Stability field of phase Egg, AlSiO$_3$OH at high pressure and high temperature: possible water reservoir in mantle transition zone

Ko FUKUYAMA*, Eiji OHTANI**, Yuki SHIBAZAKI***, Hiroyuki KAGI* and Akio SUZUKI**

*Geochemical Research Center, Graduate School of Science, The University of Tokyo, Hongo, Tokyo 113-0033, Japan
**Department of Earth Science, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
***Frontier Research Institute for Interdisciplinary Sciences, Tohoku University, Sendai 980-8578, Japan

High-pressure and high-temperature experiments were conducted to determine the stability field of phase Egg, AlSiO$_3$OH, in the pressure range of 16.5–23.5 GPa and in the temperature range of 800–1500 °C. We found that phase Egg decomposes to δ-AlOOH + stishovite below ~ 1200 °C (16.5 GPa and 800 °C; 20.6 GPa and 1000 °C) and to Al-phase D + corundum + stishovite above ~ 1200 °C (21.8 GPa and 1500 °C) at P-T conditions corresponding to the mantle transition zone.

This indicates that phase Egg is unstable at the top of the lower mantle and can be a water reservoir only in the mantle transition zone. In addition, the present results imply that the superdeep diamonds that include phase Egg do not originate from the lower mantle but from the wet mantle transition zone.

Keywords: Water in the mantle, Phase Egg, Thermodynamic stability, Mantle transition zone, Superdeep diamond

INTRODUCTION

Water in Earth’s interior is one of the main research topics in geophysics and geodynamics because water is known to affect physical properties of materials in the mantle such as rheology (Karato et al., 1986) and electric conductivity (Ishido and Mizutani, 1981). Sediments enriched in SiO$_2$ and Al$_2$O$_3$ in the oceanic crust (Miller, 1985) transport water into the deep earth mantle via subducting slabs (Peacock, 1990). Recently, it has been reported that Al$_2$O$_3$ bearing hydrous phases have broad stability fields (e.g., Sano et al., 2008; Ohira et al., 2014; Pamato et al., 2015), and these phases are considered to play an important role in the water cycle in the mantle. Phase Egg, AlSiO$_3$OH, which was first synthesized in 1978 (Eggleton et al., 1978) is one of the most important hydrous phases in the mantle originating from the sedimentary layers in the slabs and can contain 7.5 wt% of H$_2$O as hydroxyl ions. Phase Egg has also been discovered as inclusions in superdeep diamonds (Wirth et al., 2007). Therefore, phase Egg is also important for determining the origin of depth onsuperdeep diamonds. However, two previous studies (Sano et al., 2004; Pamato et al., 2015) have reported different stability fields of phase Egg (Fig. 1): Sano et al. (2004) reported that phase Egg is stable only in the transition zone, whereas Pamato et al. (2015) reported that it could be stable down to the top of the lower mantle. The difference partly results from the use of different pressure scales: Au (Anderson et al., 1989) in Sano et al. (2004) and MgO (Speziale et al., 2001) in Pamato et al. (2015). Here we modified the stability filed of phase Egg determined by Sano et al. (2004) based on the post-spinel boundaries determined by Fei et al. (2004) (Fig. 1). Even after the modification and taking into account the difference in pressure scales, there remains a discrepancy of 4–5 GPa in the stability fields of phase Egg between Sano et al. (2004) and Pamato et al. (2015). This inconsistency leads to different geological outlooks on the water cycling system via subducting slabs: whether phase Egg can store water at the top of the lower mantle or not and whether superdeep diamonds containing phase Egg (Wirth et al., 2007) originate from the lower mantle or not. If phase Egg in the diamonds
originates from the top of the lower mantle, this may indicate that the lower mantle is wet. Here, we conducted high-pressure and high-temperature experiments using a Kawai-type multi-anvil apparatus in order to determine the stability field of phase Egg.

SAMPLE AND METHODS

We used a powdered mixture of Al(OH)₃, Al₂O₃, and SiO₂ (cristobalite) as a starting material with the ideal phase Egg composition, AlSiO₃OH. The compositions of the starting materials used in this study and previous studies are listed in Table 1. High-pressure and high-temperature experiments were conducted using the Kawai-type 3000 ton multi-anvil apparatus and Kawai-type 1000 ton multi-anvil apparatus installed at Tohoku University, Japan. Tungsten carbide anvils (Tungaloy F-grade and Fujilloy TF05) with 3 mm truncated edge length (TEL) were used. The cell assembly used in this experiment is shown in Figure 2. The starting material was enclosed in a Pt double-capsule that was insulated from the heater by a magnesia (MgO) spacer. The Pt capsule was made from two Pt tubes with a wall thickness of 0.1 mm and outer diameters of 0.8 and 1.0 mm, respectively. The end of each capsule was welded. Temperature was measured using a W-Re (W3%Re-W25%Re) thermocouple inserted in the octahedron and attached to the Pt capsule as shown in Figure 2. No pressure effect was taken into account on the emf-temperature calibration.

We used forsterite as a pressure marker. Forsterite was synthesized from a stoichiometric mixture of MgO and SiO₂ (cristobalite) by heating at 1400 °C for 81 h using an electric furnace at 1 atm and was placed below the Pt capsule inside the heater (Fig. 2). In this research, pressure calibration was conducted using the metallic transition of ZnS (15.5 GPa) and GaAs (18.8 GPa) (Onodera and Ohtani, 1980). The pressure calibration curve at high temperature was obtained based on the wadsleyite-ringwoodite (β-γ) transition of Mg₂SiO₄, 17.5 GPa at 1000 °C and post-spinel boundaries, 23.5 GPa at 1200 °C, both estimated using the MgO pressure scale (Fei et al., 2004). The pressure uncertainty is about 1.5 GPa based on our previous calibrations at high temperature (Litasov and Ohtani, 2005; 2009). Recovered samples were analyzed using SEM-EDS, FE-SEM-EDS, X-ray diffraction, and micro-Raman spectroscopy. The SEM-EDS (JSM-5410) installed at Tohoku University and FE-SEM-EDS (JSM-7000F) at The University of Tokyo were employed for chemical composition analysis of quenched minerals with operating conditions of 15 kV and 50-54 µA and 15 kV and 98.4-99.2 µA, respectively. X-ray diffraction was carried out for the identification of phases of the recovered samples with the wavelength of 0.4246 Å at AR-NE7A beamline of the PF-AR synchrotron facility at KEK in Japan. Raman spectra were also obtained for the phase determination using Raman micro-

### Table 1. Compositions of starting materials in wt%

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃</th>
<th>Al(OH)₃</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>28.30</td>
<td>21.65</td>
<td>50.04</td>
</tr>
<tr>
<td>Sano et al. (2004)</td>
<td>0.00</td>
<td>56.49</td>
<td>43.51</td>
</tr>
<tr>
<td>Pamato et al. (2015)</td>
<td>13.59</td>
<td>39.27</td>
<td>47.15</td>
</tr>
</tbody>
</table>

Figure 1. Stability fields of phase Egg in previous studies (Sano et al., 2004 (Dotted line); Pamato et al., 2015). The phase boundaries of phase Egg illustrated by the solid line are modified from Sano et al. (2004) based on the difference in pressure scales evaluated by Fei et al. (2004). Dia, diaspore; To, Topaz-OH; Coe, coesite; Cor, corundum; St, stishovite; Ky, kyanite; δ, δ-ÅOOH; Egg, phase Egg; L, liquid; Al-D, aluminous phase D. HB, Slab geotherm by Hellfrich and Brodholt (1989). KOR, Slab geotherm by Kirby et al. (1996). The mantle geotherm was based on Akaogi and Ito (1993). Pressure of the post-spinel phase boundary is estimated by the equation of state of MgO (Speziale et al., 2001; Fei et al., 2004).

Figure 2. Cell assembly in this study. The cell assembly was composed of a ZrO₂ pressure medium, a LaCrO₃ heater, Mo electrodes, and a W3%Re-W25%Re thermocouple with a diameter of 0.1 mm.
scopes installed at The University of Tokyo or Tohoku University using Ar ion lasers of 514.5 nm with 6 mW or 488 nm with 24 mW, respectively.

RESULTS AND DISCUSSION

Experimental conditions and results are summarized in Table 2. The phase diagram of phase Egg obtained in this study is shown in Figure 3. At 20.6 GPa and 1000 °C, coexistence of δ-AlOOH + stishovite (SiO2) was observed based on XRD and SEM–EDS. Phase Egg was not observed in the XRD pattern (Fig. 4) nor in BSE image (Fig. 5a) of the recovered sample quenched at 20.6 GPa and 1000 °C (Run no. Egg01). A sample quenched at 16.5 GPa and 800 °C also implied the decomposition reaction of phase Egg → δ-AlOOH + stishovite based on the BSE image of FE–SEM–EDS (Fig. 5b). In addition, forsterite near the Pt capsule enclosing samples transformed into ringwoodite (γ) at 20.6 GPa and 1000 °C (Egg01) and into wadsleyite (β) at 16.5 GPa and 800 °C (Egg12). These results indicate that the decomposition of phase Egg to δ-AlOOH + stishovite occurs at pressures and temperatures lower than those reported by Pamato et al. (2015), suggesting decomposition at 27-28 GPa and 1200-1500 °C (see Fig. 1).

At higher temperatures, the decomposition of phase Egg to Al-phase D [Al2SiO4(OH)2] + corundum + stishovite was observed by SEM–EDS and micro–Raman observations (Fig. 6) at 21.8 GPa and 1500 °C. The decomposition pressure in the present study is notably lower than that reported by Pamato et al. (2015) (24-27 GPa and 1500-1750 °C shown in Fig. 1).

Figure 3 shows the decomposition boundaries of phase Egg obtained in this study. In addition, forsterite placed near the Pt sample capsule (Fig. 2) transformed into ringwoodite (γ) in Egg 01, Egg 02, Egg 06, Egg 10, Egg 11, and Egg 13 (Table 2). The pressure marker of Mg2SiO4 was used in the present experiments to investigate the stability of phase Egg in the transition zone conditions; in other words, A1–D + Cor + St is stable in the stability field of ringwoodite (Run Egg11), and phase Egg decomposes to δ + St at the boundary of the decomposition of ringwoodite (Run Egg13). These critical observations indicate that phase Egg is only stable in the transition zone. Based on these observations, the decom-

Table 2. Experimental conditions and run products of this study

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Pressure1</th>
<th>Pressure2</th>
<th>Temperature</th>
<th>Duration</th>
<th>Experimental products</th>
<th>Forsterite</th>
<th>Analysis methods</th>
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</thead>
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<tr>
<td>Egg01</td>
<td>20.2</td>
<td>20.6</td>
<td>1000 ±5</td>
<td>60</td>
<td>δ, St</td>
<td>γ</td>
<td>SEM–EDS, XRD</td>
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<tr>
<td>Egg02</td>
<td>19</td>
<td>19.3</td>
<td>1000 ±5</td>
<td>2</td>
<td>Egg, δ, St</td>
<td>γ</td>
<td>SEM–EDS, XRD</td>
</tr>
<tr>
<td>Egg04</td>
<td>17.2</td>
<td>17.5</td>
<td>1000 ±5</td>
<td>60</td>
<td>Egg, δ, St</td>
<td>β, γ, α**</td>
<td>SEM–EDS, XRD</td>
</tr>
<tr>
<td>Egg06</td>
<td>20.2</td>
<td>20.6</td>
<td>1200 ±5</td>
<td>60</td>
<td>Egg, δ, St, Cor†</td>
<td>γ</td>
<td>SEM–EDS, XRD</td>
</tr>
<tr>
<td>Egg08</td>
<td>21</td>
<td>21.3</td>
<td>1200 ±5</td>
<td>60</td>
<td>Egg, δ, St, Cor†</td>
<td>-</td>
<td>SEM–EDS</td>
</tr>
<tr>
<td>Egg10</td>
<td>21.5</td>
<td>21.8</td>
<td>1200 ±5</td>
<td>60</td>
<td>Egg, δ, St, Cor†</td>
<td>γ</td>
<td>SEM–EDS</td>
</tr>
<tr>
<td>Egg11</td>
<td>21.5</td>
<td>21.8</td>
<td>1500 ±5</td>
<td>30</td>
<td>Al-D, Cor, St</td>
<td>γ</td>
<td>SEM–EDS, Raman</td>
</tr>
<tr>
<td>Egg12</td>
<td>16</td>
<td>16.5</td>
<td>800 ±7</td>
<td>300</td>
<td>δ, St, Cor†</td>
<td>β, α**</td>
<td>SEM–EDS, Raman</td>
</tr>
<tr>
<td>Egg13</td>
<td>22</td>
<td>23.5</td>
<td>120040*</td>
<td>60</td>
<td>Egg, δ, St, Cor†</td>
<td>P, P, γ</td>
<td>SEM–EDS</td>
</tr>
</tbody>
</table>

1 Pressure calculated by the equation of state of Au (Anderson et al., 1989). 2 Pressure calculated by the equation of state of MgO (Speziale et al., 2001). 3 The pressure uncertainty is estimated to be ±1.5 GPa. 4 The temperature was estimated from the supplied power. *A possible metastable phase, because corundum grains are surrounded by δ-AlOOH. **Metastable existence of α-phase due to the temperature gradient of the cell. From SEM–EDS and FE–SEM–EDS analyses, stishovite included 0.91–4.14 wt% Al2O3 and δ-AlOOH included 0–3.65 wt% SiO2. Corundum included no SiO2. The Al/Si ratio of phase Egg was almost unity. Al/Si ratio of Al-D was 1.14 in Run Egg11.
position of phase Egg occurs under conditions corresponding to base of the mantle transition zone, i.e., pressures about 3–4 GPa lower than that reported by Pamato et al. (2015). The difference between this study and Pamato et al. (2015) may be caused by the pressure calibration curve Pamato et al. (2015) used. Pamato et al. (2015) extrapolated the saturated pressure calibration curve, which might cause errors in estimating pressure.

We observed the decomposition of phase Egg at pressures lower than those reported by Pamato et al. (2015). The decomposition reaction occurs at pressures corresponding to those of the mantle transition zone (Fig. 3). This implies that phase Egg cannot be a water reservoir at the top of the lower mantle. According to previous experiments (e.g., Sano et al., 2004), phase Egg is stable essentially within the transition zone conditions, and it is not stable in the upper mantle or the lower mantle. The stability field of phase Egg in our study is close to that of Sano et al. (2004). Thus, the superdeep diamonds containing phase Egg (Wirth et al. 2007) originated in the mantle transition zone.

**CONCLUSION**

High-pressure and high-temperature experiments in this study revealed that phase Egg can store water in the mantle transition zone but not in the lower mantle. Water is transported by δ-AlOOH (Sano et al., 2008) and/or alumino-phase D (Pamato et al., 2015) into the lower mantle. The superdeep diamonds with phase Egg inclusions (Wirth et al., 2007) originate in the mantle transition zone.
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