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Hydrogen partitioning between iron and ringwoodite: Implications for water transport into the Martian core

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ABSTRACT

We determined the exchange partition coefficients of hydrogen between solid iron and ringwoodite between 16.6 and 20.9 GPa at temperatures up to 1273 K using a Kawai-type multianvil high-pressure apparatus with synchrotron X-ray radiation at the BL04B1 beamline at SPring-8, Japan. The hydrogen concentration in iron hydride was estimated from the volume expansion of iron caused by hydrogenation determined by in situ X-ray diffractions at high pressure and high temperature, and the water content of ringwoodite in the recovered samples was estimated using the Fourier transform infrared spectroscopy (FTIR). According to our results, the exchange partition coefficients of hydrogen between the solid iron and ringwoodite were almost constant, 26, with pressure between 16.6 and 20.9 GPa and 1273 K. These results revealed that hydrogen was strongly partitioned to metallic iron and that iron hydride formed, coexisting with dry ringwoodite under the experimental pressures.

Ringwoodite, found in the Martian core–mantle boundary region, is an important hydrogen reservoir. The pattern of quasi-parallel bands of uniformly magnetized crust with alternating positive and negative polarity measured by the Mars Global Surveyor spacecraft strongly shows that a magnetic field did exist in ancient Mars suggesting a possible plate tectonic activity on ancient Mars. Thus, water could have been transported to the deep Martian interior by hydrous minerals during the plate subduction process and stored in ringwoodite in the deep Martian slabs, as is suggested on the Earth today. Our experiments suggested that hydrogen stored in ringwoodite was absorbed by the Martian core at the Martian core–mantle boundary. Thus, water from the ancient Martian ocean may be stored now in the Martian core.

1. Introduction

Based on topographic features such as sinuous valleys, outflow channels, and depositional basins (e.g. Masson et al., 2001; Baker, 2001; Irwin et al., 2005), and also on the existence of sulfate minerals that constitute several tens of percent of some surface rocks by weight (Squyres et al., 2004), recent astronomical surveys suggest that a large amount of water may have existed on the ancient Martian surface. The pattern of quasi-parallel bands of uniformly magnetized crust with alternating positive and negative polarity measured by the Mars Global Surveyor spacecraft strongly shows that a magnetic field did exist in ancient Mars suggesting a possible plate tectonic activity on ancient Mars (e.g. Solomon et al., 2005; Connerney et al., 2005).

On the present Earth, water in the oceanic crust is transported to the Earth's deep interior in the form of a hydroxyl OH in hydrous minerals, absorbed water in minerals (e.g. Ohtani et al., 2004), or a supercritical fluid captured at the grain boundaries of minerals (Ono et al., 2002) by subducting slabs. Then, wadsleyite and ringwoodite can be major water reservoirs in the mantle transition zone on Earth because the maximum water contents of wadsleyite and ringwoodite are 2.2 wt.% (Demouchy et al., 2005) and 2.6 wt.% (Kohlstedt et al., 1996), respectively. Recent magnetotelluric observation of mantle conductivity also suggested the possible presence of water in the mantle transition zone below the western Pacific subduction zone (Koyama et al., 2006). If there was plate tectonic activity on ancient Mars, the ancient Martian ocean water could have been entrained in the hydrous minerals and transported into the Martian interior by subducting slabs; and wadsleyite and ringwoodite could have been major water reservoirs in Mars, as is suggested on Earth today (e.g. Huang et al., 2005; Koyama et al., 2006).

Several Martian internal structure models have been proposed based on the calculation using the satellite observation data and high-pressure experimental data (e.g. Ohtani and Kamaya, 1992; Bertka and Fei, 1997, 1998; Sanloup et al., 1999; Zharkov and Gudkova, 2000; Gudkova and Zharkov, 2004; Zharkov et al., 2009). In these previous models, the pressure of the Martian core–mantle boundary condition was estimated to be 19–25 GPa. This pressure significantly depends on the amount of light elements in the core because the size of the core increases with increasing light elements in the core in order to match

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the observational data such as the mean density and the moment of inertia factor of Mars. Many chemical models of Mars showed that the Martian core contains some amount of sulfur based on mainly Martian SNC meteorites, Earth's materials, and chondrites (e.g. Dreibus and Wänke, 1987: 14.2 wt.%; Ohtani and Kamaya, 1992: 14.0 wt.%; Lodders and Fegley, 1997: 10.6 wt.%; Sanloup et al., 1999: 16.2 wt.%). In addition, Gudkova and Zharkov (2004) estimated the maximum amount of hydrogen in the iron core of Mars. They used the chemical model (DW) proposed by Dreibus and Wänke (1989) as the bulk composition of Mars. Dreibus and Wänke (1989) proposed that Mars was formed with 60% volatile depleted highly reduced material (component A), and 40% primitive C1 material (component B). The component A is highly reduced and free of all elements with equal or higher volatility than Na, but contains all other elements in C1 abundance ratios. Fe and all siderophile elements are metallic, and even Si is present partly in metallic form. The component B is oxidized and contains all elements, including the volatiles, with abundances like in C1 meteorites. Fe and all siderophile and lithophile elements are present mainly as oxides. The oxidized component B is assumed to have a composition of C1 carbonaceous chondrites containing ~7.3 wt.% water (Dreibus and Wänke, 1989). Under the assumption that component B has the same composition as C1 chondrites, the mass of the iron–nickel ($Fe_{0.9}Ni_{0.1}$) is $\sim 1.2\times10^{26}$ g and that of the hydrogen (H_2) is $\sim 2.0\times10^{24}$ g in the DW model. If all these hydrogen becomes a constituent of the Martian core, the upper bound for the hydrogen content in the iron core of Mars is $x\sim 1$ in FeH_x (~1.8 wt.% H).

Many researchers carried out the high-pressure–high-temperature experiments of the solubility of hydrogen in the metallic iron (e.g. Antonov et al., 1980, 1982, 1998; Fukai et al., 1982, 2003; Badding et al., 1991; Yamakata et al., 1992; Yagi and Hishinuma, 1995; Ohtani et al., 2005; Sakamaki et al., 2009). Okuchi (1997) showed the metal–silicate melt partitioning behavior of hydrogen. According to his results, in primordial Earth, more than 95 mol% of H_2O in the magma ocean was partitioned into the molten iron at the bottom of the magma ocean, where molten metal may have stagnated as iron ponds. Therefore, if a magma ocean formed in primordial Mars (e.g. Elkins-Tanton et al., 2005; Debaille et al., 2007) and almost all of H_2O accreted to Mars ($\sim 1.8\times10^{25}$ g H_2O in the DW model) dissolved into the magma ocean, more than 95 mol% of H_2O should have reacted with the molten iron ($\sim 1.2\times10^{26}$ g Fe in the DW model) to form liquid iron hydride at the bottom of the magma ocean. Then, the iron hydride ponds sank by large-scale gravitational instability (Stevenson, 1990) and the hydrogen-rich core formed, in which the hydrogen concentration was at least $x\sim 0.9$ in FeH_x (~1.6 wt.% H). Therefore, the Martian core probably contains some amount of sulfur and hydrogen. Gudkova and Zharkov (2004) showed that, if the Martian core contained volatile elements, such as about 14.0 wt.% S and 1.6 wt.% H, the core–mantle boundary condition would be about 20 GPa with no perovskite layer.

Therefore, it is important to investigate the partitioning behavior of water between iron and ringwoodite under the Martian core–mantle boundary conditions because the ringwoodite is in direct contact with the Martian core and iron possibly reacts with ringwoodite, which retains the water of the Martian ocean, at the Martian core–mantle boundary.

It is proposed that Mars had at least a liquid outer core for a model core composition with 14.2 wt.% S, assuming that the Martian core–mantle boundary condition is about 23 GPa and 2000 K (Fei and Bertka, 2005). Iron hydride melts at this condition (Sakamaki et al., 2009). Even if the silicate mantle comes in contact with the molten metal alloy at the Martian core–mantle boundary, the partition coefficient between solid iron and ringwoodite could be the lower bound, because the amount of hydrogen in molten iron hydride is larger than in coexisting solid iron hydrides; i.e., the partitioning coefficient of hydrogen between molten and solid iron hydrides, x_L/x_S, is 1.87 (where x_L and x_S are the concentration in liquid and solid, respectively) (Fukai, 1991) and the water content of ringwoodite is likely to decrease with increasing temperature (e.g. 2.6 wt.% at 1373 K and 19.5 GPa (Kohlstedt et al., 1996), and 0.7 wt.% at 1773 K and 21.5 GPa (Smyth et al., 2003)). In this study, we determined the partition coefficients of water (hydrogen) between solid iron and ringwoodite to constrain the lower bound of hydrogen content in the Martian core.

In previous high-pressure experiments on the systems of iron–silicate–water, it was showed that the reaction between these components yields iron-rich silicate minerals and iron hydride at high pressure and temperature (e.g. Suzuki et al., 1984; Yagi and Hishinuma, 1995), and that hydrogen is partitioned into molten iron compared with the coexisting silicates (Okuchi, 1997). However, because these experimental conditions were up to 7.5 GPa, there was no experiment which investigates a partitioning behavior of hydrogen between iron and ringwoodite at higher pressure, such as the Martian core–mantle boundary condition.

In fcc-FeH lattice, hydrogen can occupy interstitial octahedral sites which are surrounded by regular octahedra of Fe atoms, and one hydrogen atom occupies one interstitial site (Fukai, 2005, Chapter 2 and 4). When iron coexists with hydrous ringwoodite at high pressure and temperature, the following reaction is expected in equilibrium:

$$\underset{\text{metal}}{\mathrm{Fe}} + \underset{\text{ringwoodite}}{\mathrm{H_2O}} = \underset{\text{ringwoodite}}{\mathrm{FeO}} + \underset{\text{metal}}{\mathrm{2H}} \qquad (1)$$

Hydrogen is a univalent cation in ringwoodite, whereas it is neutral in iron hydride (Fukai, 1983). Therefore, during iron hydride formation, the H^+ in ringwoodite accepts one electron from an Fe atom in iron, and 2H and Fe^{2+} are formed. At the M site of ringwoodite, these 2H are likely to be exchanged by this Fe^{2+} and iron-rich ringwoodite ($(Mg, Fe)_2SiO_4$) is formed because, in ringwoodite, iron occupies the M site which hydrogen occupies in hydrous ringwoodite (Kudoh, 2001). In this paper, we use “iron hydride” when the hydrogen concentration is a stoichiometric (or nearly stoichiometric) or unknown, and “FeH_x” when we discuss on the hydrogen concentration itself.

2. Experimental

Experiments were carried out between 16.6 and 20.9 GPa at temperatures up to 1273 K using a Kawai-type multianvil high-pressure apparatus with synchrotron X-ray radiation at the BL04B1 beamline at SPring-8, Japan. Starting materials were prepared as powder mixtures of pure iron, $Mg(OH)_2$, and SiO_2 at a molar ratio of 2:1:1 and we synthesized iron hydride and hydrous ringwoodite at high pressure and temperature. The starting materials were enclosed in a boron nitride (BN) capsule, and a cylindrical BN composite (TiB_2+BN) was used as a heater. Fig. 1 shows a sample assembly of the present experiments. The temperature was measured by a W3%Re–W25%Re thermocouple, which was placed above the capsule inside the heater. A mixture of NaCl and MgO was placed outside the heater for determination of the experimental pressure. The temperature of the pressure marker materials was estimated based on the two equations of state of NaCl (Decker, 1971) and MgO (Jamieson et al., 1982). The temperature difference between the sample and the pressure marker was about 200 K. The energy-dispersive method was employed for X-ray diffraction study using a white X-ray from the bending magnet of the Accumulation Ring, which was operated at about 8 GeV and 95 mA (Utsumi et al., 1998). A Ge-solid state detector (SSD) was placed at a fixed angle of 5.5° from the incident X-ray beam, and diffracted X-rays were energy-analyzed. The diffraction patterns of the sample and the pressure marker were collected for 300 s at every 100–200 K temperature step between 300 and 1273 K. Under these conditions, ringwoodite coexists with solid iron hydride.

3. Analytical

We determined the partition coefficients of hydrogen between solid iron and ringwoodite by measuring the amount of hydrogen in solid iron hydride and ringwoodite.