ilmenite transitions. The powdered starting material was put into a cylindrical Pt furnace which was placed in the MgO octahedron. The furnace size was 1.0–2.0 mm in diameter and 3.0–4.5 mm in length, depending on the anvil size. A tubular $LaCrO_3$ sleeve was placed outside of the furnace for thermal insulation. Temperature at the central part of the heater was measured by a Pt/Pt−13% Rh thermocouple, whose hot junction was in contact with the outer surface of the furnace. After the sample was held at the desired P-T conditions for certain duration, the central part of the recovered sample was examined by powder x-ray diffraction and electron microprobe analysis. Lattice parameters of hollandite was refined using six to nine diffraction lines of (521), (600), (141), (150), (301), (420), (211), (130), and (220) by powder x-ray diffraction using CuK α_1 radiation. Compositions of the coexisting phases in the run products were determined by the microprobe analysis. The microprobe was operated with an acceleration voltage of 15 kV and a beam current of 12 nA. Single crystals of wollastonite, corundum, albite, and adularia were used for standards of Si, Al, Na, and K, respectively. In order to avoid vaporization of alkali elements from the samples, the electron beam was expanded to 10–20 μm in diameter. The compositions of hollandite and jadeite were determined using the grains about 30–50 μm in diameter. However, the compositions of calcium ferrite in the run products could not be determined because of the very small grain size (about 1–2 μm).

Results

The experimental results for the $KAlSi_3O_8$ composition are summarized in Table 1, and the phase relations are illustrated in Fig. 1. $KAlSi_3O_8$ sanidine stable at 1 atm dissociates into a mixture of wadeite-type $K_2Si_4O_9$, kyanite, and coesite at about 6–7 GPa at 700–1200° C. The three phases combine into a single phase of $KAlSi_3O_8$ hollandite at about 9–10 GPa. this boundary is placed at slightly higher pressure than the coesite-stishovite

Table 1. Experimental results on $KAlSi_3O_8$, using the Bridgman anvil apparatus

Run no.	Pressure (GPa)	Temperature (°C)	Time (min)	Phases
K23	6.0	700	130	Sa
K24	6.5	700	130	Sa, Wa, Co, Ky
K25	7.0	700	130	Wa, Co, Ky
K28	8.5	700	130	Wa, St, Co, Ky
K27	9.0	700	130	Ho, Wa, St, Ky
K26	9.5	700	130	Ho > Wa, St, Ky
K19	6.0	800	120	Sa
K30	6.5	800	120	Sa, Wa, Co, Ky
K32	8.5	850	120	Wa, Co, St, Ky
K29	9.0	850	120	Ho, Wa, St, Ky
K9	5.0	1000	120	Sa
K22	5.5	1000	120	Sa
K21	6.0	1000	120	Sa
K17	6.5	1000	120	Wa, Co, Ky, Sa
K16	7.0	1000	120	Wa, Co, Ky > Sa
K15	7.5	1000	110	Wa, Co, Ky > Sa
K13	9.0	1000	120	Wa, Co, Ky, St
K14	9.5	1000	120	Ho > Wa, St, Ky
K11	10.0	1000	120	Ho > > Wa, St, Ky
K10	11.0	1000	120	Ho
K4	12.0	1000	120	Ho
K31	6.5	1200	40	Sa
K33	7.0	1200	40	Wa, Co, Ky, Sa

Sa: sanidine, Wa: wadeite, Co: coesite, St: stishovite, Ky: Kyanite, Ho: hollandite

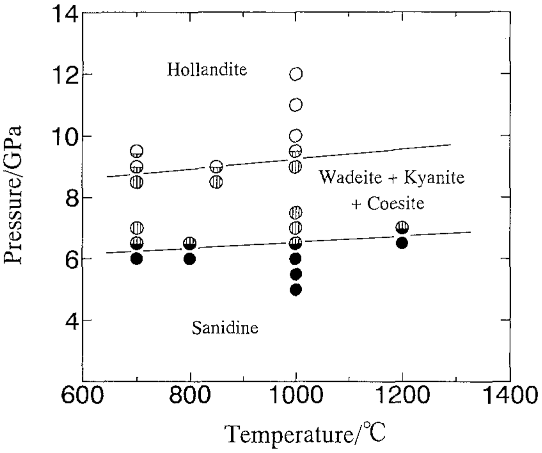

Fig. 1. Phase relations in $KAlSi_3O_8$. Circles represent the experimental runs. Areas of different symbols in one circle correspond roughly to the volumes of the different phases (or assemblages). Stishovite was found to coexist with coesite, kyanite, and wadeite at pressures within 0.5 GPa below the upper boundary

Table 2. Experimental results on the system $NaAlSi_3O_8-KAlSi_3O_8$, using the multianvil apparatus

Run no.	Composition $NaAlSi_3O_8$ mol%	Pressure (GPa)	Temperature (°C)	Time (min)	Phases
84	100	22.0	800	90	Jd + St
83	100	23.0	800	90	Cf + Jd + St
69	100	22.0	1000	20	Jd + St
66	100	23.0	1000	20	Cf + St
82	100	22.0	1200	60	Jd + St
81	100	23.0	1200	60	Cf + St
93	71	22.0	1000	60	Jd + St + Ho
57	50	16.0	1000	60	Ho + Jd + St
56	50	18.5	1000	60	Ho + Jd + St
54	50	20.5	1000	60	Ho + Jd + St
63	50	20.5	1000	120	Ho + Jd + St
78	50	22.0	1000	60	Ho + Jd + St
75	50	23.0	1000	60	Ho + Cf + St
77	50	23.0	1000	60	Ho + Cf + St
60	33	15.5	1000	60	Ho + Jd + St
55	33	17.5	1000	30	Ho + Jd + St
58	33	18.5	1000	40	Ho + Jd + St
90	33	22.0	1000	90	Ho
53	17	18.5	1000	60	Ho + Jd + St
94	17	22.0	1000	60	Ho
85	17	22.5	1000	60	Ho
59	9	13.0	1000	60	Ho + Jd + St
86	9	22.0	1000	60	Ho
91	0	20.0	1000	60	Ho

Cf: calcium ferrite, Jd: jadeite, Ho: hollandite, St: stishovite

transition boundary (Yagi and Akimoto 1976), because stishovite was found in the upper portion of the field of the wadeite-bearing assemblage. The location of the boundary between the fields of sanidine and the three-phase assemblage was determined at the pressure where wadeite, kyanite, and coesite first appeared, because a small amount of sanidine was still present together with the three phases at the P, T conditions just above the boundary due to rather sluggish reaction. The boundary between the field of hollandite and that of wadeite, kyanite, and stishovite was also determined at the pressure at which hollandite firstly appeared. Although the above two boundaries were not examined by reversed runs, our boundaries are expected to be close to equilibrium, because the boundaries are consistent with those determined by Urakawa et al. (1994), where the normal and reverse reactions were confirmed by in situ x-ray observation, as shown below.

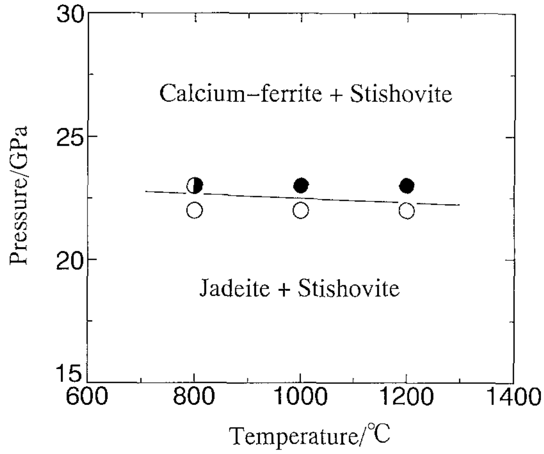

Fig. 2. Phase relations in $NaAlSi_3O_8$

Kinomura et al. (1975) examined the phase relations of $KAlSi_3O_8$ under hydrous conditions at pressures to 11 GPa and temperatures to 1000° C, using a cubic anvil press. They reported that at pressures below 7 GPa $KAlSi_3O_8 \cdot H_2O$ with cymrite structure was synthesized, which decomposed into wadeite, kyanite, coesite, and water at about 8 GPa. In our experiments performed in anhydrous conditions, the cymrite phase was not observed. Kinomura et al. (1975) also reported that the boundary from wadeite, kyanite, plus stishovite into hollandite was placed at about 11–12 GPa at 700–900° C. This transition pressure is about 2 GPa higher than our data, probably due to inaccurate pressure calibration in Kinomura et al.'s study, because the pressure values above the Bi III-V point (7.7 GPa) were estimated by extrapolation and the effect of temperature on pressure was not corrected. Urakawa et al. (1994) have examined the phase relations of $KAlSi_3O_8$ at 5–12 GPa by means of a cubic anvil apparatus with synchrotron radiation x-ray diffraction, using the gel and crystalline sanidine as the starting materials. In their study, pressure was determined accurately based on NaCl scale by in situ x-ray measurements. Although they made most of the runs at temperatures above 1000° C, their experimental data on both of the boundaries for dissociation of sanidine and for recombination into hollandite are in good agreement with our boundaries within about ±0.5 GPa. Our boundary for the sanidine dissociation and that by Urakawa et al. (1994) are consistent with that calculated

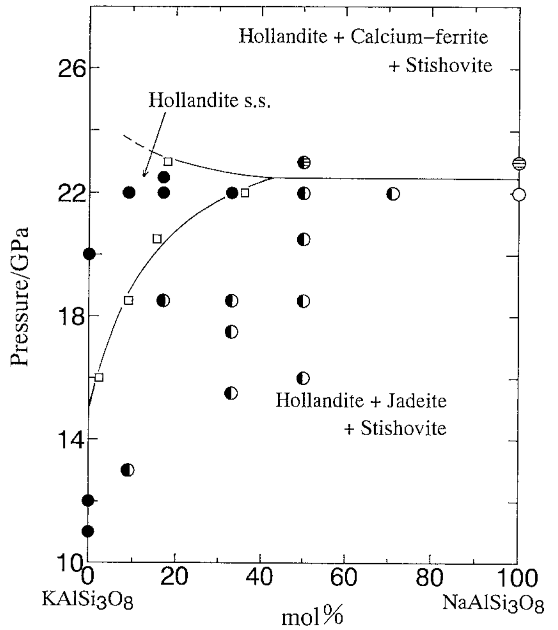

Fig. 3. Phase relations in the system $KAlSi_3O_8-NaAlSi_3O_8$ at 1000° C. Circles represent the experimental runs. Areas of different symbols in one circle correspond roughly to the volumes of the different phases (or assemblages). Small squares show the compositions of hollandite coexisting with jadeite (or calcium ferrite) plus stishovite

from thermodynamic data by Geisinger et al. (1987) within about ±0.7 GPa.

The experimental results in the system $KAlSi_3O_8-NaAlSi_3O_8$ are shown in Table 2. The transition boundary of $NaAlSi_3O_8$ is illustrated in Fig. 2. This figure shows that the assemblage of $NaAlSi_2O_6$ jadeite plus stishovite changes into a mixture of calcium ferrite-type $NaAlSiO_4$ and stishovite at about 22.5 GPa. This confirms that jadeite dissociates into calcium ferrite-type $NaAlSiO_4$ plus stishovite at that pressure. Figure 2 also shows that $NaAlSi_3O_8$ hollandite is not stable at 800–1200° C in this pressure range, because hollandite is expected to have a density intermediate between the two assemblages, as shown below.

Table 4. Lattice parameters and cell volumes of hollandite solid solutions in the system $KAlSi_3O_8-NaAlSi_3O_8$

Composition	a_0(Å)	c_0(Å)	V_0(Å^3)
$KAlSi_3O_8$	9.328(1)	2.726(1)	237.2(1)
$(K_{0.91}, Na_{0.09})AlSi_3O_8$	9.327(1)	2.724(1)	237.0(1)
$(K_{0.83}, Na_{0.17})AlSi_3O_8$	9.326(1)	2.725(1)	237.0(1)
$(K_{0.67}, Na_{0.33})AlSi_3O_8$	9.322(1)	2.725(1)	236.8(1)

Figure 3 shows the phase relations in the system $KAlSi_3O_8-NaAlSi_3O_8$ at pressures up to 24 GPa at 1000° C. Table 3 shows the compositions of hollandite and jadeite in the run products in this system. The phase boundary for the hollandite solid solution in Figure 3 was determined by the compositions of hollandite coexisting with jadeite (or calcium ferrite) plus stishovite in Table 3. Above about 14 GPa, $NaAlSi_3O_8$ dissolves gradually into $KAlSi_3O_8$ hollandite with increasing pressure. At about 22.5 GPa, hollandite solid solution with the maximum $NaAlSi_3O_8$ component of about 40 mol% is stable. At higher pressures, the solubility of $NaAlSi_3O_8$ in hollandite decreases. Therefore, the $NaAlSi_3O_8$ solubility in hollandite is rather limited at 1000° C. Compositions of jadeite coexisting with hollandite and stishovite in Table 3 show that jadeite contains zero or negligible amount of $KAlSi_2O_6$ component.

Lattice parameters and unit cell volumes of hollandite solid solutions are shown in Table 4 and illustrated in Fig. 4. With increasing $NaAlSi_3O_8$ component in hollandite, the a_0 axis decreases, and the c_0 axis is almost constant, resulting in decrease of the cell volume. Linear extrapolation of a_0 and c_0 of the solid solutions gives a_0 of 9.310 Å, c_0 of 2.723 Å and calculated density of 3.690 g/cm^3 for $NaAlSi_3O_8$ hollandite. These edge lengths and density are in good agreement with those reported by Liu (1978a): a_0 of 9.30±0.03 Å, c_0 of 2.73±0.01 Å, and density of 3.69±0.04 g/cm^3.

Table 3. EPMA analyses of hollandite and jadeite in the run products in the system $KAlSi_3O_8-NaAlSi_3O_8$

Run no.	57		58	63	93		77
Pressure (GPa)	16		18.5	20.5	22		23
Temperature (°C)	1000		1000	1000	1000		1000
Phase	Ho	Jd	Ho	Ho	Ho	Jd	Ho
SiO_2 (wt%)	68.92	59.24	66.69	65.27	64.39	58.75	61.53
Al_2O_3	16.85	25.82	18.72	17.57	19.01	27.41	20.04
Na_2O	0.23	15.01	0.87	1.73	4.13	15.23	1.98
K_2O	13.85	0.00	14.93	14.46	11.00	0.21	13.56
Total	99.85	100.07	101.21	99.03	98.53	101.60	97.11
O	8.00	6.00	8.00	8.00	8.00	6.00	8.00
Si	3.12	1.99	3.01	3.03	2.97	1.95	2.91
Al	0.90	1.02	1.00	0.96	1.03	1.07	1.12
Na	0.02	0.98	0.08	0.16	0.37	0.98	0.18
K	0.80	0.00	0.86	0.86	0.65	0.01	0.82
Na/(Na+K)	0.02	1.00	0.09	0.16	0.36	0.99	0.18

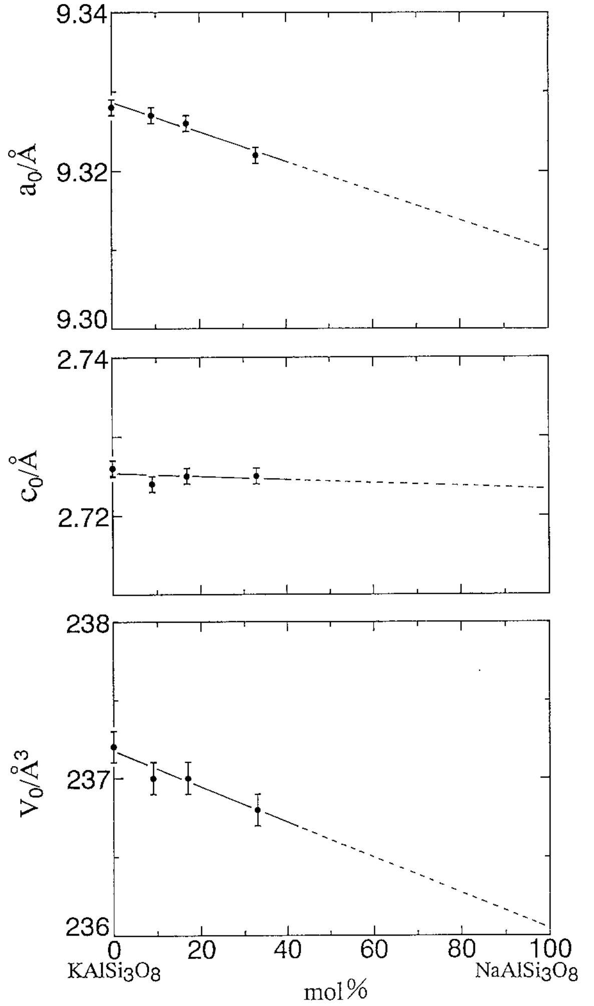

Fig. 4. Lattice parameters and unit cell volumes of hollandite solid solutions in the system $KAlSi_3O_8-NaAlSi_3O_8$. Vertical bars show the experimental errors

Discussion

Density changes for reactions involving $NaAlSi_3O_8$ hollandite are calculated, using our estimated density of $NaAlSi_3O_8$ hollandite together with the published data on calcium ferrite-type $NaAlSiO_4$ (Liu 1977; Yamada et al. 1983) and those on jadeite and stishovite (Robie et al. 1978). The density increases for the reactions:

$$\underset{\text{jadeite}}{NaAlSi_2O_6} + \underset{\text{stishovite}}{SiO_2} = \underset{\text{hollandite}}{NaAlSi_3O_8} \qquad (1)$$

$$\underset{\text{hollandite}}{NaAlSi_3O_8} = \underset{\text{calcium ferrite}}{NaAlSiO_4} + \underset{\text{stishovite}}{2\,SiO_2} \qquad (2)$$

are calculated to be 4.7 and 10.5%, respectively. The intermediate density of $NaAlSi_3O_8$ hollandite between jadeite + stishovite and calcium ferrite + stishovite is consistent with change of solubility of $NaAlSi_3O_8$ component into hollandite solid solution at pressures above and below 22.5 GPa, as shown in Fig. 3.

From the phase transition experiments by the diamond anvil cell with YAG laser heating, Liu (1978a) concluded the stability of $NaAlSi_3O_8$ hollandite at about 1000° C in the small, limited pressure range of about 20–23 GPa. This result is inconsistent with those in our study. In Liu's experiments, identification of $NaAlSi_3O_8$ hollandite was complicated by overlapping of the diffraction peaks with those of the other phases, and was based only on two, relatively weak diffraction lines which did not overlap with lines of any other phases. Therefore, it would be likely that $NaAlSi_3O_8$ hollandite was a minor phase synthesized probably at much higher temperature than 1000° C in the local hot spots by the YAG laser heating.

Sekine and Ahrens (1992) interpreted the previous Hugoniot data of albite-containing minerals (McQueen et al. 1967; Ahrens et al. 1969; Ahrens and Liu 1973), and concluded that albite transforms to hollandite structure in the pressure range of 40–80 GPa in the shock compression experiments. Recently, Mori (1990) identified a hollandite phase with the composition of $Na_{0.9}Ca_{0.1}Al_{1.1}Si_{2.9}O_8$ in a naturally shocked meteorite by electron diffraction. He found the hollandite phases in the glass veins, where majorite and ringwoodite also occurred. Comparing these results with the present data by the static experiments, where $NaAlSi_3O_8$ hollandite is not stable at 800–1200° C, it is likely that $NaAlSi_3O_8$ hollandite may be stable at much higher temperatures.

In the last decade, extensive studies on phase transitions of mantle minerals have been carried out. These studies have clarified that major constituent minerals in the lower mantle are $MgSiO_3$-rich perovskite and magnesiowüstite, with a small amount of $CaSiO_3$ perovskite. However, host minerals of alkali elements in the lower mantle have not yet been sufficiently clarified. Calcium ferrite-type $NaAlSiO_4$ would be a major host mineral for Na in the lower mantle, as already suggested by Ringwood (1975) and Liu (1978a). The assemblage of calcium ferrite plus stishovite is denser than $NaAlSi_3O_8$ hollandite, as discussed above, and the calcium ferrite phase is expected to be stable in the deep lower mantle.

Our results also suggest that hollandite solid solution in the system $KAlSi_3O_8-NaAlSi_3O_8$ may be an important candidate for the host phase of K as well as Na in the transition zone and the uppermost lower mantle. The hollandite structure is the only known K-bearing phase stable under the lower mantle conditions, because Liu (1978b) confirmed that $KAlSi_3O_8$ hollandite is stable at pressures at least 30 GPa around 1000° C. Since abundance of K in the mantle is much smaller than Na, the amount of hollandite in the lower mantle would probably depend on solubility of K into calcium ferrite-type $NaAlSiO_4$, which unfortunately could not be determined in this study due to the small grain size of calcium ferrite. In order to discuss further the host phase of K in the lower mantle, further studies are required to examine possible transition of the K-bearing hollandite at high pressure and to clarify the K solubility into the calcium ferrite phase.

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