Iron-Water Reaction and Composition of the Earth's Core

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Introduction

Water influences the melting temperatures of solids very significantly, and in recent years, it has become widely investigated as a component of the earth's interior. Following Stevenson's suggestion of hydrogen as a light element in the core [1], Fukai and Suzuki established the stability of iron hydride (FeH$_x$) the iron-water system through experiments [2]. They discussed the possible role of water in the formation and evolution of protoplanetary bodies. Several studies designed to demonstrate the formation of hydrides at high pressures [2-6] have clearly established that iron hydride forms stably at pressures from a few GPa to 7.5 GPa both in the Fe-H$_2$ and the Fe-H$_2$O systems. This discovery has led to the important proposal of including water (and thereby hydrogen and oxygen) in the core [2, 3]. Studies of the temperature effect on these systems have been performed to 1800K at low pressures. With the work discussed here, we have extended the pressure and temperature range of the previous studies on the iron-water reaction to nearly 40 GPa and ~1700K.

Methods and Materials

We conducted the experiments by using a Mao-Bell design diamond-anvil cell (DAC) for single-sided laser heating and Merrill-Bassett design cell for double-sided YLF-laser heating [7]. *In situ* x-ray data were collected on laser-heated samples at the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) sector at the APS. Stainless steel or rhenium gaskets were used. They had a 100- to 125-µm hole in which a sample of iron powder (99% purity, ~5 µm in size) was sandwiched between layers of a thoroughly wetted MgO powder. An additional drop of water was added before the cell was closed. Pressure was measured by using the lattice parameters of iron in unheated samples. The pressure could not be measured at high temperatures because of reactions. The energy-dispersive x-ray data were processed with the Topas software of Bruker GMBH.

Results

Figure 1 shows the results of single-sided laser heating. The use of the Mao-Bell cell does not permit double-sided laser heating at GSECARS, and in such cells, one may easily encounter substantial temperature gradients in the axial direction variously estimated at 200K or more under such conditions. The initial mixture contained iron, MgO, and water. At the start of heating, at temperatures of ~1200K, a significant reaction occurred. The products continued to develop upon further heating. The data at 1500K were fitted with a three-phase assemblage of double hexagonal close-packed (dhcp) iron, the hexagonal phase of FeO, and periclase (Table 1). Fei and Mao [8] described the hexagonal FeO phase at much higher pressures (96 GPa) as a NiAs-type (B8) structure. Because of the multiphase assemblage in this experiment, we cannot be absolutely sure that this is the correct interpretation of the data, but we could not fit the peak at a d-spacing of ~2.17 Å in any other way. The calculated cell parameters at such pressures are consistent with expectations. The results of this experiment establish that (a) an iron oxide phase formed at the start of heating (Fig. 1, ~1200K), followed by iron hydride, and (b) both phases remained stable to 1500K (Fig.1).
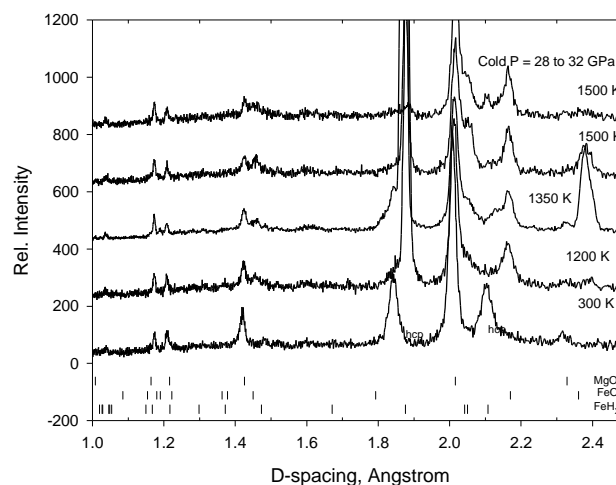

FIG. 1. Single-sided laser heating of iron, MgO, and water at GSECARS. The cold pressures are measured by using the equation of state of hcp iron and MgO. At the start of the experiment, hcp iron and MgO are at ~25 GPa. Upon heating to 1200K, iron peaks disappear, giving rise to some new peaks. The diffraction pattern has been analyzed with the TOPAS software for a three-phase assemblage consisting of hexagonal FeO and dhcp iron hydride and MgO (Table 1).
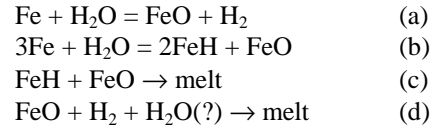
Table 1. Crystallographic fitted parameters.

MgO Spacegroup Fm-3m a = 4.03313 Å				dhcp Iron hydride Spacegroup P63/mmc a = 2.43393 Å c = 8.23280 Å				FeO Spacegroup P63/mmc a = 2.72630 Å c = 5.51184 Å			
h	k	l	d-space	h	k	l	d-space	h	k	l	d-space
1	1	1	2.32853	0	0	2	4.11640	1	0	0	2.36104
2	0	0	2.01656	1	0	0	2.10784	1	0	1	2.17031
2	2	0	1.42593	0	0	4	2.05820	1	0	2	1.79302
3	1	1	1.21603	1	0	1	2.04198	1	0	3	1.44999
2	2	2	1.16426	1	0	2	1.87618	0	0	4	1.37796
4	0	0	1.00828	1	0	3	1.67165	2	-1	0	1.36315
3	3	1	0.92526	1	0	4	1.47261	2	-1	2	1.22185
				0	0	6	1.37213	1	0	4	1.19010
				1	0	5	1.29759	2	0	0	1.18052
				2	-1	0	1.21696	2	0	1	1.15434
				2	-1	2	1.16703	2	0	2	1.08515
				1	0	6	1.14995	1	0	5	0.99886
				2	0	0	1.05392	2	0	3	0.99317
				2	-1	4	1.04755	2	-1	4	0.96909
				2	0	1	1.04539				
				0	0	8	1.02910				
				1	0	7	1.02705				
				2	0	2	1.02099				
				2	0	3	0.98386				
				2	0	4	0.93809				

A second set of experiments was carried out in a double-sided laser-heated cell. Brucite appears to form at 3.5 GPa but dissociates again to MgO and water (not observed) as the pressure increases to 40 GPa. In this experiment, we oxidized all iron at 1425K (Fig. 2), and no hydride phase was formed. Also, the refraction data matched the data of cubic FeO and not the hexagonal. The newly formed FeO, with possibly some MgO, melted between 1425 and 1525K. The inference regarding melting was based on an observation of vigorous reaction and convectional motion at the heated spot. When this starts to happen, the temperature cannot be increased, even at the maximum power of the laser, as would be typical of melting or another phase transition.

Discussion

The difference in the results of the two experiments may be related to (a) the nature of heating and (b) oxidation conditions. Single-sided laser heating may stress the sample, which may lead to the formation of hexagonal rather than cubic FeO. When water is mixed with MgO and iron, the composition of the starting mixture is not well determined. In the presence of water, we could consider the following reactions:

$$Fe + H_2O = FeO + H_2 \qquad (a)$$
$$3Fe + H_2O = 2FeH + FeO \qquad (b)$$
$$FeH + FeO \rightarrow melt \qquad (c)$$
$$FeO + H_2 + H_2O(?) \rightarrow melt \qquad (d)$$

If excess water is present, all iron may be oxidized without the formation of the hydride phase, which appears to be the case in the second experiment (Fig. 2). Since it is difficult to control the initial mixture composition of water and iron and the oxygen fugacity in a DAC, the results are expected to show considerable scatter on first appearance and melting of the reaction products. An important result of this study is that in the system Fe-FeO [9-12], melting temperature is significantly lowered by the addition of water.

As the iron hydride stability extends to high pressures (~30 GPa) and temperatures (~1500 K), the iron hydride could form in a primitive iron core and become a part of the melt if the temperature exceeded the melting temperature (~2000K) at the outer-core pressures.

Since the experiments were conducted in the presence of periclase (and wuestite [Fe_xO]), both of which show normal cell constants appropriate to the ambient pressure, it is obvious that the major part of the water does not remain in the oxide phases.
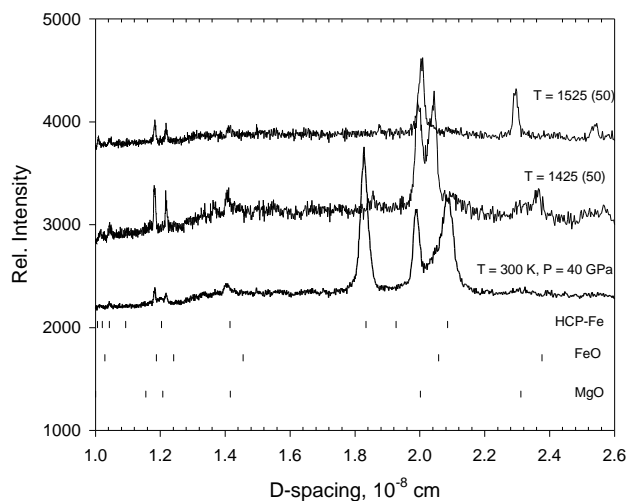
FIG. 2. Double-sided laser heating of iron, MgO, and water at a pressure of 40 GPa. Upon heating at 1425K, all iron disappears with the formation of an oxide mixture, with one phase being close to pure MgO (the pressure medium) and the other phase being FeO (with possibly some MgO, as estimated from the d-spacings). Upon further heating at 1525K, the iron oxide phase melts, and the peaks disappear. MgO, the pressure medium, remains with d-spacing that is indicative of a pressure of ~35 GPa after quenching.

We could not determine the influence of water on direct melting of iron because of the hydride and oxide reactions that preceded melting. In spite of this difficulty, we demonstrated the melting of wuestite or ferropericlase (a solid solution between periclase and wuestite) below 1525K in the presence of water. Wuestite is estimated to be present in abundance in the mantle. It could be an important constituent of the primitive Earth, formed by direct reaction between iron and water. Although from the experiment (Fig. 2), we could ascertain only that Fe was first oxidized and then melted, the experiment does give us an estimate of the possible effect of water on the melting of Fe. According to Boehler [13], dry Fe_xO melts at a temperature of ~2500K at a pressure of 35 GPa. Thus water may reduce the melting temperature of the pure phase by close to 1000K. If the melting temperature of iron is similarly reduced in a fluid-saturated system, the effect could be large. In a less saturated system, it may lower the melting by some hundred degrees Kelvin.

To summarize this work, then, the reaction of iron with water was studied to a pressure of 40 GPa and a temperature of ~1700K by using laser-heated DACs. Both wuestite and iron hydride exist stably under these conditions. They melt at temperatures of ~1500K and above. The results favor the dissolution of water in iron at high temperatures and pressures. The dissolved water components in the core would depress the melting temperature of iron (or iron-nickel alloy) significantly and reduce the density.

Acknowledgments

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