



Formation of iron hydride and high-magnetite at high pressure and temperature

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Abstract

Iron hydride (FeH_x) is considered as suitable storage for hydrogen in the earth's interior and possibly in the core [J. Geophys. Res. 91 (B 9) (1986) 9222]. Most experimental data on its stability pertain to low pressures (<10 GPa) and temperatures. We studied the reaction of iron with brucite (water) at pressures 75 GPa and temperatures of ~ 2000 K using the double-side laser-heated diamond-anvil cell. A high-pressure phase of magnetite (Fe_3O_4) (orthorhombic) and iron hydride (double hcp) were found to exist stably under these conditions. The results indicate that at pressures corresponding to the earth's lower mantle, the hydride phase is stable, and that orthorhombic high-magnetite ($\text{h-Fe}_3\text{O}_4$) may also be stabilized in lieu of or in addition to magnesiowuestite. The stability of these phases open up the possibility that water (as a component of a fluid phase or hydrous solids) may be present not only in the mantle but also in the core (as dissolved hydride and oxide), which helps melting and dynamic movements. The core may have been the reservoir of oceans of fluid. A percent of water (by weight) in the core is equivalent to about 10 times the water in all the oceans. The dissolved water components in the core would depress the melting temperature of iron (or iron–nickel alloy) significantly, reduce the density and effectively promote convection.

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1. Introduction

The occurrence of fluids and fluid bearing systems in the earth's interior is considered important for the formation of melts and facilitating the dynamic process (Murkami et al., 2002). Water significantly influences the melting temperatures of solids (King and Holloway, 2002; Kawamoto et al., 1996). Water may be present in many silicate minerals (Murkami et al., 2002), and in a primitive earth setting it may have

played an important role by reacting with iron and thus, exercising significant influence on oxidation of the mantle and the growing core. Fukai and Suzuki (1986) followed Stevenson's (1981) suggestion of hydrogen as a light element in the core and established the stability of iron hydride (FeH_x) in the iron–water system through experiments. They discussed the possible role of water in the formation and evolution of protoplanetary bodies. Studies demonstrating the formation of hydrides at high pressures (Okuchi, 1997; Takahashi et al., 2002; Badding et al., 1991; Yagi and Hishinuma, 1995) have clearly established that iron hydride forms stably at pressures from a few to 7.5 GPa, both in the Fe-H_2 and the $\text{Fe-H}_2\text{O}$ systems.

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The stability of iron hydride and oxide at high pressures has been predicted based on thermodynamic calculations (Williams and Hemley, 2001). These results have led to the important proposal of including water (and thereby hydrogen and oxygen) in the core (Fukai, 1981; Takahashi et al., 2002). The information on the temperature effect on the Fe–H₂ and Fe–H₂O systems is available to 1800 K at low pressures. With this work, we have extended the Pressure range of the previous studies on the iron–water reaction to nearly 75 GPa.

2. Experimental methods

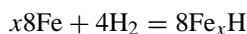
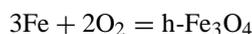
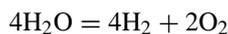
During the last 2 years, we conducted experiments with iron and brucite as starting materials. In the experiment reported here, in-situ X-ray data were collected on a laser-heated sample at GSECARS (Shen et al., 1998). Angle dispersive X-ray diffraction experiments under high pressure and temperature were performed at the GeoSoilEnviroCARS beamline (13-ID-D) at the advanced photon source (APS). A double-sided YLF laser heating system (7) was used for experiments. The laser heating spot size at the sample position was about 20–30 μm in diameter. A monochromatic X-ray beam (energy 29.200 keV) was used to produce a double crystal monochromator [silicon (1 1 1)]. The X-ray beam size was controlled by a slit system to 150 μm × 150 μm and subsequently focused by Kirkpatrick–Baez mirrors to a beam size of 7 μm (vertical) × 10 μm (horizontal) at full width at half maximum (FWHM). A charge-coupled device (CCD) detector (Bruker-2k) was used for diffraction measurements. Exposure time for the CCD was 30 s. The sample-detector distance was calibrated by diffraction patterns from a standard material (CeO₂) at one atmosphere. Pressures were determined from the lattice parameters of the iron before and after heating. We used a Merrill–Bassett design diamond-anvil cell for double-side laser heating of a sample consisting of an iron foil sandwiched between layers of brucite. A DAC, with 300 μm culet size, was used. A stainless steel gasket was pre-indented to 30 μm in thickness, and a hole of 80 μm in diameter was drilled. Three disks (brucite, iron foil, and brucite) were layered in the sample chamber. Brucite was also used as a pressure medium and thermal insulating layers for laser

heating. Pressure was determined at the start of heating and after quenching.

3. Results

The sample was pressurized to 75 GPa. Before the start of heating, diffraction peaks of hcp-phase of iron were observed with brucite diffraction disappearing at about 9 GPa. Within a few minutes of the start of heating, there was a significant development of the dhcp pattern along with some peaks of an unidentified phase (Fig. 1). After several minutes of heating a vigorous reaction was observed which continued for many minutes. Several additional peaks developed which continued to increase in intensity. Fig. 2 shows the in-situ X-ray diffraction data at an average temperature of ~2050 K (the temperature was difficult to measure due to continued reaction with some flashes). Since it is difficult to control the composition of the initial mixture of water (from brucite) and iron, the extent of reaction cannot be controlled. Brucite will always be in excess and under a temperature gradient varying over a wide range. In the pattern of the heated sample, we observed a prominent display of high-magnetite (high-pressure phase as described by Fei et al. (1999)) and iron hydride (dhcp) with some brucite, hcp-iron and periclase (Fig. 2); some brucite must have dissociated providing fluid for the reaction while the remaining recrystallized due to heating. Formation of solid solution between the magnesium component (MgO–FeO or FeFe₂O₄–MgFe₂O₄) is a possibility but cannot be ascertained here. The calculated cell constant and cell volume data (Table 1) are consistent with similar data on high-magnetite as found by Fei et al. (1999) at lower pressures (24 GPa). Similar consistency of the data on dhcp-iron hydride (Okuchi, 1997), also at low pressures, and of brucite (Fei and Mao, 1993) supports our analysis of the diffraction data in Fig. 2.

In the presence of water, we could consider the following reactions



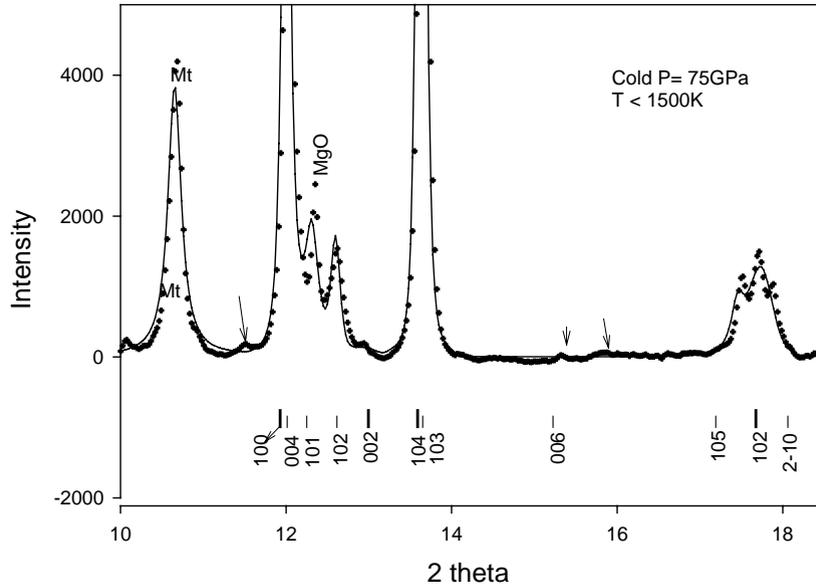


Fig. 1. In-situ X-ray diffraction from a heated sample of brucite and iron. The initial pattern of hcp-iron and brucite changes to an assemblage of dhcp-hydride (small ticks show the positions), hcp-Fe (bold ticks), and an unidentified phase (marked with arrows and later confirmed to be high-pressure magnetite, see Fig. 2). The data are fitted using the TOPAS2 software package (similar to GSAS). The identification and indexing of the dhcp-hydride phase is based on a comparison of the unheated hcp-iron at 75 GPa and the poor fit to the data if only hcp-iron is used.

Table 1
The fitted cell parameters on the five phases (cold $P = 75$ GPa)

	Periclase	dhcp-iron hydride	hcp-iron	h-Magnetite ^a	Brucite
a (Å)	3.889 (2)	2.298 (5)	2.38 (3)	2.715 (1)	2.797 (1)
b (Å)				9.393 (8)	
c (Å)		8.12 (3)	3.75 (2)	9.197 (4)	3.940 (1)
Cell volume (Å ³)	58.82	37.13	18.40	234.54	26.69

^a Fei et al. (1999) observed a high-pressure phase of magnetite and assigned it the *Pbcm* space group (CaMn₂O₄-type structure) with $a = 2.799$; $b = 9.409$; and $c = 9.483$ Å at 23.96 GPa.

Wuestite has been noted to occur in the Fe–water system at lower pressures (Fukai, 1981; Yagi and Hishinuma, 1995). The occurrence of a denser polymorph of magnetite has been reported by Fei et al. (1999). Recently Dubrovinsky et al. (2001) reported that h-Fe₃O₄ adopts the CaTi₂O₄ structure. Thermodynamically magnetite would dissociate to oxide mixture of FeO and Fe₂O₃ at high pressure. Lazor et al. (2004) noted the presence of h-Fe₃O₄ at a pressure of 19 GPa. This study finds the stability limit extended to 75 GPa. As long as both Fe and iron oxide are present the oxygen fugacity is well defined in a

volume around heated iron. Approaching equilibrium conditions in a small volume is possible but cannot be overemphasized in a diamond-anvil cell even with the double-side heating.

4. Summary

The following inferences can be drawn based on the experimental results: (a) iron hydride stability extends to high pressures (~75 GPa) and temperatures (~2000 K) and therefore, it could form in a primitive

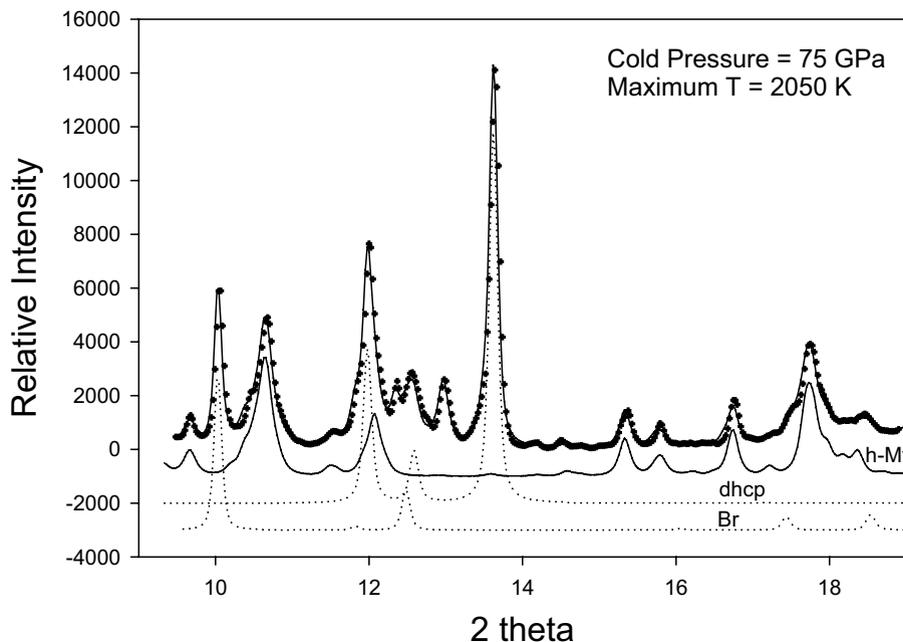


Fig. 2. X-ray diffraction of iron–brucite reaction products. A mixture of iron and brucite was heated in a Merrill–Bassett type double-side laser heating cell by YLF lasers from both sides. The sample was pressurized to 75 GPa with pressure measured by the cell constants for hcp-iron. The top curve shows the pattern after heating for nearly 30 min. The pattern was analyzed with the Bruker software Topas2 and shows the phase assemblage iron, iron hydride, and high-pressure magnetite (h-Fe₃O₄) with some periclase and recrystallized brucite. The contribution of the diffraction data from various phases to the top curve is revealed by the curves shown underneath.

mantle and core; (b) in the system iron–water, the hydride phase cannot exist without an oxide and therefore, both hydrogen and oxygen components could be part of the melt in the outer core; and (c) high-pressure h-magnetite may be a stable phase in the mantle. Simple calculations show that one percent of water (by weight) could amount to an equivalent of many oceans of fluid in the core. We may conclude that the core could be a dominant reservoir of hydrogen on the planet, with as much as 100 hydrosphere of hydrogen present in the high-pressure iron-alloy. This statement assumes that the phase relation in the system Fe–H₂O could be sustained at much higher temperature and pressure of the outer core.

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