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Electrical conductivity of dense hydrous magnesium silicates with implication for conductivity in the stagnant slab

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ABSTRACT

Electrical conductivities of dense hydrous magnesium silicates (DHMS), phase A, super-hydrous phase B (SuB) and phase D, were measured by means of impedance spectroscopy in the frequency range of 10^{-1}–10^{6} Hz at temperatures up to 775, 700 and 700 K and pressures of 10, 18 and 22 GPa, respectively. For all phases, the increase in electrical conductivity (σ) with temperature follows the Arrhenian formula: $\sigma=\sigma_0\exp(-(\Delta H/kT))$. The pre-exponential factors (σ_0) and activation enthalpies (ΔH) of phase A, SuB and phase D yield values of 7.28 ± 0.82 S/m and 0.77 ± 0.01 eV, 292 ± 48 S/m and 0.83 ± 0.01 eV and 1342 ± 154 and 0.75 ± 0.01 eV, respectively. Higher pressure DHMS phases show higher conductivity values. The electrical conductivities of phase D and super hydrous phase B are about two and one orders of magnitude higher than that of phase A in the same temperature range, respectively. Although the proton conduction is considered to be a dominant mechanism, there is no clear relationship between water content and conductivity. Rather the conductivity of DHMS phase is closely related to the O···O distance. The conductivity–depth profiles for a cold subduction zone were constructed based on the phase proportion predicted in the descending slab. The results show distinctly lower conductivity values than those geophysically observed beneath the northeastern China and the Philippine Sea, where the cold slab stagnates in the mantle transition zone. Consequently, the DHMS phases themselves cannot be a main contributor to enhance the conductivity in the stagnant slab. Dehydration of the stagnant slab would strongly enhance the conductivities in the transition zone beneath northeastern China and Philippine Sea.

1. Introduction

Water plays an important role in the Earth, such as triggering the seismic event and the arc volcanism, enhancing the deformation, grain growth and the electrical conductivity of the mantle minerals (e.g., Meade and Jeanloz, 1991; Pawley and Holloway, 1993; Mei and Kohlstedt, 2000; Nishihara et al., 2006; Karato, 1990; Yoshino et al., 2006). Water can be transported into the deep Earth's interior by hydrous minerals in descending slab, e.g., serpentine, talc, and dense hydrous magnesium silicates (DHMS). Especially, the DHMS phase has been considered to be the important water containers in the subducted slab with peridotite composition to transport water into the transition zone and even the lower mantle (e.g., Ohtani et al., 2004). Phase A, phase E, super-hydrous phase B (SuB) and phase D are stable up to 15, 17, 30 and 44 GPa, respectively (Kanzaki, 1991; Ohtani et al., 2003; Shieh et al., 1998). Therefore, phases A, E and SuB are important water reservoirs under the P–T conditions in subducting slabs shallower than the 660 km seismic discontinuity. Phase D can be the major water carriers in slabs descending into the lower mantle.

It is well known that the Pacific plate becomes stagnant in the transition zone beneath the northeastern China and the Philippine Sea (Fukao et al., 2001; Huang and Zhao, 2006). Ichiki et al. (2001) firstly reported a 1-D electrical conductivity–depth profile beneath the NE China, which showed that the stagnant slab was more conductive than those of other tectonic settings. Recently, Kelbert et al. (2009) also reported higher conductivity values beneath NE China based on the global electromagnetic induction sounding. If temperature of the stagnant slab is significantly low (less than 1300 K), it is difficult to explain such high conductivity anomalies observed in the stagnant slab using the laboratory data of proton conduction in olivine and its high-pressure polymorphs (Huang et al., 2005; Yoshino et al., 2008a; Yoshino and Katsura, 2012).

If the descending slab passes temperature conditions below choke point (e.g., Schmidt and Poli, 1998), the DHMS phases can be present within or just above the subducted slab. Despite the low temperatures in the subduction zone, the DHMS may exhibit high conductivity because of high mobility of proton and high hydrogen concentration in their crystal structures. According to the

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petrological model in the subduction zone proposed by Ohtani et al. (2004), the proportion of DHMS is as high as 20% in weight. Therefore, the DHMS can be a potential candidate to explain the high conductivity values estimated at the transition zone depth beneath the NE China and the Philippine Sea.

The main purpose of this study is to examine contribution of the electrical conductivity of the DHMS phase to the high conductivity anomaly observed in stagnant slabs. In this study, we investigated electrical conductivity of phase A ($Mg_7Si_2O_8(OH)_6$), super-hydrous phase B ($Mg_{10}Si_3O_{14}(OH)_4$) and phase D ($Mg_{1.14}Si_{1.73}H_{2.81}O_6$) at pressures up to 22 GPa and in a temperature range of 500–775 K. We will discuss a cause of high conductivity observed at the transition zone where the slab stagnates using the laboratory-based 1-D conductivity–depth profile along the subducted slab geotherm.

2. Experimental methods

2.1. Starting material

Powders of reagent-grade MgO, $Mg(OH)_2$ and natural talc (same material as used in the study of Guo et al. (2011)) were used to synthesize phase A, super-hydrous phase B (SuB) and phase D. Before weighed, talc and $Mg(OH)_2$ powders were kept in a vacuum furnace for 6 h at 473 K, and MgO powder was baked for 1 h at 1273 K. Phase A was synthesized from a powder mixture of $Mg(OH)_2$, MgO and $Mg_3Si_4O_{10}(OH)_2$ in a molar ratio of 5:6:1 at 10 GPa and 1200 K for 2 h. SuB was synthesized from a mixture of $Mg(OH)_2$, MgO and $Mg_3Si_4O_{10}(OH)_2$ in a mole ratio of 5:26:3 at 18 GPa and 1273 K for 2 h. Phase D was synthesized from a mixture of $Mg(OH)_2$ and SiO_2 in a mole ratio of 1.14:1.73 and about 0.02 ml water at 22 GPa and 1273 K for 2 h. The synthesis experiment was performed in a sealed Pt capsule. The run product, observed by a field emission scanning electron microscope (FE-SEM), showed large porosity ($\sim$5 vol%) filled with saturated water (Fig. 1a, c, and e). For such a sample, the grain interior conduction cannot be observed by large contribution of the conductivity of grain boundary water. In order to reduce porosity in the sample, “sintering” experiments were conducted at the same experimental conditions used in the synthesis experiments. The run product was confirmed to be the desired phase by a microfocus X-ray diffractometer. The textural observation by FE-SEM showed the large porosity reduction (Fig. 1b, d, and f). The recovered samples contain small amounts of minor phases (Table 1). These isolated minor phases would have a negligible effect on the conductivity of DHMS.

2.2. Experimental cell

The cell assembly for the synthesis and sintering experiments of DHMS samples includes a pre-sintered Cr_2O_3-bearing MgO octahedral pressure medium, ZrO_2 thermal insulator and cylindrical TiB_2-doped BN heater. The edge lengths of each pressure medium for synthesizing of phase A, SuB and phase D are 18, 14 and 10 mm, respectively. Temperature was monitored with $W_{97}Re_3$–$W_{75}Re_{25}$ thermocouple. Eight tungsten carbide cubes with a truncation edge length of 11, 6 and 3 mm were used as a second stage anvil for the synthesis, sintering and conductivity measurement of phase A, SuB and phase D, respectively.

The sintered samples were cored to disks with a thickness of 0.5 mm and a diameter of 1.5 mm using an ultrasonic drilling machine. The sample was placed in an MgO capsule, by which the sample was insulated from the TiB_2 heater, and sandwiched by two molybdenum electrodes with a diameter of 1.5 mm and a thickness of 0.5 mm. Two sets of $W_{97}Re_3$-$W_{75}Re_{25}$ thermocouples were connected to each Mo electrode, and were insulated from the heater by Al_2O_3 tubes. Fig. 2 shows the cell design for electrical conductivity measurement.

2.3. Impedance spectroscopy analysis

Before the conductivity measurements, all samples were baked for 3 h in a vacuum furnace at 473 K to eliminate adsorbed water. The conductivity measurements of phase A, SuB and phase D were carried out using a complex impedance analyzer (Solartron 1260) with a frequency range of 10^{-1}–10^6 Hz at 10, 18 and 22 GPa, respectively. A typical measurement was performed by the following procedures: (1) the sample was compressed to the desired pressure; (2) complex impedance spectra were measured in a 50 K step until the sample was heated to the desired temperature; (3) the samples were kept at this temperature until the sample resistance became constant by removal of the absorbed water; (4) the samples were cooled to 500 K and the impedance spectra were obtained at each 25 K interval; and (5) the samples were heated up to the highest temperature and measured at 50 K intervals to check the reproducibility of measurements. Since the conductivity in the first heating usually was influenced by absorbed water in the assembly (Yoshino, 2010), we adopted the conductivity data obtained from the cooling path in the following sections. The sample conductivity was calculated from the sample resistance and dimension after conductivity measurement.

The difficulties of electrical conductivity measurements of hydrous phases are due to (1) synthesis of the sample without free water at high pressure; (2) selection of material to avoid chemical reaction and to insulate electrically between sample and heater; and (3) determination of an appropriate experimental temperature range to avoid dehydration of the sample. The previous studies on the conductivity measurement of hydrous minerals have shown that the sample conductivity is strongly enhanced by the presence of a small amount of free fluid at temperatures above 800 K even if the temperature is below the dehydration temperature (Fuji-ta et al., 2007; Guo et al., 2011). The free water might originate from the partial dehydration of hydrous minerals or the reaction between the sample and the container. Because dehydration temperature is different for each hydroxyl species in crystal, tiny amount of water might be released below the dehydration temperature showing complete decomposition. In this study we carefully confirmed the partial dehydration temperature for phase A, SuB and phase D. Both low and high temperature measurements were performed to obtain the grain interior (proton) conduction for the DHMS phases and check the water effect on the bulk conductivity. The experimental conditions and results are summarized in Table 1.

3. Experimental results

Fig. 3a shows the heating and cooling paths for the conductivity measurement of SuB aggregate at temperatures up to 1000 K. When heating to 1000 K, we kept it for 10 min and simultaneously measured the conductivities. The sample conductivity continuously increased, and then we obtained impedance spectra in the cooling path. Although the dehydration temperatures of phase A, SuB and phase D are 1350 K at 10 GPa (estimated from Yamamoto and Akimoto (1977)), 1600 K at 18 GPa (Ohtani et al., 2003) and 1600 K at 22 GPa (Frost and Fei, 1998), respectively, the conductivity always increased considerably at 800 K during heating. The increase of the sample conductivity at 800 K would correspond to a dehydration reaction of ($5Mg_{10}Si_3O_{14}(OH)_4+MgO=3Mg_{14}Si_5O_{24}+9Mg(OH)_2+H_2O$) between sample and MgO capsule, although this reaction was not identified based on the observation of run product due to the low temperature and short duration.