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Supercritical fluid in the mantle transition zone deduced from H–D interdiffusion of wadsleyite

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ABSTRACT

Knowledge of the distribution of water in the Earth's mantle is key to understanding the mantle convection and geochemical evolution of the Earth. As wadsleyite and ringwoodite can incorporate large amounts of water in their crystal structures, proton conduction has been invoked to account for the widespread conductive anomalies observed in the mantle wedge, where descending slab stagnates at the transition zone. However, there is a lot of controversy on whether proton conduction by itself is able to explain such anomalies, because of large discrepancy in the extent of the water effect deduced from previous electrical conductivity measurements on hydrous polycrystalline wadsleyite and ringwoodite. Here we report the hydrogen self-diffusion coefficient obtained from H–D interdiffusion experiments in wadsleyite single-crystal couples. Our results demonstrate that the effect of water on the electrical conductivity of wadsleyite is limited and hydrous wadsleyite by itself is unable to explain conductive anomalies in the transition zone. In contrast, the expected hydrogen effective diffusion does not allow the wide propagation of water between the stagnant slab and surrounding mantle, probably leading to persistence of local water saturation and continuous release of supercritical fluids at the stagnant slab roof on geological time scales. This phenomenon provides an alternative explanation for both the high-conductivity and seismic-velocity anomalies observed in the mantle wedge at the transition-zone depth.

1. Introduction

The most notable feature of electrical conductivity structures in the mantle transition zone obtained by magneto-telluric and geomagnetic deep sounding observations is the presence of a zone of enhanced conductivity along the circum-Pacific margin that extends from western North America, through the Aleutian arc and East Asia, and into the Indian Ocean and Australia (Kelbert et al., 2009). Extremely conductive areas have been found at the depth from 410 to 550 km beneath Argentina (0.3 S/m) (Booker et al., 2004), northeastern China (0.1–0.3 S/m) (Ichiki et al., 2006) and the Philippine Sea (0.1–0.3 S/m) (Baba et al., 2010; Shimizu et al., 2010): these values are more than one order of magnitude higher than those for the central Pacific (Kelbert et al., 2009). As wadsleyite and ringwoodite, which are the most dominant minerals in the transition zone, have high water solubility (Kohlstedt et al., 1996; Bolfan-Casanova et al., 2000; Demouchy et al., 2005; Litasov and Ohtani, 2009), such conductive regions have been considered in terms of hydration of nominally anhydrous minerals in the transition zone (Baba et al., 2010; Ichiki et al., 2006; Kelbert et al., 2009).

To examine the hypothesis, laboratory-based electrical conductivity measurements have been performed on hydrous wadsleyite and ringwoodite during the last decade (Huang et al., 2005; Yoshino et al., 2008; Dai and Karato, 2009; Manthlake et al., 2009; Yoshio and Katsura, 2012). However, the relationship between conductivity and hydrogen content has not become clear because of large uncertainties and discrepancies between laboratories. One laboratory reported relatively high electrical conductivities in hydrous wadsleyite (Huang et al., 2005; Dai and Karato, 2009), which could explain the extremely conductive zone in the mantle wedge with less than 1 wt.% H_2O incorporated in wadsleyite. In contrast, another laboratory demonstrated a significantly weaker effect of water (by more than one order of magnitude) in the same conditions (Yoshino et al., 2008; Manthilake et al., 2009). Because dehydration unavoidably occurs during heating, especially at high water

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content, achieving reliable, consistent results from direct electrical conductivity measurements on hydrous polycrystals is very difficult (Yoshio and Katsura, 2012). A different method to estimate electrical conductivity from hydrogen self-diffusivity is useful to resolve the controversies from direct measurements and to understand further the origin of the conductive anomalies. Hydrogen self-diffusivity can be obtained from H–D interdiffusion experiments by employing a diffusion couple composed of H- and D-doped wadsleyite single crystals that includes no contribution from grain-boundary diffusivity.

In previous H–D exchange experiment, the center of H-doped single crystal was utilized for one semi-infinite end and the other semi-infinite end locates in the interface between single crystal and D-rich water bath (Du Frane and Tyburczy, 2012). The composition of semi-infinite end in the interface, C_1, is difficult to be determined by Secondary ion mass spectrometry (SIMS). However, fitting of diffusion profile using 1-D solutions to Fick's second law for a semi-infinite solid (Crank, 1975) can be tricky due to C_1 and D_H,

$$\frac{C_{(x,t)} - C_0}{C_1 - C_0} = erfc\left(\frac{x}{2\sqrt{D_H t}}\right), \tag{1}$$

where $C_{(x,t)}$ is the concentration at distance x (m) and time t (s), C_0 and C_1 are the concentrations at two semi-infinite ends, and D_H is the hydrogen self-diffusion coefficient. Indeterminism of C_1 largely constrains the validity for approximating hydrogen self-diffusion. In this study we employ H- and D-doped single crystals for two semi-infinite ends to realize determination of C_1 by SIMS, which has been broadly performed in Fe–Mg interdiffusion (Holzapfel et al., 2009) and is helpful to obtain accurate hydrogen self-diffusivity.

2. Experimental approach

2.1. Synthesis of hydrous wadsleyite single crystals

A Cr-doped MgO octahedron with edge lengths of 14 mm and tungsten carbide cubes with truncation edge lengths of 6 mm were used for synthesis of wadsleyite in a Kawai-type multi-anvil apparatus (Table 1). The silicate source was powder (grain size <1 µm) of natural San Carlos olivine and the water source was composed of an oxide mixture of $Mg(OH)_2$ or $Mg(OD)_2$ + SiO_2 + FeO (Mg# = 90 and ~10 wt.% H_2O or D_2O). The bulk water content in the starting material was around 6–7 wt.%. A welded Au capsule (2.5 mm in length and diameter) was loaded in an MgO sleeve surrounded by a stepped $LaCrO_3$ cylindrical heater. The center of the capsule was shifted 0.6 mm from the center of the heater along the axial direction to create a monotonic thermal gradient in the axial direction. The silicate and water sources were placed in the hot and cool regions, respectively. After heating to 1923 K at 16 GPa, the sample was slowly cooled to 1723 K at a cooling rate of 1 °C/min (gradual crystallization from silicate partial melts). The sample was kept at 1723 K for more than 5 h before quenching to homogenize the water and iron contents in single crystals, because partitioning of water and Fe between wadsleyite and a coexisting hydrous melt is sensitive to temperature (Litasov et al., 2011). The largest grain size of synthetic wadsleyite was ~1.8 mm. Most of the single crystals were transparent and free from inclusions. The homogeneity of the H_2O (D_2O) contents in single crystals was confirmed by unpolarized Fourier-transformed infrared (FTIR) spectroscopy with unpolarized light. The *Paterson* calibration was used to calculate the water content from infrared absorption (Paterson, 1982). The homogeneity of the Fe content in Fe-bearing crystals was confirmed using an electron probe micro-analyzer (EPMA).

Table 1
Composition determined by EPMA and FTIR of synthetic H-doped and D-doped wadsleyite single crystals used in diffusion experiments, and the results of H–D inter-diffusion runs conducted in a Kawai-type multi-anvil apparatus.

Synthesis				
Run.		EPMA	FTIR	
		Mg#	D/(H+D)	Total (wt.%)
1K1890	H-wad	90.27 ± 0.39	n.d.	0.95 ± 0.03
5K2300	D-wad	90.02 ± 0.19	0.78 ± 0.01	1.04 ± 0.02

Diffusion				
Run.	Axis	T (K)	Dur (min)	log D_H (m^2/s)
1k2403	*a*	1000	77	−12.05 ± 0.01
1k2184	*a*	1100	12	−11.68 ± 0.03
1k1943	*a*	1200	21	−11.40 ± 0.02
5k2493	*b*	1000	90	−13.05 ± 0.02
1k2066	*b*	1000	124	−12.92 ± 0.02
1k2075	*b*	1100	41	−12.36 ± 0.02
1k2181	*b*	1200	5	−11.74 ± 0.02
1k2102	*c*	1000	132	−12.45 ± 0.02
1k2198	*c*	1100	11	−12.12 ± 0.03
1k2193	*c*	1200	5	−11.58 ± 0.01

We also conducted another synthesis experiments by slow cooling from 1923 to 1373 K to obtain wadsleyite single crystals with a higher water content. As the grain size of those crystals was not large enough for the diffusion experiment, only the water solubility was determined.

2.2. H–D interdiffusion experiment

The crystallographic orientations of the synthetic single crystals were determined before the diffusion experiments using a precession camera to investigate the anisotropy of hydrogen diffusion. After determination of the crystallographic orientation, H- and D-doped crystals were double-polished along the same orientation with 1-µm diamond paste and tightly coupled together. The couple was put into a gold capsule (inner diameter 1.8 mm, length 2 mm) and fine-grained gold powder (1 µm) was used to fill up the remaining space. The edge length of the octahedral pressure media and the truncation edge length of the tungsten carbide cube used in the diffusion experiments were same as those used in crystal synthesis. Because of the short length of the crystal pair (<0.7 mm), the temperature gradient seems to be not crucial, although straight $LaCrO_3$ heaters were used for diffusion experiments. The welded Au capsule was kept at 353 K in a vacuum oven for ~8 h before compression. The diffusion experiments were conducted at the same pressure of 16 GPa as synthesis in a Kawai-type multi-anvil apparatus and at variable temperatures between 1000 and 1200 K. To minimize diffusion during heating up to the target temperature, the heating rate was set to greater than 10 K/s. After annealing at the target temperatures, the samples were quenched by cutting power off to <320 K in seconds.

Recovered samples were polished to the center of diffusion couples and then mounted in Bi–Sn alloy to minimize hydrogen background during SIMS analysis. The mounts were coated with Au layer of ~30 nm by plasma sputtering. H–D interdiffusion profiles were determined by SIMS, a Cameca 6f and 1270 at Hokkaido University along an array of spot analyses from one crystal edge to another crystal edge perpendicular to the interface (Fig. 1). A primary Cs^+ ion beam operated at 17 ~ 20 nA, and was focused to form an 20 ~ 30 µm spot on the sample, and the secondary $^1H^-$, $^2H^-$ and $^{30}Si^-$ ions were collected from the center region (10 µm in diameter) of the sputtered area using a mechanical aperture to minimize artifacts arising from hydrogen adsorption on the pol-