A new high-pressure form of $KAlSi_3O_8$ under lower mantle conditions

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[1] In situ X-ray diffraction measurements have been made on $KAlSi_3O_8$ hollandite using diamond anvil cell and multianvil apparatus combined with synchrotron radiation. Both of the measurements with different techniques demonstrated that K-hollandite transforms to a new high-pressure phase (hollandite II) at ~22 GPa upon increasing pressure at room temperature. The X-ray diffraction peaks of the new phase were reasonably indexed on the basis of a monoclinic cell with *I*2/*m* space group. Hollandite II was also confirmed to be formed at high temperatures to 1200°C and pressures to 35 GPa, which was quenched to room temperature under pressure but converted back to hollandite at about 20 GPa on release of pressure. The present result is contradictory to earlier studies based mainly on quench method, which concluded that hollandite is stable up to 95 GPa at both room temperature and high temperatures up to 2300°C. *INDEX TERMS:* 1025 Geochemistry: Composition of the mantle; 3630 Mineralogy and Petrology: Experimental mineralogy and petrology; 3675 Mineralogy and Petrology: Sedimentary petrology; 3924 Mineral Physics: High-pressure behavior; 3954 Mineral Physics: X ray, neutron, and electron spectroscopy and diffraction. **Citation:** Sueda, Y., T. Irifune, N. Nishiyama, R. P. Rapp, T. Ferroir, T. Onozawa, T. Yagi, S. Merkel, N. Miyajima, and K. Funakoshi (2004), A new high-pressure form of $KAlSi_3O_8$ under lower mantle conditions, *Geophys. Res. Lett.*, *31*, L23612, doi:10.1029/2004GL021156.

1. Introduction

[2] $KAlSi_3O_8$-rich feldspar is a major constituent mineral in granitic continental crust, parts of which are believed to be transported deep into the mantle via subduction of oceanic lithosphere [*Armstrong*, 1981; *Dupre and Allegre*, 1983; *Hofmann*, 1997; *Sobolev and Shatsky*, 1990]. $KAlSi_3O_8$ feldspar transforms to a high-pressure form with a hollandite structure [*Ringwood et al.*, 1967; *Yamada et al.*, 1984] at pressures greater than ~9 GPa and at temperatures 1000–1400°C via a mixture of $K_2Si_4O_9$ wadeite + Al_2SiO_5 kyanite + SiO_2 coesite, a reaction that has been confirmed on the basis of both quench [*Kinomura et al.*, 1975; *Yagi et al.*, 1994] and in situ X-ray diffraction experiments [*Urakawa et al.*, 1994]. The $KAlSi_3O_8$-rich hollandite (K-hollandite, hereafter) has also been shown to be a major phase in continental crust and marine sediment lithologies, as well as in some basalts, at depths equivalent to the deeper part of the upper mantle and throughout the mantle transition region [*Irifune et al.*, 1994; *Schmidt*, 1996; *Ono*, 1998; *Wang and Takahashi*, 1999].

[3] Only few studies have been made on the stability of K-hollandite under lower mantle conditions. Quench experiments using multianvil apparatus (MA) on a K-rich basalt demonstrated that K-hollandite is a major subsolidus phase at pressures to 27 GPa and at 1700°C, equivalent to the conditions of the uppermost lower mantle [*Wang and Takahashi*, 1999]. These authors also suggested that there is a possibility of occurrence of a phase transition in K-hollandite at pressures of 20–22.5 GPa at 1700°C from some indirect evidence.

[4] More recently, an experimental study with diamond anvil cell (DAC) demonstrated that K-hollandite is stable at pressures up to 95 GPa and temperatures to ~2300°C, leading to a conclusion that hollandite is the major host of potassium down to a depth of 2200 km in the lower mantle [*Tutti et al.*, 2001]. However, this conclusion relies on the results of quench experiments, and no in situ X-ray diffraction measurements under simultaneous high pressure and high temperature corresponding to those of the lower mantle have been conducted to date.

2. Experimental Method

[5] We made in situ X-ray diffraction observations using both DAC and MA combined with synchrotron radiation. We used a polycrystalline sintered piece of pure $KAlSi_3O_8$ hollandite, synthesized by MA, as the starting material for the DAC experiment. This sample was polished to a square block with sides of ~80 μm and ~25 μm thick. Helium pressure medium was used and the pressure, as determined by the changes in unit-cell volume of gold calculated with an equation of state [*Anderson et al.*, 1989], was also cross-checked by the ruby scale [*Mao et al.*, 1986]. While the sample was maintained at high pressure, a monochromatized (λ = 0.4258 Å) and collimated (~30 μm) X-ray from synchrotron source at the Photon Factory, Tsukuba, was directed on the sample, and the diffracted X-ray was acquired using an imaging plate, typically for 15 minutes in each measurement. Further details of the experimental set-up are given elsewhere [*Yagi et al.*, 2001]. The X-ray diffraction measurements were conducted every ~2 GPa as pressure was increased, and the phases present were identified on the basis of the diffraction profiles.

[6] In situ X-ray diffraction experiments at simultaneous high pressure and high temperature were also conducted using MA with sintered diamond anvils at SPring-8. The cell assembly used in the present study was virtually the same as that of our earlier study [*Irifune et al.*, 2002]. An energy-dispersive method was adopted for X-ray diffraction

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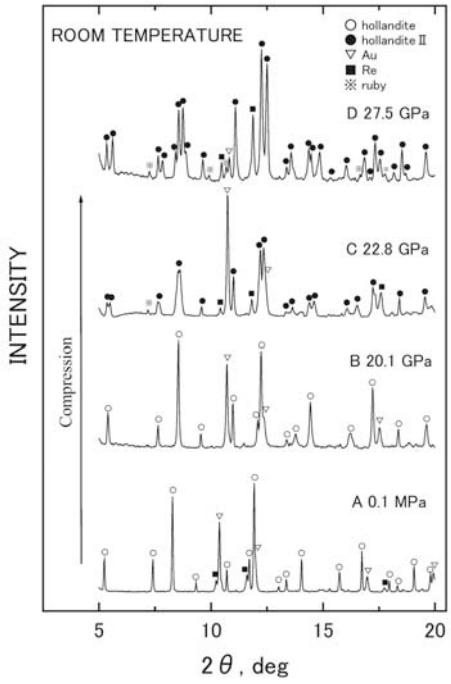

Figure 1. X-ray diffraction profiles of $KAlSi_3O_8$ in DAC with increasing pressure at room temperature. Only the diffraction peaks of K-hollandite, in addition to those of Au and Al_2O_3 as the pressure scales and Re gasket, were observed at ambient conditions (a) and at 20.1 GPa (b). The diffraction profile started to change at ~22–23 GPa (c), and hollandite II was formed at higher pressures (d).

measurements with a white X-ray beam of ~50 μm, and a new 1500-ton MA (SPEED-MkII [*Katsura et al.*, 2004]) was used for the experiments with sintered diamond anvils. Temperature was measured with a $W_{97}Re_3$-$W_{75}Re_{25}$ thermocouple and the pressure was evaluated by the volume change in gold [*Anderson et al.*, 1989]. The starting material was a glass of pure $KAlSi_3O_8$ composition with some minor quench crystals, which had previously produced single phase K-hollandite in earlier quench experiments performed at 15 GPa and at 1200°C in the MA.

3. Experimental Results

[7] Figure 1 shows the variations of the X-ray diffraction profile for the $KAlSi_3O_8$ sample as a function of pressure at room temperature in the DAC. The overall pattern of the diffraction peaks for hollandite did not change with increasing pressure to about 20 GPa (Figures 1a and 1b), but some peaks started to split or broaden at ~22–23 GPa (Figure 1c), and a diffraction pattern quite different from that of the hollandite structure was obtained at higher pressures (Figure 1d). The diffraction peaks were found to be reasonably indexed on the basis of a monoclinic symmetry with $I2/m$ space group, as listed in Table 1. The cell parameters obtained by least-square fitting of the observed diffraction data at 27.5 GPa were; a = 9.146 (3) Å, b = 2.640 (1) Å, c = 8.725 (3) Å, β = 91.54 (3) deg., and V = 210.6(1) $Å^3$, giving a density of 4.39 g/cm^3 under this pressure. Further detailed studies of the crystal structure and the compressibility of this phase are currently being pursued (T. Ferroir et al., manuscript in preparation, 2004).

[8] Variations of the X-ray diffraction profile in a run using MA (run M080) are depicted in Figure 2. K-hollandite was first synthesized from the glass starting material at 18 GPa, at 1200°C for one hour, and then further pressurized at the room temperature (Figure 2a). Upon compression, the diffraction peaks clearly became broader at pressures above ~22–23 GPa (Figure 2b), and some of the original single peaks began to split at the highest pressure of 31.4 GPa at room temperature (Figure 2c). This observation is consistent with the results in the DAC experiment, although much clearer peak splitting was noted in the latter experiment at room temperature because of the use of the helium pressure medium, which provides a quasi-hydrostatic environment for the sample at high pressure.

[9] Temperature was then increased gradually at fixed press load, and the X-ray diffraction data were collected for 5–10 minutes at a number of specific temperatures up to 1200°C. Upon increasing temperature, the diffraction peaks became sharper and were completely split into several peaks above ~800°C. The whole X-ray diffraction pattern obtained at 33.4 GPa, 1200°C (Figure 2d), was virtually the same as that observed in the DAC experiment with helium pressure medium at similar pressures and at the room temperature (Figure 1d). The high-pressure phase was preserved upon decreasing temperature under pressure (Figure 2e), and the lattice parameters (a = 9.123 (1) Å, b = 2.644 (1) Å, c = 8.686 (2) Å, β = 91.55 (2) deg., and V = 209.4(1) $Å^3$) measured at 29.4 GPa at the room temperature were consistent with those obtained in the DAC experiment. The new phase, however, converted back to the hollandite structure at about 20 GPa during decompression, and the diffraction profile at ambient conditions was that of the hollandite structure (Figure 2f).

[10] Another MA run (run M039) was made with the same glass starting material, by pressurizing the sample to 35.4 GPa without first synthesizing the hollandite phase at lower pressure, and temperature was then increased to 1200°C at fixed press load. The same diffraction peaks that were observed in the run using the K-hollanite starting material were present. This indicates that the new phase (hollandite II, hereafter) is indeed stable under these pressure and temperature conditions, because the same phase was obtained from the different starting material (glass and K-hollandite), an important criterion in testing the thermodynamic stability of the new phase. Again, hollandite II was preserved in run M039 at the room temperature under pressure after quenching, but it transformed to the hollandite structure at the ambient pressure.

4. Discussion

[11] Figure 3 summarizes the present experimental conditions and the results in a P-T diagram. We recently made measurements of the P-V-T relations in K-hollandite using MA at pressures up to 25 GPa and temperatures up to ~1500°C (N. Nishiyama et al., manuscript in preparation, 2004). These experiments confirmed that the hollandite structure is stable under these conditions, as shown in Figure 3 (for run M044), although notable broadening of some diffraction peaks is apparent at temperatures below

Table 1. X-ray Diffraction Data of Hollandite II at 27.5 GPa, at Room Temperature[a]

h	k	l	d_{obs} (Å)	d_{cal} (Å)	$(d_{obs}/d_{cal}) - 1$
2	0	2	4.566	4.571	−0.0011
0	0	2	4.359	4.361	−0.0003
−2	0	2	3.195	3.199	−0.0012
2	0	2	3.118	3.114	0.0013
−3	0	1	2.903	2.901	0.0005
3	0	1	2.8529	2.8531	−0.0001
−1	0	3	2.7912	2.7924	−0.0004
1	0	3	2.7473	2.7492	−0.0007
1	1	0	2.5330	2.5360	−0.0012
2	1	1	2.2033	2.2039	−0.0003
0	0	4	2.1839	2.1804	0.0016
3	1	0	1.9937	1.9952	−0.0007
0	1	3	1.9550	1.9543	0.0004
−3	1	2	1.8276	1.8266	0.0006
3	1	2	1.8001	1.8023	−0.0012
2	1	3	1.7853	1.7853	0.0000
−4	1	1	1.7024	1.7016	0.0005
4	1	1	1.6892	1.6884	0.0005
−1	1	4	1.6581	1.6595	−0.0008
1	1	4	1.6462	1.6473	−0.0006
−4	0	4	1.6009	1.5994	0.0010
6	0	0	1.5254	1.5238	0.0011
−5	1	2	1.4555	1.4536	0.0013
5	1	2	1.4121	1.4114	0.0005
−2	1	5	1.3952	1.3958	−0.0004
2	1	5	1.3763	1.3778	−0.0008
0	2	0	1.3210	1.3198	0.0009
−6	1	1	1.3080	1.3093	−0.0010
−5	1	4	1.2498	1.2506	−0.0006
5	1	4	1.2252	1.2249	0.0002
4	1	5	1.2148	1.2153	−0.0003

[a]Monoclinic symmetry with *I*2/*m* space group. a = 9.146 (3) Å, b = 2.640 (1) Å, c = 8.725 (3) Å, β = 91.54(3) deg., V = 210.6 (1) $Å^3$, ρ = 4.39 g/cm^3.

∼700°C, indicative of the commencement of the phase transition to hollandite II. Thus it is most likely that the boundary between K-hollandite and hollandite II has a steep positive slope and locates at about 24 GPa at high temperature as shown by the dashed line in Figure 3, although further study is needed to define the phase boundary more quantitatively.

[12] It was reported that K-hollandite is stable at pressures and temperatures far exceeding those of the present study, on the basis of quench experiments with DAC [*Tutti et al.*, 2001]. In this study, in situ X-ray diffraction measurements were also made after laser heating under high pressure and at room temperature. No structural changes were apparent at pressures up to at least 50 GPa, except for possible amorphization at higher pressures, although no detailed descriptions on the diffraction profiles, the P/T conditions, and heating durations were reported for these in situ X-ray measurements.

[13] These results are totally inconsistent with our results based on in situ X-ray observations using both MA and DAC. It is understandable that these authors [*Tutti et al.*, 2001] concluded that K-hollandite does not transform to any other structures based on the analyses of the recovered sample, because, as we found in our experiments, hollandite II converts to the hollandite structure at ambient conditions. The transition could have been overlooked due to relatively poor resolution in the observed diffraction profiles, because of the use of a small CCD detector and/or the effect of the non-hydrostatic stress produced in the sample without pressure medium in their experiments. Alternatively, the presence of small amounts of other cations, such as Na, Ba, Mg, and Ca, in the natural K-feldspar that was used as the starting material [*Tutti et al.*, 2001] might affect the stability of hollandite II under pressure.

[14] On the other hand, the presence of a phase transition in K-hollandite at 20–22.5 GPa and 1700°C was suggested, on the basis of abrupt changes in both the chemical composition of this phase and in melting relations of a K-rich basaltic composition [*Wang and Takahashi*, 1999]. Although the pressure range for the proposed phase transition is slightly lower than that of our study (∼24 GPa), the discrepancy may be due to difference in estimates of pressure at high temperature between the two studies. Thus it is likely that the predicted phase transition in K-hollandite observed in the K-rich basalt corresponds to the K-hollandite to hollandite II transition discovered in the present study. A significant change in the Hugoniot data on $KAlSi_3O_8$ was noted at pressures of 12–30 GPa in shock compression experiments, and this was interpreted as proposed being due to the formation of a mixed phase assemblage [*Ahrens and Liu*, 1973]. This may also be explained by the K-hollandite to hollandite II transition at about 24 GPa, taking into account the uncertainty of the pressure estimation in these experiments.

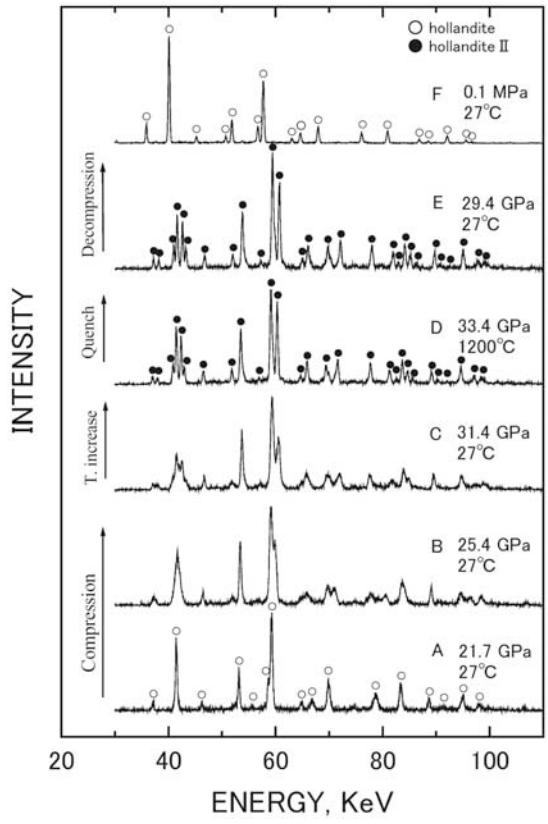

Figure 2. Variations of X-ray diffraction profile of $KAlSi_3O_8$ in MA with increasing pressure (a–c), and at high temperature under the maximum load (d). Hollandite II was quenchable to room temperature under pressure (e), but converted to the hollandite structure when the pressure was released (f).

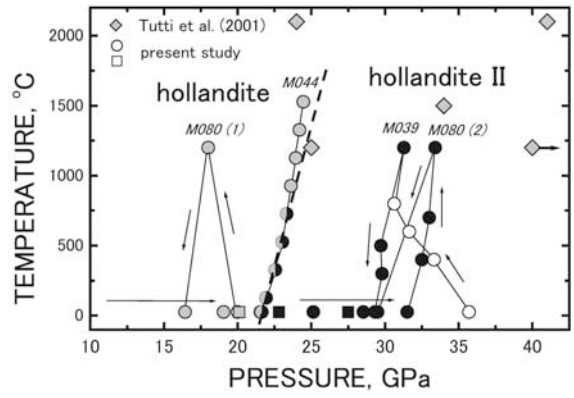

Figure 3. P-T conditions of the present in situ X-ray diffraction measurements using DAC (squares) and MA (circles). The diamond symbols are those of an earlier study [*Tutti et al.*, 2001] based mainly on quench experiments using DAC. Open symbols denote glass starting material, while filled symbols represent the P-T conditions where hollandite II was formed and the shadow symbols are those where K-hollandite was formed. The dashed line indicates the possible phase boundary between K-hollandite and hollandite II.

[15] It has been demonstrated that K-hollandite is present near the liquidus in both K-rich basalt and continental crust materials at pressures above ~20 GPa [*Irifune et al.*, 1994; *Wang and Takahashi*, 1999]. K-hollandite has a peculiar crystal structure possessing relatively large tunnels surrounded by four double chains of edge-shared octahedra along the c-axis, and has been demonstrated to retain some trace elements with large ionic radii, such as La, Pb, K, and Sr, whereas Nb and U are excluded. It follows that chemical fractionation due to partial melting in the presence of K-hollandite may introduce some distinctive geochemical signatures in the deep mantle, which are inconsistent with the characteristics of enriched mantle reservoirs for EMI, EMII, and HIMU ocean island basalts [*Irifune et al.*, 1994]. The present results suggest that such arguments are invalid for chemical fractionation at the lower mantle depths, because the transition of K-hollandite to the new structure should change the element partitioning and melting behaviors under these conditions. Abrupt enrichments of Ca and Na components in K-hollandite, presumably converted from hollandite II on release of pressure, were indeed noted in a K-rich basaltic composition coexisted with the melt at pressures 22.5 and 25 GPa [*Wang and Takahashi*, 1999]. Thus further studies on partitioning of the key trace elements between hollandite II and the coexisting melts in continental crust or basaltic lithologies should provide important constraints on the origin of distinctive geochemical components in the deep mantle.

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