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1 **"Revision 1"First principles study on the high-pressure**

2 **phase transition and elasticity of KAlSi$_3$O$_8$ hollandite**

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10 **ABSTRACT**

11 **In order to understand the fate of the host phase for potassium subducted into the**

12 **deep Earth's interior, we have studied the high-pressure stability and elastic**

13 **properties of KAlSi$_3$O$_8$ hollandite (K-hollandite) by means of the first principles**

14 **computation method. Based on experimental observations, the tetragonal K-**

15 **hollandite I phase was found to undergo the ferroelastic second-order phase**

16 **transition to the monoclinic K-hollandite II phase at 14.9 GPa. This K-hollandite II**

17 **phase was mechanically stable up to 150 GPa (i.e., entirely in the Earth's lower**

18 **mantle), being consistent with previous studies. The Born's elastic stability criteria**

19 **indicate that the tetragonal mechanical instability occurs at similar pressure of**

20 **16.9 GPa with shear softening. This causes anomalous pressure dependence of the**

21 **wave velocities across the instability. Taking a Clapeyron slope of 7 MPa/K and a**

22 **temperature of 1800 K, the transition pressure becomes ~28 GPa corresponding to**

23 **about 770 km depth, which would be seismologically detectable and could be**

24 **comparable to seismic scatterers observed at the shallowest lower mantle. Next, we**

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25 **studied the solid solution effect of sodium to K-hollandite, indicating that it is very**

26 **limited on the phase stability, though the Na-end member phase was found to be**

27 **metastable. Elasticity demonstrates strong anisotropy around 15 GPa due to the**

28 **ferroelastic nature.**

29

30 Keywords: elastic property, phase transition, hollandite, first principle,

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33   **INTORODUCTION**

34   Long-lived radiogenic nuclides such as ^{40}K, ^{232}Th, ^{235}U, and ^{238}U are essential to

35   understanding the Earth's long-term evolution, while short-lived such as ^{26}Al are

36   important only for the very early Earth (Urey 1955). It is believed that these elements

37   are distributed in the continental and oceanic crust and mantle and are concentrated

38   especially in the continental crust. Since recent studies have demonstrated that even

39   continental crust could be subducted into the Earth's deep interior despite of its

40   buoyancy as well as subducted slab (Scholl and von Huene 2007; Kawai et al. 2009), it

41   is important to understand the stability of the host phases of radiogenic nuclides such as

42   ^{40}K.

43   Alkali feldspars in the $KAlSi_3O_8$-$NaAlSi_3O_8$ system are the most abundant group

44   of minerals in the Earth's crust. While alkali feldspars are minerals that can survive the

45   initial stage of subduction, hollandite-type aluminosilicates with the large square tunnels

46   formed by four double chains of edge-shared octahedra are a candidate for host phases

47   of large elements and incompatible large-ion lithophile elements (LILEs) such as Rb,

48   Ba Sr, K, Pb, La, Ce, and Th in the deep mantle. It is, therefore, essential to investigate

49   stability and elasticity of hollandite in the Earth's deep interior.

50   Potassium feldspar is one of the most abundant minerals in the continental crust.

51   Previous experimental studies on host phases of potassium show that $KAlSi_3O_8$ felspar

52   dissociates into an assemblage of $K_2Si_4O_9$ wadeite, Al_2SiO_5 kyanite, and SiO_2 coesite at

53   6-7 GPa and 1500 K, and the three phases further recombine into $KAlSi_3O_8$ hollandite

54   (hereafter called as K-hollandite I) at about 9 GPa and 1500 K (Urakawa et al. 1994;

55   Yagi et al. 1994). While experiments on K-rich alkali basalt using multi-anvil cell

56   implied a phase transition of K-hollandite I at 22.5 GPa and 2000 K because quenched

57   K-hollandite became Na- and Ca-richer (Wang and Takahashi 1999), some reported that

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58   K-hollandite I remains stable in the pressures range between 20 and 95 GPa at 900 K

59   (Tutti et al. 2001). On the other hand, a new high-pressure $I2/m$ monoclinic structure of

60    $KAlSi_3O_8$ (K-hollandite II) from an $I4/m$ tetragonal structure at 22 GPa and room

61   temperature was confirmed by in situ X-ray diffraction measurements (Sueda et al.

62   2004). Later, the phase transition was suggested to be second-order (ferroelastic)

63   because of marginal volume change by high-pressure studies up to 32 GPa and room

64   temperature using laser-heated anvil cell (Ferroir et al. 2006) and then stability of K-

65   hollandite II was investigated up to 128 GPa (Hirao et al. 2008). In contrast to the phase

66   stability, elasticity of the K-hollandite I and II phases was studied by theoretical studies

67   (Mookherjee and Steinle-Neumann 2009). However, these previous studies are

68   controversial in both the phase transition pressure and elasticity. Some studies reported

69   a second-order phase transition pressure of about 23 GPa (Caracas and Boffa Ballaran

70   2010; Deng et al. 2011), while the other suggested a first-order phase transition of 33

71   GPa (Mookherjee and Steinle-Neumann 2009). As for elasticity, one reported that the

72   K-hollandite I phase becomes mechanical unstable at 50 GPa (Mookherjee and Steinle-

73   Neumann 2009), while another suggested a pressure of about 22 and 23 GPa (Caracas

74   and Boffa Ballaran 2010).

75   While hollandite is the host phase for large elements such as LILEs, potassium

76   could be replaced by sodium (Wang and Takahashi 1999). $K_{0.8}Na_{0.2}AlSi_3O_8$ hollandite I

77   was reported to undergo a phase transition to hollandite II at 17-18 GPa (Boffa Ballaran

78   et al. 2009). Then, $K_{0.8}Na_{0.2}AlSi_3O_8$ and $KAlSi_3O_8$ hollandite were theoretically

79   predicted to undergo phase transitions at 13 and 23 GPa, respectively, suggesting that

80   solid solution effect of sodium to K-hollandite be significant (Caracas and Boffa

81   Ballaran 2010). The high-pressure behaviour of the end member $NaAlSi_3O_8$ albite

82   composition has also been debatable. While some diamond-anvil cell experiments

83   reported that $NaAlSi_3O_8$ hollandite (Na-hollandite) could be stable at some pressure (Liu

84   1978; Tutti 2007), some multi-anvil experiments and theoretical studies suggested that

85   Na-hollandite be metastable phase (Yagi et al. 1994; Liu 2006; Akaogi et al. 2010;

86   Deng et al. 2010). In this paper, we have studied the high-pressure stability and

87   elasticity of the $KAlSi_3O_8$ hollandite, and solid solution effect of sodium to K-hollandite

88   by means of *ab initio* density functional computation methods.

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90   **CRYSTAL STRUCTURE MODELS**

91   The $KAlSi_3O_8$ hollandite I phase has a tetragonal crystal structure with the space

92   group *I4/m*, which has a large square tunnel formed by double chains of edge-shared

93   $(Al,Si)O_6$ octahedra, and K resides in the tunnel (Fig. 1a) (Ringwood et al. 1967;

94   Yamada et al. 1984). As the large square tunnels formed by four double chains supply a

95   space for large-ion elements such as K, Ba, Sr, Na and Pb, hollandite-type silicate are

96   considered as a possible repository of large alkali elements, especially potassium, in the

97   lower mantle. On the other hand, the K-hollandite II phase has a monoclinic crystal

98   structure with the space group *I2/m*, which has a distorted square formed by four double

99   chains (Sueda et al. 2004; Ferroir et al. 2006; Hirao et al. 2008; Mookherjee and Steinle-

100 Neumann et al. 2009; Caracas and Boffa Ballaran 2010). There is, however, no

101 experimentally formal description in the crystallographic literature for the K-hollandite

102 II phase, while a theoretical study predicted the atomic positions satisfying the space

103 group *I2/m* monoclinic symmetry (Mookherjee and Steinle-Neumann et al. 2009).

104   The disorder in $(Al,Si)O_6$ octahedra in a single unit cell breaks the tetragonal

105 symmetry. While a previous calculation using a single unit cell with 26 atoms breaks

106 the symmetry (Deng et al. 2011), we therefore consider three supercells in order to

107 maintain the tetragonal symmetry (Fig 1.b-d). First, a $1\times1\times2$ supercell consists of two

108 layer of $K_2Al_2Si_6O_{16}$ along *c*-axis, where one layer is stacked along *c*-axis on another

109 layer with a 90° rotation around the *c*-axis (Fig. 1b; model A). Next, a $2\times2\times1$ supercell

110   consists of four cells of $K_2Al_2Si_6O_{16}$ in the *c*-plane, where one cell is adjacent to another

111   cell with a 90° rotation around the *c*-axis (Fig. 1c; model B). Finally, a 2×2×2 supercell

112   consists of two layers of $K_8Al_8Si_{24}O_{64}$ model B, where one layer is stacked along *c*-axis

113   on another layer with a 90° rotation around the *c*-axis (Fig. 1d; model C). Although

114   conventional unit cells for model A, B, and C include 52, 104, and 208 atoms,

115   respectively, all the primitive unit cells include 52 atoms. Previous studies used a 104

116   atom 1×1×4 supercell in computation (Mookherjee and Steinle-Neumann et al. 2009)

117   but their supercell is exactly identical to our model A with translation symmetry

118   (personal communication with M. Mookherjee), and it is quite unclear why they chose

119   the reducible cell.

120   In order to investigate solid solution effect of sodium, we consider five 1×1×2

121   supercells (model A) with Na content of 25 (Fig. 2a-b), 50 (Fig. 2c), 75 (Fig. 2d), 100

122   (Fig. 2e) mol%. The disorder effects are taken into account for Na content of 25 mol%.

123   We consider two configurations of Na. One maintains the tetragonal symmetry (Fig. 2a),

124   while another breaks the symmetry (Fig. 2b).

125

126   **FIRST PRINCIPLES COMPUTATION DETAILS**

127   Our first principles calculations are based on the density functional theory

128   (Hohenberg and Kohn 1964; Kohn and Sham 1965) within the local density

129   approximation (LDA) (Ceperley and Alder 1980; Perdew and Zunger 1981). One

130   electron wavefunction satisfying the Kohn-Sham equation describes an electronic

131   ground state, which was expanded by using the plane wave basis set. Ionic core

132   potentials were approximated based on the pseudopotential method, which were

133   generated using the Vanderbilt's method (Vandelbilt 1990) for K, Na, and O and

134   Troullier and Martins' methods (Troullier and Martins 1991) for Al and Si. The electric

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135   configurations included in these pseudopotentials are $3s^23p^64s^1$ for K, $2s^22p^63s^1$ for Na,

136    $3s^23p^1$ for Al, $3s^23p^23d^0$ for Si, and $2s^22p^4$ for O. Most of these have been well tested in

137   our previous studies (Tsuchiya et al. 2004, 2005; Kawai and Tsuchiya 2010, 2012a,b).

138   The plane wave energy cutoff was set to 50 Ry, and the irreducible part of Brillouin

139   zone was sampled on 2×2×2 for the supercells of the K-hollandite I and II phases (52

140   atoms as mentioned above) using the Monkhorst-Pack method (Monkhorst and Pack

141   1976). Effects of using the larger cutoff and k -points on the calculated properties were

142   found insignificant. The full elastic constant tensors of the class *4/m* tetragonal and *2/m*

143   monoclinic structures have seven and thirteen independent components, respectively.

144   They were calculated using the stress-strain relation with applying strains of ±0.01

145   (Kawai and Tsuchiya 2010, 2012a,b; Karki et al. 2001; Tsuchiya et al. 2004). We

146   confirmed that the linear relation was ensured enough for this strain range. All structural

147   parameters were fully relaxed to a static (0 K) configuration using the damped variable

148   cell shape constant pressure molecular dynamics technique (Wentzcovitch 1991) using

149   the PWSCF code until residual forces became less than $5.0×10^{-5}$ Ry/a.u. Computations

150   for the K-hollandite II were performed from the structure which was initially distorted

151   in the *c*-plane until the structure was fully relaxed.

152   **Results and discussion**

153   In order to investigate the phase stability we calculated enthalpy for each supercell

154   model for both K-hollandite I and II phases (Fig. 3a). We found that model A is the

155   most stable, model C is the second for both K-hollandite I and II phases, although the

156   enthalpy difference between model A and C is little. The supercells were found to have

157   an enthalpy difference of about 30 kJ/mol between model A and B, which is produced

158   clearly due to the difference in the configurations of Si/Al. Si and Al locally generate

159   positive and negative charges, respectively. While Si is fairly randomly distributed in

160   model A, Al is aligned both in the *c*-plane and along the *c*-axis in the cell shown in

161   model B. This causes an enthalpy difference between model A and B. It is a little

162   surprising that model C is about 3 kJ/mol more unstable than model A because model C

163   is more symmetric than model A. Hence, in this study we consider model A to be the K-

164   hollandite phase.

165   Next, we investigated the phase stability between the K-hollandite I and II phases.

166   The enthalpy of K-hollandite II phase deviates from that of K-hollandite I phase at

167   about 15 GPa and becomes lower than that of K-hollandite I phase above this pressure.

168   The enthalpies for the K-hollandite I and II phases asymptotically converge at about 15

169   GPa with decreasing pressure. This kind of behavior is a typical feature for a second-

170   order phase transition, which is likely expected to have a positive Clapeyron slope. If

171   extrapolating experimental phase boundaries with a positive slope of ~ 7MPa/K

172   (Nishiyama et al. 2005; Ferrior et al., 2006), we obtain phase transition pressures of

173   16~18 GPa at static temperature. This pressure is consistent well with our results. On

174   the other hand, a previous theoretical study (Mookherjee and Steinle-Neumann 2009)

175   reports that enthalpies for the K-hollandite I and II phases cross over one another at

176   about 33 GPa, indicating a typical feature for a first-order phase transition, even though

177   the asymptotic feature can be seen in their enthalpy of the K-hollandite II phase around

178   20 GPa. They seem to have failed in computation of the reference structure of the K-

179   hollandite I phase. Meanwhile, a previous theoretical study determined the transition

180   pressure to be 23 GPa without any consideration of enthalpy difference between the K-

181   hollandite I and II phases (Deng et al. 2011).

182   Pressure-volume relations calculated for the K-hollandite I and II phases are

183   shown in Fig. 4. Their equations of state parameters (zero-pressure bulk modulus, B_0,

184   and its pressure derivative, B_0') determined by least-squares fitting to the third-order

185   Birch-Murnaghan equation (Table 1) are $B_0 = 205.07$ GPa and $B_0' = 4.18$ for the K-

186   hollandite I phase and $B_0 = 192.26$ GPa and $B_0' = 4.16$ for the K-hollandite II phase. We

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187   can obtain good agreement with experimental data for the K-hollandite I phase (Ferroir

188   et al. 2006; Nishiyama et al. 2005; Zhang et al. 1993), although our computed volume

189   for the K-hollandite I phase is about 1.4 % smaller than experimental results due to no

190   thermal effect for a static condition (Fig. 4 and Table 1). The K-hollandite II is more

191   compressible than the K-hollandite I phase. Zero-pressure volume obtained by the

192   recent calculations within the generalized gradient approximation (GGA) (Deng et al.

193   2011) is larger than that computed in this study within LDA as usually seen. While the

194   zero-pressure volumes obtained in this study for both K-hollandite I and II phases match

195   well with each other, previous theoretical study shows difference in zero-pressure

196   volumes between K-hollandite I and II phases (Mookherjee and Steinle-Neumann 2009),

197   indicating that their computation is shy of convergence.

198   Computed lattice parameters for the K-hollandite I and II phases are shown in Fig.

199   5 as a function of pressure. These are in excellent agreement with the experimental data

200   for both the K-hollnadite I (Ferroir et al. 2006; Zhang et al. 1993) and II (Sueda et al.

201   2004; Ferroir et al. 2006; Hirao et al. 2008) phases. Although the bulk volume

202   compressibility does not differ significantly between the K-hollanidte I and II phases

203   (Fig. 4), the splitting of cell parameters (*a* and *b*) and the change of the angle γ start

204   rapidly at 20 GPa. The mean value (*a*+*b*)/2 and *c* do not change rapidly after the phase

205   transition as reported by experimental studies (Ferroir et al. 2006; Hirao et al. 2008).

206   Second-order phase transitions are critical phenomena. When we take a cell angle

207   related to the monoclinic distortion, γ, as an order parameter, it can be described based

208   on the Landau theory (Landau and Lifshitz 1994) as $\gamma \bullet [(P-P_c)/P_c]^q$, where P_c and q

209   are the critical pressure and the critical exponent related to the long-range order in the

210   system, respectively. Calculated pressure variation in γ was well fitted by this formula

211   in the pressure range from 15 and 40 GPa and to provide $P_c = 14.9$ GPa and $q = 0.463$

212   (inset of Fig. 5c). This critical exponent is found close to the ideal value for classical

213   second-order transitions of 1/2.

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214   Elastic constants of the K-hollandite I and II phases calculated are shown in Fig. 6

215   as a function of pressure from 0 to 150 GPa. Elastic constants of K-hollandite I and II

216   are almost the same up to 10 GPa. Note that the relation $C_{16} = -C_{26}$ is satisfied in the

217   class *4/m* tetragonal structure (Nye 1985). This relation between the K-hollandite I and

218   II phases is seen for the monoclinic K-hollandite II below 10 GPa, indicating that the

219   monoclinic K-hollandite II spontaneously becomes tetragonal with decrease in pressure.

220   In contrast, the softening in C_{11} and C_{66} of the tetragonal K-hollandite I phase occurs

221   with increasing pressure over 40 GPa. This is consistent with previous theoretical

222   studies (Mookherjee and Steinle-Neumann 2009; Caracas and Boffa Ballaran 2010).

223   For $1 \leq k \leq n$, the *k*-th principal submatrix of matrix **A** is the $k \times k$ submatrix

224   formed from the first *k* rows and first *k* columns of matrix **A**. Its determinant is called as

225   the (leading) *k*-th principal minor (Gilbert 1991). From Sylvester's criterion, a real,

226   symmetric matrix is positive definite if and only if all its principle minors are positive.

227   Since the energy density must be positive definite quadratic form (Born and Huang

228   1954), all the six (leading) principal minors of elastic tensor **C** should be positive. For

229   the class *4/m* tetragonal structure, principal minors are as follows:

$$
\begin{aligned}
C(6) &= C_{66}, \\
C(5,6) &= C_{44}C_{66}, \\
C(4,5,6) &= C_{44}^2 C_{66}, \\
C(3,4,5,6) &= C_{33}C_{44}^2 C_{66}, \\
C(2,3,4,5) &= (C_{11}C_{33}C_{66} - C_{13}^2 C_{66} - C_{16}^2 C_{33})C_{44}^2 \\
C(1,2,3,4,5,6) &= [(C_{11}^2 - C_{12}^2)C_{33}C_{66} - 2(C_{11} - C_{12})C_{13}^2 C_{66} + 4C_{13}^2 C_{16}^2 \\
&\quad - 2\{(C_{11} + C_{12})C_{33} - 2C_{13}^2\}C_{16}^2]C_{44}^2
\end{aligned}
\qquad (1).
$$

230

231   We computed all the values and found $C(1,2,3,4,5,6)$ the mechanical stability condition

232   for the tetragonal K-hollandite I phase. Hence, we computed a principal minor,

233     $C(1,2,3,4,5,6)$, in the pressure from 0 to 60 GPa and found that the mechanical

234   instability occur around 16.9 GPa (Fig. 7a).

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235   The class *4/m* tetragonal symmetry with seven independent elastic constants is

236   also known as *4/m* (TII) Laue symmetry (Farley et al. 1975; Blanchfield et al. 1982).

237   When the components of the elastic tensor of a *4/m* (TII) Laue symmetry crystal are

238   transformed by rotation around *c*-axis through an angle

239    $$\phi = \frac{1}{4}\tan^{-1}\left(\frac{4C_{16}}{C_{11}-C_{12}-2C_{66}}\right)_,$$ (2)

240   then the transformed elastic constant C_{16}' becomes zero, the number of independent

241   elastic constants is reduced from 7 to 6 and the elastic constant tensor C_{ij}' makes the

242   form of that of a *4/mmm* (TI) Laue symmetry crystal. For elasticity tensor to be positive

243   definite, the requirements obtained in the same manners as noted above are as follows:

244    $$C_{11}-C_{12} > 0, (C_{11}+C_{12})C_{33}-2C_{13}^2 > 0, C_{44} > 0, \text{ and } C_{66} > 0 .$$ (3)

245   Since C_{11}-C_{12} > corresponds to the stability criterion for tetragonal stability for K-

246   hollandite I phase, we found that the mechanical instability occurs 16.9 GPa (Fig. 7b),

247   which is equal to the above computed results. This is of course quite reasonable because

248   this rotational transformation operation is just algebraic and should not affect the

249   elasticity of material itself.

250   Previous theoretical study (Caracas and Boffa Ballaran 2010) shows that $C_{66} < 0$

251   instead of C_{11}-$C_{12} < 0$ but we did not confirm $C_{66} < 0$ even using the values reported in

252   their paper. Instead, we found using their data tetragonal instability of C_{11}-$C_{12} < 0$ at

253   about 31 GPa for a *4/m* (TII) Laue symmetry crystal with six independent elastic

254   constants and also found C(1,2,3,4,5,6) negative at almost the same pressure as 31 GPa

255   even for a *4/mmm* (TI) Laue symmetry crystal with seven independent elastic constants,

256   although their data are too sparse in pressure to determine the critical pressure

257   accurately. The difference in critical pressures may depend on their adopted method.

258   They use the virtual crystal approximation, as it is called as *alchemical* approximation,

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259   for the Al/Si disordered sites. This approximation allows us to reduce the cell size and,

260   thereby, computational cost. On the other hand, since *alchemical* pseudopotential for the

261   disordered sites seems to make crystal more symmetric, the K-hollandite I phase

262   becomes more stable and the critical pressure increases. We suspect that *alchemical*

263   pseudopotential causes this discrepancy in the transition pressure (de Gironcoli and

264   Baroni 1992).

265   Taking the Voigt-Reuss-Hill averages of the calculated elastic constants, we have

266   obtained the isotropic bulk (B) and shear moduli (G), and isotropic compressional (V_P),

267   shear (V_S), and bulk sound velocities (V_φ) of the both K-hollandite I and II phases as a

268   function of pressure (Fig. 8). While no significant anomaly is seen in the bulk modulus,

269   a softening appears in the shear modulus associated with the K-hollandite I-II transition

270   (Fig. 8b). The present calculations, therefore, show that the phase transition of K-

271   hollandite I phase at 15.7 GPa produces the shear elastic instability (Fig. 8b).

272   Next, the single crystal elastic wave velocities of both the K-hollandite I and II

273   phases are calculated. Taking a Fourier transformation over space and time of the elastic

274   equation of motion, we obtain Christoffel's equation:

275    $$\rho c^2 u_i = n_j n_l C_{ijkl} u_k ,$$ (4)

276   where ρ, c, and **u** are density, phase velocity and displacement vector respectively and

277    $(n_x, n_y, n_z) = (\sin\theta\cos\phi, \sin\theta\sin\phi, \sin\theta)$ is the direction cosine normal to wave

278   surface. For eq. 4 to be satisfied, it is necessary that

279    $$\left| \rho c^2 \delta_{ik} - n_j n_l C_{ijkl} \right| = 0 ,$$ (5)

280   where δ_{ij} is the Kronecher's delta (Fryer and Frazer 1987). Solving this characteristic

281   equation, we can obtain seismic velocities for three quasi-waves such as quasi-P, quasi-

282   S1 and quasi-S2 waves because polarizations may not be along the dynamic axis. The

283   azimuthal dependence of three phase velocities for the K-hollandite I phase at 0 and 20

284   GPa and the K-hollandite II phase at 20 and 100 GPa is shown in Fig. 9. While we do

285   not see changes of the anisotropic style, i.e., the fast and slow directions, for K-

286   hollandite I phase between 0 and 20 GPa, quasi-S2 wave becomes very slow along

287   [110] suggesting mechanical instability. φ-dependence of the K-hollandite I and II

288   phase has periods of 180° and 90° due to the difference between tetragonal and

289   monoclinic systems. The fast and slow directions, in particular for the S waves, change

290   very much with pressure for the K-hollandite II phase, although the magnitude of

291   anisotropy decreases with increasing pressure. Next we define the azimuthal anisotropy

292   for the P and S waves by following relations as follows:

293    $$A_P = \frac{V_{P_{max}} - V_{P_{min}}}{V_P} \times 100; \quad A_S = \frac{V_{S_{max}} - V_{S_{min}}}{V_S} \times 100 \quad , \tag{6}$$

294   where V_P and V_S are the isotropic aggregate velocities (Fig. 7). The K-hollandite

295   becomes strongly anisotropic around 20 GPa (Fig. 10). In particular, the S wave

296   anisotropy diverges. This clearly reflects the ferroelastic nature of the phase transition.

297   Finally, the solid solution effect of sodium to K-hollandite is considered. In

298   order to investigate the phase stability, we compute enthalpy for each symmetric

299   supercell for Na content of 25 (Fig. 2a), 50 (Fig. 2c), 75 (Fig. 2d), 100 (Fig. 2e) mol%

300   for both K-hollandite I and II phases (Fig. 3d). Significant solid solution effects to phase

301   stability cannot be found via enthalpy comparison. We also compute the mechanical

302   stability conditions for each supercell and find that the instability occurs in the pressure

303   range from 16 to 18 GPa for all the Na content (Fig. 7). This also suggests that solid

304   solution effect is insignificant. This pressure is very consistent with previous

305   experimental results which reported that $K_{0.8}Na_{0.2}AlSi_3O_8$ hollandite undergo phase

306   transition to hollandite II at 17-18 GPa [14]. On the other hand, previous theoretical

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307   studies predicted that $K_{0.8}Na_{0.2}AlSi_3O_8$ and $KAlSi_3O_8$ hollandites undergo phase

308   transitions at 13 and 23 GPa, respectively, and the solid solution effect of sodium to K-

309   hollandite is significant (Caracas and Boffa Ballaran 2010). As noted above, we suspect

310   that *alchemical* pseudopotential causes this discrepancy in the transition pressure (de

311   Gironcoli and Baroni 1992). We also compute enthalpy differences between

312    $K_{0.75}Na_{0.25}AlSi_3O_8$ hollandite I and $KAlSi_3O_8$ hollandite I and between

313    $K_{0.75}Na_{0.25}AlSi_3O_8$ hollandite II and $KAlSi_3O_8$ hollandite II. Since these values are

314   coincident within 0.001 kJ/mol both before and after the phase transition. This suggests

315   that the solid solution effects of sodium to both K-hollandite I and II are almost the

316   same in contrast to previous experimental results (Wang and Takahashi 1999). This may

317   be caused by other effects such as the solid solution effects of sodium to other phases in

318   their sample.

319   Then, the disorder effect in (K,Na) in the tunnel (Fig. 2a-b) is studied. Although

320   the supercell without the tetragonal symmetry (Fig. 2b) becomes spontaneously strained

321   with increasing pressure, this pressure of about 17 GPa is rarely different from the

322   pressure at which the supercell with the tetragonal symmetry (Fig. 2a) undergoes phase

323   transition to monoclinic hollandite II (Fig. 3b). The supercell without the symmetry (Fig.

324   2b) is about 2.5 kJ/mol less stable than with the symmetry (Fig. 2a). Since this enthalpy

325   difference is very small, both configurations with and without tetragonal configurations

326   will be randomly distributed under high-*P,T* condition in the mantle. In order to

327   understand random configuration effects to the phase transition between K-hollandite I

328   and II, we investigate the pressure dependence of a cell-parameter, γ, for configurations

329   both with and without tetragonal symmetry (Fig. 5d). Although a configuration without

330   tetragonal symmetry (green line) has a distorted structure in all the pressure range,

331   distortion is very small up to 15 GPa and γ without tetragonal symmetry increases in the

332   same manner as that with tetragonal symmetry (blue line). This suggests that even for a

333   configuration without tetragonal symmetry phase transition occurs at the same pressure

334 as with tetragonal symmetry. Hence, random distribution of structure with and without

335 tetragonal symmetry would not influence phase transition pressure. Also, although it

336 may be monoclinic locally, due to random distributions K-hollandite should be

337 tetragonal up to the phase transition pressure.

338   Next, phase stability in $NaAlSi_3O_8$ system is considered. We calculate enthalpy

339 for an assemblage of jadeite ($NaAlSi_2O_6$) and stishovite (SiO_2), an assemblage of a CF-

340 type phase ($NaAlSiO_4$) and stishovite ($2SiO_2$), and $NaAlSi_3O_8$ hollandite I and II, and

341 have found that an assemblage of jadeite and stishovite is stable up to 18 GPa and an

342 assemblage of a CF-type phase and stishovite is stable over 18 GPa. This is consistent

343 with previous theoretical studies (Deng et al. 2010; Kawai and Tsuchiya 2010, 2012c),

344 although the transition pressure of 18 GPa (Kawai and Tsuchiya 2010, 2012c) is

345 different from that of 33.6 GPa (Deng et al. 2010). The former matches well with

346 experimental results (Akaogi et al. 2010). Our calculation suggests that the Na-

347 hollandite be metastable phase as previous studies noted.

348

349   **GEOPHYSICAL IMPLICATIONS**

350   Sediment and Archaean granites become less dense near the Earth's surface but

351 contain about 20 volumetric% of the K-hollandite I phase above 9 GPa in the upper

352 mantle, respectively (Irifune et al. 1994; Wu et al. 2009). Taking a temperature of 1300

353 (cold geotherm) 1800 K (normal geotherm) into account, the mechanical instability

354 (Fig. 7b) of the K-hollandite I occurs at 24.8 and 28.3 GPa, with a Clapeyron slope of 7

355 MPa/K (Nishiyama et al. 2005), corresponding to the depth of 692 and 771 km,

356 respectively. In depth range between the depth at which mechanical stability starts and

357 the depth at which phase transition is completed, the velocity changes due to both

358 softening of shear modulus of the K-hollandite I phase and phase transition between the

359   K-hollandite I and II phase can be observed. This is consistent with evidence on the

360   seismic scatterers observed in the shallowest lower mantle (Kaneshima 2009),

361   suggesting that buoyant granitic material can be subducted into the deep mantle and be

362   carried to another gravitationally stable depth range other than the Earth's surface

363   (Kawai et al. 2009).

364   Since the K-hollandite is stable entirely in the lower mantle, they can be host

365   phase for large elements in the Earth's deep interior. The K-hollandite controls a

366   significant proportion of the whole-rock budget of incompatible elements. Recycling of

367   continental sediments including the K-hollandite subducted into the mantle transition

368   zone can explain the geochemical trace element abundance in EM-I type ocean-island

369   basalts (Rapp et al. 2008). Also, geochemical studies on potassium-rich lamproites from

370   Gaussberg, Antarctica (Murphy et al. 2002) suggested that the source of lamproites

371   should be effectively isolated for 2-3 Gyr in the mantle. Since the granitic materials

372   including the K-hollandite are gravitationally stable in the mantle transition zone

373   (Kawai et al. 2009), the mantle transition zone could be reservoir of incompatible

374   LILEs, solving the terrestrial Pb-isotope paradox (Murphy et al. 2002; Kawai et al.

375   2010).

376

377   **CONCLUSIONS**

378   Using theoretical methods, first we examined the phase stabilities of the K-

379   hollandite I and II phases and confirmed that the K-hollandite I phase becomes

380   mechanically unstable at 15.7 GPa and undergoes the ferroelastic (second order) phase

381   transition to the K-hollandite II phase at about 15.7 GPa and that the K-hollandite II is

382   stable entirely in the lower mantle and can be the host phase for geochemically

383   important large elements. Next, we investigated elasticity of both the K-hollandite

384 phases and found softening of shear modulus and velocity changes due to phase

385 transition, consistent with seismic observation. Finally, we studied the solid solution

386 effect of sodium to K-hollandite and found that this effect to phase stability is very

387 small in contrast to previous studies and that Na-hollandite is metastable phase.

388

396

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542

543 Fig. 1 (a) Crystal structures of the $KAlSi_3O_8$ hollandite phases. Deep purple,

544 light blue, dark blue and red spheres represent K, Al, Si, and O atoms,

545 respectively. (b) 1×1×2 tetragonal supercell (model A), (c) 2×2×1 tetragonal

546 supercell (model B), and (d) 2×2×2 tetragonal supercell (model C). (See

547 supplemental data for details of atomic positions for each model.)

548 Fig. 2 (a) Crystal structures of the $(K,Na)AlSi_3O_8$ hollandite phases. Deep purple,

549 yellow, light blue, dark blue and red spheres represent K, Na, Al, Si, and O

550 atoms, respectively. 1×1×2 supercell with Na content of 25 mol% with (e; conf

551 A) and without (f; conf B) the tetragonal symmetry. 1×1×2 supercell with Na

552 content of 50 (g), 75 (h), and 100 (i) mol% with tetragonal symmetry. (See

553 supplemental data for details of atomic positions for each model.)

554 Fig. 3. (a) The calculated enthalpy difference of the K-hollandite I and II phases

555 for three supercell models relative to model A of the K-hollandite I phase (see

556 Fig. 1). The phase transition pressure from K-hollandite I to II is determined to

557 be 15 GPa by fitting the cell angle γ (see text for details). (b) The calculated

558 enthalpy differences of the hollandite with Na content of 25 mol% between conf

559 B and tetragonal conf A (red) and between conf B and monoclinic conf A (blue).

560 (c) The enthalpy differences among an assemblage of jadeite ($NaAlSi_2O_6$) and

561 stishovite (SiO_2), an assemblage of a CF-type phase ($NaAlSiO_4$) and stishovite

562 ($2SiO_2$), and $NaAlSi_3O_8$ hollandite I and II. The enthalpy of hollandite II is taken

563 as a reference. (d) The enthalpy differences of the K-hollandite I and II phases

564 with Na content of 0, 25, 50, 75, and 100 mol% relative to K-hollandite I phase

565 with each Na content.

566 Fig. 4. Volumes calculated for model A of the K-hollandite I (circles) and II

567 (triangles) phases. Fitting curves are computed using a third-order Birch-

568 Murnaghan equation of state. We also show experimental results for the K-

569   hollandite I (circles) (Ferroir et al. 2006; Zhang et al. 1993) and II (triangles)

570   (Sueda et al. 2004; Ferroir et al. 2006; Hirao et al. 2008) in addition to

571   theoretical results by Mookherjee and Steinle-Neumann (2009).

572   Fig. 5. Lattice parameters (a and b in a; c in b; γ in c) calculated for model A of

573   the K-hollandite I (circles) and II phases (triangles). We also show experimental

574   results for the K-hollandite I (open circles) (Ferroir et al. 2006; Zhang et al.

575   1993) and II (open triangles) (Sueda et al. 2004; Ferroir et al. 2006; Hirao et al.

576   2008) phases. (inset of c) calculated cell angle, γ, (red triangle) with a fit (green

577   line) (see text for details). (d) Calculated lattice parameters, γ, for K-hollandite I

578   (red line) and II phases (blue line) with tetragonal symmetry and K-hollandite

579   without tetragonal symmetry (green line) with Na content of 25 mol%.

580   Fig. 6. Elastic constants calculated as a function of pressure for model A of the

581   K-hollandite I (0-60 GPa) and II (0-150 GPa) phases. (a)-(c) show longitudinal,

582   off-diagonal, and shear components for the tetragonal K-hollandite I and

583   monoclinic K-hollandite II phases.

584   Fig. 7. Mechanical stability criterion computed for the K-hollandite I phase with

585   Na content of 0, 25, 50, 75, and 100 mol%. (a) C(1,2,3,4,5,6) for the class $4/m$

586   tetragonal structure. (b) C_{11}-C_{12} for the class $4/mmm$ tetragonal structure.

587   Fig. 8. (a) Aggregate bulk and shear moduli of the K-hollandite I (red) and II

588   (blue) phases. (b) Longitudinal, bulk and shear wave velocities and densities of

589   the K-hollandite I and II phases. The vertical bold lines represent the calculated

590   transition pressure of hollandites.

591   Fig. 9. Velocities of quasi-waves (qV_P, qV_{S1}, and qV_{S2}), where qS1 is the faster

592   of the two split shear waves, as a function of the propagation direction for the K-

593 hollandite I phase at 0 and 20 GPa and the K-hollandite II phase at 20 and 100

594 GPa.

595 Fig. 10. Pressure dependence of the elastic anisotropy of the K-hollandite I and

596 II phases.

597 **Table 1** Equation of state parameters for the K-hollandite I and II phases
598 calculated at the static temperature. Results of previous theoretical and
599 experimental studies are also shown.

	V_0 (cm³/mol)	B_0 (GPa)	B'_0
Hollandite-I (calc:this study)	140.70	205.07	4.18
Hollandite-I (calc)[a]	137.09	225.0	4.3
Hollandite-I (calc)[b]	147.43	174.0	3.99
Hollandite-I (exp)[c]	142.3	180	4.0
Hollandite-I (exp)[d]	143.1	183	4.0
Hollandite-I (exp)[e]	142.7	201	4.0
Hollandite-II (calc:this study)	140.7	192	4.16
Hollandite-II (calc)[a]	137.3	221	3.9
Hollandite-II (calc)[b]	147.4	168	4.0

600   [a] Mookherjee and Steinle-Neumann (2009)

601   [b] Deng et al. (2011)

602   [c] Zhang et al. (1993)

603   [d] Nishiyama et al. (2005)

604   [e] Ferroir et al. (2006)

605

606   **Table 2** Elastic constants (c_{ij}), aggregate bulk (B) and shear (G) moduli of the

607   K-hollandite I and II phases calculated at 0 GPa. We also show results of

608   previous theoretical studies.

	Hollandite-I (This study)	Hollandite-I [a]	Hollandite-I [b]	Hollandite-II (This study)	Hollandite-II[a]
C_{11} (GPa)	290	342	303	290	382
C_{22}	-	-	-	290	395
C_{33}	530	568	517	530	575
C_{44}	154	165	175	154	177
C_{55}	-	-	-	154	182
C_{66}	112	129	139	112	48
C_{12}	181	186	202	181	132
C_{13}	103	118	123	103	140
C_{23}	-	-		103	107
C_{16}	-42	-	44	-42	-16
C_{26}	-	-		42	4
C_{36}	-	-		-0.1	38
C_{45}	-	-		0.0	13

B	207	230	224	204	220
G	111	124	143 (117)*	110	134
V_P (km/s)	9.46	9.87	10.19 (9.74)*	9.45	9.92
V_s	5.28	5.53	5.98 (5.41)*	5.28	5.75
V_{ϕ}	7.23	7.53	7.49	7.23	7.37

609
610 [a] Mookherjee and Steinle-Neumann (2009)
611 [b] Caracas and Boffa Ballaran (2010)
612 * recomputed using the data by Caracas and Boffa Ballaran (2010)
613

(a)   (b) model A   (c) model B   (d) model C

(a) Na25% conf A (b) Na25% conf B (c) Na50% (d) Na75% (e) Na100%

(a)

(b)