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Electrical conductivity of mantle clinopyroxene as a function of water content and its implication on electrical structure of uppermost mantle

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ABSTRACT

The electrical conductivity of San Carlos clinopyroxene aggregates with various water contents were measured under Ni–NiO buffer at 1.5 GPa and 600–1200 K in a DIA-type apparatus. The conductivity increases with increasing water content in clinopyroxene. Hidden conduction mechanism was detected because of the much smaller iron content in clinopyroxene, which was usually covered by small polaron conduction in other nominally anhydrous minerals. The identified activation enthalpies ranged from 0.70–0.75 eV to 1.23–1.37 eV. Our result reveals that the dominant charge-carrying species in electrical conductivity could change with temperature and water content. At high temperatures relevant to asthenospheric condition, activation enthalpy for the conductivity agrees well with that for the hydrogen self-diffusion. The dominant charge carrier therefore might be M site vacancy. However, contrary to previous view that all hydrogens contribute to increasing conductivity equally, our result shows that only a limited amount (20%–40%) of hydrogen acts as effective charge carrier in clinopyroxene. On the other hand, the activation enthalpy for the conductivity at low temperatures is significantly lower than that for the hydrogen self-diffusion, similar to what has been observed in olivine and orthopyroxene. This type of conduction is probably caused by fast diffusion of specific hydrogen or fast hydrogen grain boundary diffusion. At low temperatures, the proton conduction of clinopyroxene is nearly one order and two orders of magnitude lower than those of olivine and orthopyroxene, respectively, and tends to converge at high temperatures. Using the present data combined with conductivity of olivine and orthopyroxene, a laboratory-based conductivity-depth profile in the uppermost mantle shows that hydrous clinopyroxene cannot account for the high conductive regions observed beneath the ocean floor near Eastern Pacific Rise. The presence of partial melt would be unavoidable.

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1. Introduction

The high conductive region (60–120 km) observed from magnetotelluric data near the East Pacific Rise (e.g. Evans et al., 2005; Baba et al., 2006) has been mainly ascribed to two hypotheses: 1) high electrical conductivity of hydrous olivine (Wang et al., 2006; Dai and Karato, 2014) and 2) partial melting of peridotite (Gaillard et al., 2008; Yoshino et al., 2006). Although water could enhance electrical conductivity, some studies suggested that the conductivity enhanced by hydrous olivine and orthopyroxene was insufficient to account for this anomaly (Du Frane and Tyburczy, 2012; Poe et al., 2010; Schlechter et al., 2012; Yoshino et al., 2009; Zhang et al., 2012).

Clinopyroxene, one of the main constituent minerals in the upper mantle, could be a possible candidate because water tends to partition into it rather than olivine and orthopyroxene ($D^{cpx/ol}$ = 12.5–88) (Aubaud et al., 2004; Grant et al., 2007). Although substantial hydrogen-enhanced conductivities in natural clinopyroxenes were demonstrated (Wang et al., 1999; Yang et al., 2011; Yang and McCammon, 2012), none of these previous studies could provide robust estimation of the conductivity of mantle clinopyroxene, either due to their large compositional deviation from mantle clinopyroxene (Yang et al., 2011; Yang and McCammon, 2012) or poor constraint on water content (Hinze et al., 1981; Huebner and Voigt, 1988; Wang et al., 1999). Thus a systematic and well-constrained determination of electrical conductivity of mantle clinopyroxene originating from peridotite as a function of water content is essential to understand such high conductivity anomalies occasionally observed in oceanic asthenosphere and construct realistic laboratory conductivity-depth model.

Hydrogen diffusivity, obtained from H–D exchange experiments, offers an alternative way to evaluate electrical conductivity indirectly (Du Frane and Tyburczy, 2012). However, conductivities of clinopyroxene calculated from hydrogen diffusion (Hercule and Ingrin, 1999) gave significantly different values from those directly measured ones in both magnitude and activation enthalpy. Such discrepancy was also observed in olivine and orthopyroxene (Du Frane and Tyburczy, 2012). To explain this discrepancy, Karato (2013) proposed the hybrid model composed of multi-species hydrogen diffusion. Dai and Karato (2014) argued that $(2H)_M^X$ diffusion process with higher activation enthalpy becomes dominant at high temperatures. However, more efforts are needed to test it and unravel the microscopic mechanism of hydrogen enhanced conductivity in nominally anhydrous minerals. At high temperatures, proton conduction in olivine and its high-pressure polymorphs is usually masked by larger contribution of small polaron conduction to the bulk conductivity (Yoshino et al., 2006, 2008). The Fe-bearing hydrous clinopyroxene thus provides an opportunity to detect $(2H)_M^X$ diffusion, because of its much smaller iron content.

In this study, we determined the electrical conductivity of San Carlos clinopyroxene aggregates as a function of water content at 600–1200 K and 1.5 GPa. A detailed discussion about the mechanism of hydrogen-involved electrical conductivity in clinopyroxene is presented. Compared the conductivity of clinopyroxene between those of olivine and orthopyroxene, a possible reason resulting in the difference is proposed. Assuming constant water-partitioning coefficients among olivine, orthopyroxene and clinopyroxene, we estimate the electrical conductivity-depth profile in the oceanic mantle with varying bulk water contents, and then evaluate the origin of conductivity anomalies observed beneath the ocean floor near Eastern Pacific Rise.

2. Experimental procedure

2.1. Sample preparation

Clinopyroxene aggregates with various water contents were synthesized under Ni–NiO buffer from San Carlos clinopyroxene powder at 1273–1373 K and 1.5 GPa in a piston cylinder apparatus. San Carlos clinopyroxene crystals initially contained ∼0.020 wt.% H_2O. To synthesize clinopyroxene with high water content (∼0.200 wt.%), a mixture of the clinopyroxene powder and 2 wt.% powder mixture of talc and brucite (1.4:1 by weight) was placed in platinum capsule (PC419-1). Melt-bearing clinopyroxene was synthesized in the same run (PC419-2) using platinum capsule with free water. To synthesize less hydrous clinopyroxene aggregates, clinopyroxene powder was carefully protected from moisture before and after being loaded into Ni (occasionally Fe) capsule. Before annealed at 1373 K the sample was kept at 873 K and low press load for several hours. After recovering, the oxygen fugacity was confirmed to be controlled near NNO buffer because of the coexistence of Ni and NiO powder mixture. The sintered clinopyroxene aggregates were cut into several pieces. Sliced pieces were cylindrically cored to disks with 2 mm diameter by ultrasonic coring machine to remove the reacted zone with capsule and used for subsequent examinations and measurement. The sintering experimental conditions for each run are summarized in Table 1.

2.2. Electrical conductivity measurement

One piece of the sintered clinopyroxene aggregate with a thickness of 400–500 μm was used to measure the electrical conductivity at 600–1200 K and 1.5 GPa in a DIA-type apparatus. The cell assembly was composed of a cubic pyrophyllite pressure medium, a ZrO_2 thermal insulator and a cylindrical graphite heater (Fig. 1). The disc-shaped sample was placed between two surface-oxidiz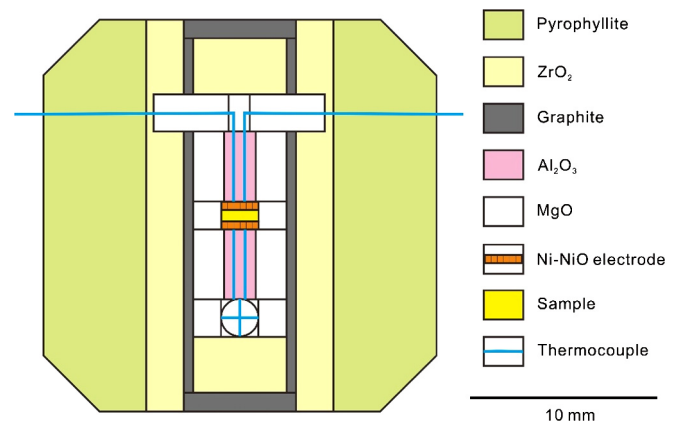ed nickel electrodes, of which one oxidized-surface was carefully removed so that the sample could be in direct contact with

Fig. 1. The configuration of the cell assembly for electrical conductivity measurement in a DIA-type apparatus.

Table 1
Summary of sintering experimental conditions.

Run No.	Starting material	Capsule	T (K)	Duration (h)
PC419	Cpx + H_2O source/Cpx	Pt	1373	2.5
PC426	Cpx	Fe foil	1473	5
PC428	Cpx	Fe foil	1473	5
PC429	Cpx	Ni foil	1273	5
PC432	Cpx	Pt	1473	5
PC449	Cpx	Ni foil	1373	10
PC451	Cpx	Ni foil	1373	10

All these experiments were conducted at 1.5 GPa. For PC419, two different starting material was loaded into two independent Pt capsules, one was Cpx powder + H_2O source mixture (PC419-1), the other was Cpx powder (PC419-2). The starting material for all the other runs was Cpx powder with different amounts of absorbed moisture from the air. For each run, abundant amount of Ni and NiO powder mixture was loaded outside capsule to control the oxygen fugacity.

nickel. This partly oxidized nickel electrodes also served as oxygen buffer during electrical conductivity measurement. Two sets of WRe_3–WRe_{25} thermocouples were connected to the upper and lower Ni electrodes, and insulated from graphite heater by MgO or Al_2O_3 insulators.

In situ electrical conductivity data were acquired using a combination of Solartron 1260 impedance Gain-Phase Analyzer and Solartron 1296 interface, with an applied voltage 1 V in amplitude and impedance frequencies ranging from 1 MHz to 0.1 Hz. After compression, preheating at 500 K or 800 K helped to remove free water in the cell assembly and created an environment with high insulation resistance. Conductivity measurements were performed at 600–900 K and 800–1200 K for the most hydrous and other samples, respectively. The reproducibility of conductivity measurements was ensured after three heating–cooling cycles. The maximum temperature interval for measurement of each heating path was 100 K. Within each cycle, impedance spectra were obtained at every 50 K during heating and every 25 K during cooling. Sample resistances were obtained after fitting the impedance spectra to an equivalent parallel circuit composed of a resistor and a capacitor. The electrical conductivities of clinopyroxene aggregates were calculated using the equation:

$$\sigma = L/(SR) \tag{1}$$

where L is the thickness of sample, S is the cross-section area of electrode, R is the resistance calculated from complex impedance spectra. To examine possible current leakage to the surrounding material, the resistance of the cell where polycrystalline MgO was used as a sample, was measured in a separate run. This test was