Effects of Al content on water partitioning between orthopyroxene and olivine: Implications for lithosphere–asthenosphere boundary

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ABSTRACT

To investigate the partitioning coefficient of water between orthopyroxene (Opx) and olivine (Ol) ($D_{(Opx/Ol)}$) under low-water concentrations ($3\sim387$ wt. ppm) similar to the Earth's mantle conditions, high-pressure experiments have been conducted at pressures of 1.5–6 GPa and a temperature of 1573 K. The experiments were performed with Kawai-type multi-anvil and piston-cylinder apparatus by using starting materials of natural Ol and synthetic Opx with various Al contents. The water contents were obtained with a vacuum type Fourier transform infrared spectrometer (FT-IR6100, IRT5000). IR-spectra of Ol and Al-bearing Opx in this study are similar to those obtained by high-pressure experiments (Bai and Kohlstedt, 1993) and natural rocks (Grant et al., 2007), respectively. It is believed that broad bands in IR spectra of natural Opx are due to effect of crystal distortion by large Al substitution. On the contrary, IR-spectra of Al-free Opx are not consistent with those reported by Rauch and Keppler (2002) likely because of the large difference of water fugacity. $D_{(Al-free\ Opx/Ol)}$ is ~1 at all pressure conditions or decreases with increasing pressure. However, the water contents of Al-bearing Opx are significantly larger than those of Ol at the same conditions. In addition, the effect of Al concentration in Opx on $D_{(Opx/Ol)}$ becomes larger with increasing pressure. The high Al content in Opx significantly increases $D_{(Opx/Ol)}$ and the trend increases with increasing pressure. $D_{(Opx/Ol)}$ drops sharply at the pressure at which the Al concentration of Opx becomes nearly 0 in the Earth's mantle conditions. This conclusion indicates that viscosity of the upper mantle decreases sharply at depths larger than those in which orthopyroxene contains no Al. The dramatic change of $D_{(Opx/Ol)}$ may explain the lithosphere–asthenosphere boundary beneath oceans and continents.

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1. Introduction

Most anhydrous minerals in the Earth's mantle contain a small amount of hydrogen (i.e. water), structurally bound as hydroxyl. This small amount of water has an important influence on the behaviors of rock systems. Physical properties of minerals such as ionic diffusion rates, electric conductivity, and viscosity are significantly affected by the presence of water in minerals (e.g., Goldsmith, 1987; Zhang et al., 2012; Karato and Jung, 2003). A large viscosity contrast of more than two orders of magnitude was detected at depths of 70 km to 100 km beneath ocean and was defined as the lithosphere–

asthenosphere boundary (Anderson, 1989). Partial melting models (e.g. Anderson and Sammis, 1970; Hirth and Kohlstedt, 1996; Kawakatsu et al., 2009) and sub-solidus models (e.g. Faul and Jackson, 2005; Karato and Jung, 1998) were proposed for explaining the presence of the boundary. However, the origin of the lithosphere–asthenosphere boundary remains an enigma. In both models, water distribution in the Earth is critical to the nature of the boundary. Therefore, precise knowledge on the distribution of water among mantle minerals is very important for understanding the Earth's dynamics.

The water solubility in the Earth's mantle minerals (e.g. Kohlstedt et al., 1996; Mierdel and Keppler, 2004; Zhao et al., 2004) and the water partitioning coefficient among mantle minerals (e.g. Bolfan-Casanova et al., 2000) were determined by high-pressure and high-temperature experiments conducted under water-saturated or high water fugacity conditions. However,

the water contents of mantle minerals that were detected in a natural peridotite xenolith (e.g. Grant et al., 2007) and estimated by electrical conductivity (e.g. Karato, 2011) were one or two orders of magnitude smaller than those detected by high-pressure experiments. Such experiments under low-water concentrations similar to those of natural rocks in addition to that estimated by electrical conductivity are very limited owing to the sensitivity of traditional analytical methods. Recent development of Fourier-transform infrared (FT-IR) spectroscopy and secondary ion mass spectroscopy (SIMS) improved the sensitivity of low water contents in minerals. Several experiments that used FT-IR indicated that the incorporation mechanism of water differs among low and high water contents. Nishihara et al. (2008) indicated that the substituting mechanism of OH in wadsleyite changes considerably with OH concentration and oxygen fugacity. This fact implies that the water partitioning coefficient among mantle minerals can change with water fugacity (i.e. water content). It is necessary, therefore, to conduct several high-pressure experiments that determine the water partitioning coefficient among the Earth's mantle minerals under low water content or low water fugacity conditions.

Water content in minerals can be changed by pressure, temperature, and chemical composition (e.g. Bai and Kohlstedt, 1993). The Earth's uppermost mantle is composed mainly of Ol, Opx, clinopyroxene (Cpx), spinel, and garnet. In particular, Ol accounts for a large proportion (60 vol.%) of the Earth's uppermost mantle. In addition, Opx, which contains significantly more water than does Ol in the mantle xenolith, is the second most abundant phase of the Earth's uppermost mantle. The FeO content in mantle Ol shows very limited variation in range, whereas the Al content of Opx in the Earth's upper mantle decreases significantly with increasing pressure (Obata, 1976). Therefore, the variation of Al content in mantle minerals can be important for the solubility of water in mantle minerals.

Rauch and Keppler (2002) investigated the effect of Al content on water solubility in Opx. The water solubility significantly increased with Al content and reached values that were several times higher than those in pure enstatite. However, the Al contents in Opx revealed by these high-pressure experiments were limited (<1 wt.%) compared with those detected in a natural peridotite xenolith (<5.26 wt.%) (Grant et al., 2007). Stalder (2004) also reported influence of Al on hydrogen incorporation in Opx. He synthesized Al doped enstatite crystals (5.9 wt.%) and measured by FT-IR. The results suggested that substitutions involving Al dominate the H incorporation and water content in Opx was linearly increased with Al. Al content is considered to enhance water solubility in Opx; that with high Al contents may dominate the water budget in the Earth's uppermost mantle. Thus, $D_{(Opx/Ol)}$ could change significantly in the Earth's upper mantle because of changes of Al content in Opx occurring with depth. Férot and Bolfan-Casanova (2012) reported the influence of Al in pyroxene on H incorporation in Ol and pyroxene (Py). They investigated almost no effect of Al concentration of $D_{(Py/Ol)}$. However, their experiments conducted under water-saturated conditions at from 2.5 to 9 GPa. Shapes of IR spectra by previous experimental studies (e.g. Férot and Bolfan-Casanova, 2012) with water-saturated condition are significantly different with those of mantle xenolith (especially Opx). The dominant incorporation mechanism of H could be largely difference between previous experimental study and mantle xenolith. Therefore, it is necessary to investigate the influence of Al in Opx on $D_{(Opx/Ol)}$ under low water concentration by high-pressure and high-temperature experiments.

In this study, we conducted experiments to determine the effects of Al content in Opx and pressure on $D_{(Opx/Ol)}$ under low-water conditions similar to those in the Earth's upper mantle. The water contents of the recovered samples were measured by using vacuum-type FT-IR spectroscopy. The influence of the water par-
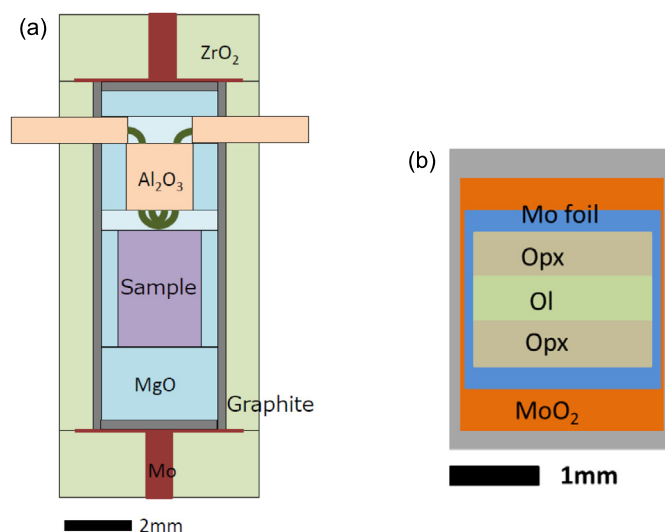

Fig. 1. (a) 18/11 M cell assembly viewed in cross section. (b) Typical capsule design used for the annealing experiments. Oxygen fugacity of the sample is buffered by presence of Mo foil and MoO_2 powder.

titioning coefficient on the lithosphere–asthenosphere boundary is discussed on the basis of these experiments.

2. Experimental procedures

2.1. Sample preparation

Natural olivine powder (Ol: $(Mg,Fe)_2SiO_4$, Mg# = 0.89) sampled from a fertile peridotite KLB-1 (Takahashi, 1986) and synthetic orthopyroxene powder (Opx: $(Mg,Fe)_{2-x}Al_{2x}Si_{2-x}O_6$, Mg# = 0.90: $x = 0, 0.1, 0.2, 0.4$) with four different Al contents and a Mg number consistent with that of KLB-1 were used as starting materials. The synthetic Opx was prepared from a powdered mixture of MgO, silicic acid (SiO_2), Al_2O_3, and Fe_2O_3. The mixture was molded into a pellet and heated at 1573 K and $f_{O_2} = QFM$ (quartz–fayalite–magnetite) – 2 [log unit] for 20 h in a 1 atmosphere gas-mixing furnace. After being quenched, the sample was finely ground in an agate mortar and was heated again under the same conditions.

2.2. High-pressure and high-temperature experiments

Annealing experiments were conducted to investigate the effects of Al content and pressure on water partitioning between Opx and Ol under the pressure conditions of the Earth's upper mantle by using a piston-cylinder apparatus for $P = 1.5$ GPa and a Kawai-type multi-anvil apparatus (SPI-1000) for $P = 2$ to 6 GPa at the Magma Factory, Tokyo Institute of Technology. A half-inch talc–Pyrex glass cell (Takahashi, 1986) was used for the piston-cylinder apparatus. With the Kawai-type multi-anvil apparatus, we used tungsten carbide cubes (Fujiroi, TN-05) with a truncated edge length of 11 mm as second anvils. The pressure medium was an octahedron with an 18 mm edge length constructed of MgO doped with 5 wt.% Cr_2O_3. The sample was heated in a cylindrical graphite furnace. A Mo metal rod and ZrO_2 were used as electrodes and a thermal insulator, respectively. A W5%Re–W26%Re thermocouple, shown in Fig. 1(a), was used to measure the temperature of the sample. Molded pellets of the starting material powder, which consisted of two or three single-phase layers each more than 300 μm thick, were loaded in a Mo metal foil capsule with a 50 μm wall thickness. The grain sizes of starting materials were several μm. The capsule was then placed in an $Au_{75}Pd_{25}$ capsule with a 0.1 mm wall thickness, which was used to close the system for water with MoO_2 powder. The $Au_{75}Pd_{25}$ capsule was then sealed by