NAL phase in K-rich portions of the lower mantle

Chie Kato,1 Kei Hirose,1,2,3 Tetsuya Komabayashi,1 Haruka Ozawa,1,3 and Yasuo Ohishi4

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[1] The stability of the K-rich new aluminous (NAL) phase was examined on the join Na0.25K0.75Mg2.00Al4.80Si1.15O12 (Na75K25)–K1.00Mg2.00Al4.80Si1.15O12 (K100) up to 144 GPa by X-ray diffraction in a laser-heated diamond anvil cell. Single-phase K100 and Na50K50 NAL were formed up to the lower mantle conditions, and the NAL phase coexisted with the calcium ferrite-type (CF) phase at 120 GPa and 2300 K for the Na75K25 bulk composition. This is a striking contrast to the K-free (Na100) NAL that becomes unstable above 27 GPa at 1850 K, which suggests that potassium stabilizes NAL at significantly higher pressures. K-rich NAL may host potassium in the lower mantle that contains K2O more than 0.09 wt %. In addition, the NAL phase likely formed owing to partial melting in the ultralow-velocity zone or because of a basal magma ocean. Future seismological observations may clarify whether NAL is a radiogenic heat source above the core-mantle boundary. Citation: Kato, C., K. Hirose, T. Komabayashi, H. Ozawa, and Y. Ohishi (2013), NAL phase in K-rich portions of the lower mantle, Geophys. Res. Lett., 40, 5085–5088, doi:10.1002/grl.50966.

1. Introduction

[2] Potassium is an important heat-producing element, but its host phases under deep lower mantle conditions remain poorly known [Wang and Takahashi, 2000; Miyajima et al., 2001; Lee et al., 2009]. The K2O content of pyroclitic mantle is considered very low (~0.03 wt %) [McDonough and Sun, 1995], but the occurrence of K-rich magmatism suggests that the mantle is locally enriched in potassium [McCulloch et al., 1983] and includes a discrete phase as a host of potassium in such K-rich portions. Previous experimental studies demonstrated that K phase III appears in K-doped pyroclitic lower mantle material (0.64 wt % K2O) at 25.5 GPa, coexisting with MgSiO3-rich perovskite, ferropericlase, and CaSiO3-rich perovskite [Wang and Takahashi, 2000]. Because the solubility of potassium in typical lower mantle phases is quite limited. Wang and Takahashi [2000] argued that the K phase III is present even in normal lower mantle.

Additional supporting information may be found in the online version of this article.

1Department of Earth and Planetary Sciences, Tokyo Institute of Technology, Tokyo, Japan.
2Earth-Life Science Institute, Tokyo Institute of Technology, Tokyo, Japan.
3Institute for Research on Earth Evolution, Japan Agency for Marine-Earth Science and Technology, Yokosuka, Kanagawa, Japan.
4Japan Synchrotron Radiation Research Institute, Sayo, Hyogo, Japan.

Corresponding author: C. Kato, Department of Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 152-8551, Japan. (kato.c.ab@m.titech.ac.jp)

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[3] K phase III should be identical to the NAL phase [Miyajima et al., 1999; Gasparik et al., 2000; Miura et al., 2000]. NAL is known to form in subducted basaltic crust under uppermost lower mantle conditions [Miyajima et al., 2001; Hirose and Fei, 2002; Ricolleau et al., 2010]. More recent experiments by Imada et al. [2011] have shown that the NAL phase only forms below 45 GPa and undergoes transformation into CF at higher pressures on the join NaAlSiO4-MgAl2O4 [Ono et al., 2009]. This is consistent with the disappearance of NAL above ~50 GPa in deeply subducted oceanic crust with mid-oceanic ridge basalt (MORB) composition [Perrillat et al., 2006; Ricolleau et al., 2008]. Nevertheless, potassium prefers NAL more than CF as demonstrated by high-pressure experiments [Miyajima et al., 2001] and by the study of inclusions in superdeep diamonds [Walter et al., 2011], indicating that potassium stabilizes NAL relative to CF.

[4] The general formula for NAL is [M3][M2][M1]O12, where M1, M2, and M3 represent small-, middle-, and large-sized cations, respectively [Miura et al., 2000; Gasparik et al., 2000]. The structure of NAL has hexagonal symmetry and consists of a double-chain framework of M1O6 that are connected to each other by sharing the edges. Two differently sized tunnel-like spaces along the c axis surrounded by three and six double chains of M1O6 provide the potential sites for cation vacancy that covers the entire lower mantle.

2. Experimental Procedure

[5] We prepared four starting materials from gels with chemical compositions of Na0.75K0.25Mg2.00Al4.80Si1.15O12 (Na75K25), Na0.50K0.50Mg2.00Al4.80Si1.15O12 (Na50K50), Na0.25K0.75Mg2.00Al4.80Si1.15O12 (Na25K75), and K1.00Mg2.00Al4.80Si1.15O12 (K100). The composition of the K end-member is taken from Kojitani et al. [2011]. The gel was dehydrated by heating to 1273 K for 15 min, and the compositions were confirmed by electron microprobe analysis. The powder sample was pressed into a disc and coated with Au in runs #1–4 and #6–8. In runs #5 and #9–12, the sample was mixed with Au powder at a mass ratio of 10:1. Au was used as a laser absorber and an internal pressure standard. The sample was loaded into
the hole of the rhenium gasket together with a pressure medium of Ar, KCl, or a pure starting material unmixed with gold (see Table S1 in the supporting information). The samples were compressed by diamond anvils with a culet size of 300 μm for pressures less than 70 GPa and a culet size of 120–150 μm for higher pressures. The samples were heated to 1800–2700 K by a multimode yttrium/aluminum/garnet laser or a couple of single-mode Yb fiber lasers at BL10XU, SPring-8. The beam-shaping optics that converts a Gaussian beam to one with a flatter energy distribution was used to reduce the radial temperature gradient. Temperature was measured from both sides by fitting the thermal radiation spectrum to the Planck radiation function using the spectroscopic method. The heating duration was 5–135 min for each run (Table S1). Temperature variations in the 15 μm area from which XRD data were collected were within ±10% [e.g., Ozawa et al., 2010]. The angle-dispersive spectra were collected on an imaging plate (Rigaku R-AXIS IV) and a charge-coupled device (Bruker APEX). The wavelength of the monochromatic incident X-ray beam was 0.412–0.415 Å. Sample pressure was calculated from the volume of Au on the basis of the thermal equation of state of Fei et al. [2007]. The pressure uncertainty is ±1.4–3.2 GPa and is mainly attributed to the temperature uncertainties.

### 3. Results

We conducted 12 separate runs and obtained 14 data sets to examine the phase relations on the join Na$_1$Mg$_{2.00}$Al$_{4.80}$Si$_{1.15}$O$_{12}$-K$_1$Mg$_{2.00}$Al$_{4.80}$Si$_{1.15}$O$_{12}$ (Table S1). While sharp diffraction peaks appeared in less than 5 min at the low-pressure range (Figure 1), crystallization was found to be rather sluggish at greater than 120 GPa. The peaks were weak even after heating to 2700 K at 141 GPa (Figure 2). The XRD patterns of NAL and CF phases are similar to each other, but their characteristic peaks, including those at 10–11° of 2-theta angle, were used for phase identification. In addition, the misfit of peak assignment was much larger when assuming the CF phase instead of the NAL phase in all experiments.

The experiments on the K end-member (K100) demonstrated that NAL was the single phase from 39 GPa and 1900 K to 141 GPa and 2700 K (Figure 3). Earlier multianvil experiments synthesized K100 NAL at 20–25 GPa [Kojitani et al., 2011]. These results indicate that K100 NAL is stable in lower mantle P-T conditions, although it might melt at the high temperatures of the core-mantle boundary (CMB) region. This strongly contrasts with the fact that K-free (Na100) NAL is stable only below 27 GPa at 1850 K [Imada et al., 2011]. Similarly, we observed only NAL in both Na$_{25}$K$_{75}$ and Na$_{50}$K$_{50}$ compositions at the entire P-T range explored in this study. Na$_{50}$K$_{50}$ NAL was formed at 144 GPa, with the pressure exceeding that of the CMB. On the other hand, both NAL and CF coexisted at 120 GPa and 2300 K for...
the Na75K25 bulk composition (see Figure S1 in the supporting information).

[10] In addition, we have obtained pressure-volume (P-V) data for the K end-member (K100) NAL at 300 K between 27 and 127 GPa (Table S2). The volume data were measured right after the synthesis of single-phase NAL in runs #1–5. The lattice constants and the unit-cell volumes were calculated from 14 to 34 diffraction peaks.

4. Stability and Incompressibility of K-rich NAL

[11] The phase relations on the join Na1.00Mg2.00Al4.80Si1.15O12-K1.00Mg2.00Al4.80Si1.15O12 (Na100-K100) are drawn in Figure 3, considering the experimental results on the join NaAlSiO4-MgAl2O4 [Imada et al., 2011]. Imada et al. [2011] reported that Na100 NAL is stable up to 27 GPa, and Na100 and CF form above 44 GPa at 1850 K. In order to draw the composition-pressure phase diagram at 2400 K (Figure 3), the experimental temperatures were corrected by adjusting the pressure on the basis of the P-T slope (+0.008 GPa/K) of the NaL-out reaction in MORB [Perrillat et al., 2006].

[12] The phase diagram in Figure 3 indicates that NAL forms a continuous solid solution on the join Na1.00Mg2.00Al4.80Si1.15O12-K1.00Mg2.00Al4.80Si1.15O12 below 32 GPa. More importantly, potassium drastically expands the stability field of NAL. This suggests that the K’ ion has a strong affinity for the M3 site in the NAL structure not only at 25 GPa [Kojitani et al., 2011] but also at deep lower mantle pressures.

[13] We fitted the third-order Birch-Murnaghan equation to state of the P-V data of K100 NAL, i.e.,

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P = \frac{3}{2} K_0 \left[ \left( \frac{V}{V_0} \right)^{-\frac{3}{2}} - \left( \frac{V}{V_0} \right)^{-\frac{1}{2}} \right] + \frac{3}{4} (K’ - 4) \left( \frac{V}{V_0} \right)^{-\frac{1}{2}} - 1 \]

where \( V_0, K_0, \) and \( K’ \) are unit-cell volume, isothermal bulk modulus, and its pressure derivative, respectively, at ambient conditions. In the fitting procedure, \( V_0 \) was fixed at 186.37(1) Å³, as reported by Kojitani et al. [2011]. The fitting yielded \( K_0 = 207(2) \) GPa and \( K’ = 4.1(0) \). The results are shown in Figure S2 and Table S3 in the supporting information and are compared with the results of previous studies on different chemical compositions. We did not observe anomalous compression behavior over the pressure range studied, implying that the 3s-4d electronic transition of potassium did not take place [Bukowskii, 1976].

[14] Imada et al. [2012], on the basis of compression experiments, reported that \( K_0 = 199(6) \) GPa and \( K’ = 5.0(6) \) for Na1.32Mg1.8Al4.8Si1.2O12 NAL, which is similar in composition to Na100. \( K’ \) was, however, not well constrained in Imada et al. [2012] because the experimental pressure range was limited to 31 GPa. We therefore fitted their P-V data with \( K’ \) fixed at 4.1, same as that obtained for K100 NAL. The results show \( K_0 = 207(5) \) GPa for Na1.32Mg1.8Al4.8Si1.2O12 NAL, which is identical to that of the K end-member. Note that the refined parameters reproduce the experimental data of Imada et al. [2012] as well as their original parameters. Both Imada et al. [2012] and the present study use the Au pressure scale proposed by Fei et al. [2007]. Hence, the similar \( K_0 \) values imply that the bulk modulus of NAL is not affected by the exchange between Na and K. It may be dominantly controlled by the (Al,Si)O₆ double chains that make up the framework of the crystal structure.

5. K-rich NAL in the Lower Mantle

[15] These results indicate that K-rich NAL has a wide stability field, which covers the entire P-T conditions of the lower mantle when the molar ratio \( K/(Na + K) \) is greater than 0.35 on the join Na1.00Mg2.00Al4.80Si1.15O12-K1.00Mg2.00Al4.80Si1.15O12 (Figure 3). The multianvil experiments of Wang and Takahashi [2000] demonstrated that the NAL phase formed at 25.5 GPa in K-rich (0.64 wt % \( K_2O \)) pyrolite mantle material with a molar ratio \( K/(Na + K) \) of ~0.85 (reported as K phase III). K-rich NAL in such natural multicomponent systems has a complex chemical formula, but the main compositional difference with the present study is the high Mg and Si at the expense of Al (see Figure S3 in the supporting information). The recent first-principles calculations by Mookherjee et al. [2012] have shown that higher Mg content stabilizes NAL relative to CF, supporting that the NAL phase can be present in the deep lower mantle.

[16] It is known that CaSiO₃ perovskite incorporates minor amounts of potassium. Previous experiments by Hirose et al. [2005] reported 0.4 wt % \( K_2O \) in CaSiO₃ perovskite at 60 GPa, whereas Kesson et al. [1998] found 1.6–1.8 wt % \( K_2O \) at 70–135 GPa. Considering that the lower mantle may include ~5% CaSiO₃ perovskite [e.g., Murakami et al., 2005], K-rich NAL may appear as a discrete phase when the \( K_2O \) content is greater than 0.09 (~1.8 × 0.05) wt %. Note that typical mantle is considered to contain ~0.03 wt % \( K_2O \) [McDonough and Sun, 1995].

[17] On the other hand, NAL transforms to CF in the middle part of the lower mantle, when the \( K/(Na + K) \) value is low (Figure 3). The NAL phase in subducted MORB crust under uppermost lower mantle conditions has a molar ratio \( K/(Na + K) \) of 0.16–0.17 [Hirose and Fei, 2002]. Such low \( K/(Na + K) \) ratio accounts for the disappearance of NAL above ~50 GPa in MORB [Perrillat et al., 2006; Ricolleau et al., 2010]. In addition, KAI₅Si₄O₁₂ hollandite II [Suéda et al., 2004] can host potassium in subducted continental crust in the uppermost lower mantle [Ishii et al., 2012] and is known to be stable at least to 128 GPa [Hirao et al., 2008].

6. Summary and Conclusion

[18] Our experiments demonstrate that potassium dramatically stabilizes NAL relative to CF. K-rich NAL appears in the shallow-to-deep lower mantle having a \( K_2O \) content higher than 0.09 wt %. The melting phase relations in a K-rich pyrolite composition shows that K-rich NAL (K Phase III) is the last phase to crystallize during cooling and can host potas-

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The in situ XRD experiments were conducted at SPring-8 (proposals 2012A0087 and 2012B0087).

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