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The melting temperature of iron hydride at high pressures and its implications for the temperature of the Earth's core

Takuo Okuchi

Department of Earth and Planetary Sciences, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 465-8602, Japan

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Abstract. The Earth's core is about 10% less dense than pure iron under the relevant pressure and temperature conditions, so elements lighter than iron should exist in it. Recent experiments support the hypothesis that hydrogen dominates this light component. The hydrogen dissolved in metallic iron has a large potential to reduce its melting temperature. To estimate the melting temperature of the iron–hydrogen core, experiments were carried out at pressures up to 10 GPa by means of a new technique to determine the melting temperature and chemical composition from the textures of rapidly decompressed iron hydride grains. The rate of reduction of the melting temperature induced by adding hydrogen to iron was obtained as $(1.8 \pm 0.2) \times 10^3$ K per unit mole fraction. If this behaviour of hydrogen persists to the much higher pressure deep inside the Earth, the isentrope in the iron–hydrogen core is about 600 K lower than the previous estimates based on experiments on the iron–sulphur–oxygen system.

1. Introduction

The possible existence of the lightest element in the universe, hydrogen, in the deepest part of the Earth has been widely discussed during the last two decades [1–7]. Despite the experimental difficulties due to the rapid decomposition of the metallic alloy of iron and hydrogen under room conditions, the stability of solid crystalline iron hydride (FeH_x) at the high pressures relevant to the Earth's core is now firmly established through the experimental results from *in situ* x-ray diffraction techniques [5, 7, 8]. By means of *in situ* observations, the chemical composition and melting temperature of solid FeH_x were simultaneously measured at pressures up to 5 GPa [7]. However, diffraction measurements cannot be applied to investigate molten FeH_x itself, although it is the principal hydrogen-bearing phase within the Earth—rather than the solid FeH_x .

Recently, the stability and possible chemical composition of molten FeH_x in the Earth's core were determined through high-pressure quenching (not *in situ*) experiments by means of a rapid-decompression technique to catch the hydrogen as numerous bubbles before its escape from iron [9, 10]. This technique provides an alternative way to measure the chemical composition and melting temperature of FeH_x even after its decomposition into iron and hydrogen at room conditions, because the volume fraction and distribution of the hydrogen bubbles reflect these properties of the host FeH_x phases. In this study, therefore, the composition and melting temperature of FeH_x were examined at pressures up to 10 GPa by the rapid-decompression technique. The rate of reduction of the melting temperature induced by adding hydrogen to iron at various pressures was calculated. Using this rate, the melting temperature of the FeH_x core was estimated, to allow us to discuss the thermal state in the Earth's deep interior.

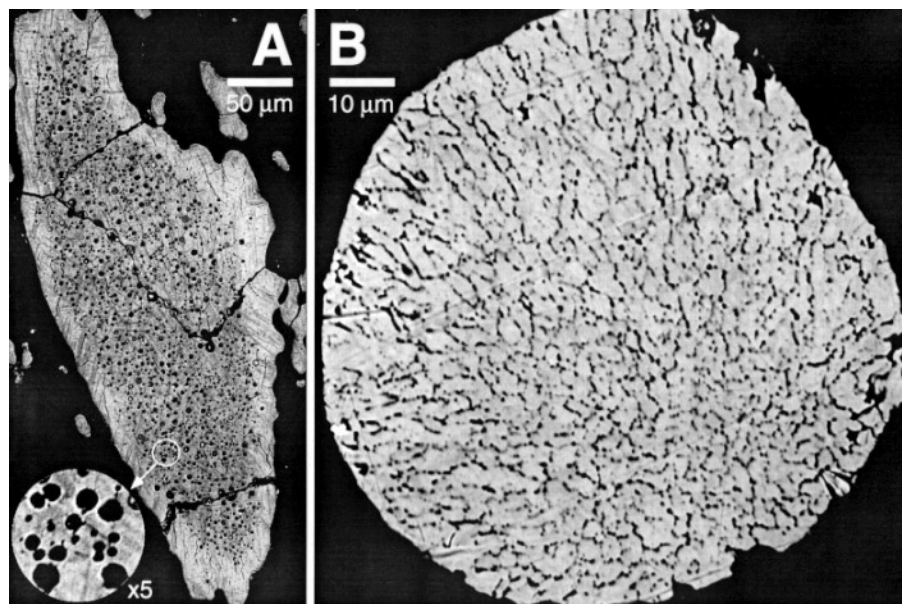


Figure 1. Back-scattered electron images of rapidly decompressed FeH_x grains in polished cross sections from the run at 7.5 GPa and 1200 °C. (A) Solid FeH_x . Because of the instant decompression, hydrogen became visible as numerous bubbles. (B) Molten FeH_x . The bubbles formed along the grain boundaries of the fine crystals. The melting of FeH_x was identified from this change in nucleation sites of H_2 .

2. Experimental procedure

All of the experiments were carried out using a uniaxial multi-anvil apparatus at Tokyo Institute of Technology [11]. The starting materials were prepared from mixtures of iron, brucite ($\text{Mg}(\text{OH})_2$) and silicic acid ($\text{SiO}_2 \cdot 0.4\text{H}_2\text{O}$) in the molar ratio of 2:1:1, and then sealed in Pt capsules of diameter 5 mm and 7 mm long. These large capsules were required to buffer the hydrogen pressure throughout the experiments. Despite the large size, temperature variations within the capsules were reduced to less than 100 K by thermal insulation [10].

The FeH_x was synthesized by electric heating at high pressures through the following iron–water reaction [3]:



The molar ratio of hydrogen to iron (x) in equation (2) depends on the pressure, temperature and activity of each component in equation (1) [9]. In previous high-pressure quenching experiments on FeH_x , this ratio could not be examined because hydrogen completely escaped from iron during decompression at a usual rate of several GPa h^{-1} [2]. The melting of FeH_x was identified only when the surrounding material was also molten; in this, ‘balls of iron’ were formed [4]. In the present experiments, the pressure was released rapidly (1.5 GPa s^{-1}) to produce numerous hydrogen bubbles in the iron grains (figure 1). The chemical composition of FeH_x was found by analysis from the volume fraction of these bubbles [9, 10]. Because of the difference in nucleation sites of H_2 between the solid and molten FeH_x phases, the melting of FeH_x was unambiguously identified even if the surrounding silicate material was not molten. Solid FeH_x is quenched without any

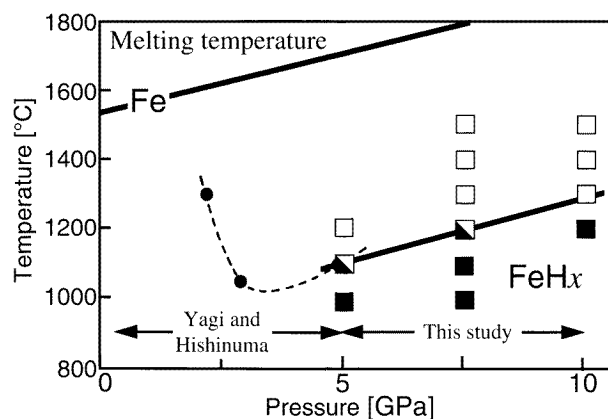


Figure 2. Run conditions and results of the melting experiments of FeH_x in the iron–silicate– H_2O system. Filled squares: solid FeH_x was synthesized. Half-filled squares: both solid and molten FeH_x were synthesized. Open squares: molten FeH_x was synthesized. The melting temperature determined from the *in situ* measurements [7] is shown with solid circles. These two types of result are in good agreement.

textural change, and the nucleation occurs homogeneously in the iron matrix. Molten FeH_x is quenched into an aggregate of fine crystals of solid FeH_x , and the nucleation occurs heterogeneously along the grain boundaries.

3. Results

Figure 2 shows the run conditions and results of the melting experiments on FeH_x . Those determined by the *in situ* measurements starting from the same iron–silicate– H_2O system are also shown for comparison [7]. The solid and molten FeH_x coexisted at 5.0 GPa and 1100 °C and at 7.5 GPa and 1200 °C. In these runs the solid and molten FeH_x should be on the solidus and liquidus of the Fe–H phase diagram [12]. At 10 GPa, all of the FeH_x grains synthesized were solid at 1200 °C and molten at 1300 °C.

The melting temperature of FeH_x is expected to decrease proportionally with its hydrogen concentration [12]. Table 1 shows the rate of reduction of the melting temperature with the change in chemical composition of the solid FeH_x on or near the solidus at each pressure used in the experiments. It was $(1.6\text{--}2.0) \times 10^3$ K per mole and not dependent on pressure within the experimental limits. Despite the variations in pressure, temperature and activity of H_2O , the solid FeH_x on its solidus synthesized by the iron–water reaction has a rather constant chemical composition of $\text{FeH}_{0.3\text{--}0.4}$ at pressures up to 10 GPa.

4. Discussion

The thermal structure deep inside the Earth is not well known despite its important implications for the dynamics and evolution of the solid Earth. The only constraint on this problem is that the inner-core boundary under the pressure of 330 GPa should be at the melting temperature of the core material. As for the widely proposed core composition of the iron–sulphur–oxygen system, the melting curve has been explored at pressures up to 200 GPa for iron and to 50 GPa for FeO and FeS by Boehler [13]. He discussed the feature that sulphur and oxygen do not reduce the melting temperature of iron much, so the inner-core boundary is just at the melting temperature of pure iron, which was estimated to be 4850 ± 200 °C. Assuming an adiabatic temperature gradient throughout the molten outer core, the top of the core was estimated to be at 3900 K, and the temperature gap across the core–mantle boundary, which is the principal parameter for the activity of the solid Earth

Table 1. The rate of reduction of the melting temperature induced by adding hydrogen to iron at various pressures ($-dT_m/dx$). The final column shows the reduction of the melting temperature induced by adding hydrogen to iron estimated for the composition of the inner core [9]. T_m^{Fe} : the melting temperature of pure Fe [14]. $T_m^{\text{FeH}_x}$: the observed melting temperature of FeH_x . x : the hydrogen/iron molar ratio of solid FeH_x on or near the solidus.

Pressure (GPa)	T_m^{Fe} (°C)	$T_m^{\text{FeH}_x}$ (°C)	x	$-dT_m/dx$	$\Delta T_m^{\text{FeH}_{0.34}}$ (K)	Reference
2.9	1640	1050	0.35	1.7×10^3	580	Yagi and
4.9 ^a	1710	1100	0.39	1.6×10^3	540	Hishinuma [7]
5.0 ^a	1710	1100	0.39	1.6×10^3	540	This study
7.5	1810	1200	0.33	1.8×10^3	610	
10.0	1900	1300	0.30 ^b	2.0×10^3	680	

^a The hydrogen density in the bubbles (figure 1) was estimated by comparing the results of these *in situ* and rapid-decompression runs under the same P - T conditions, assuming the samples of solid FeH_x synthesized in these runs to be identical in composition.

^b Estimated from the composition of molten FeH_x at 1300 °C with $D_{L/S}^{\text{H}} = 1.2$ [9].

for driving the mantle convection and the plate tectonics, was estimated to be 1300 K.

Hydrogen has been proposed as an important light element in the core [1–7], but the quantity of it that was transported to the core during the Earth’s formation was not investigated experimentally until very recently, due to the difficulties in handling molten FeH_x . Okuchi [9] showed that hydrogen transported to the molten iron during the core formation may reach $x = 0.41$ and that hydrogen in the inner core, once it begins to crystallize, may reach $x = 0.34$. This large amount of hydrogen may considerably reduce the melting temperature of iron at the inner core, although its existence was not considered by Boehler [13]. Table 1 shows that the melting temperature of iron decreases by about 600 K on adding 0.34 mol of hydrogen to iron. Then the temperature at the top of the core may decrease to about 3300 K, and the temperature gap across the core–mantle boundary also decreases, to only 700 K, which is almost a half of the previous estimate obtained without considering the effect of hydrogen. This reduction of the temperature gap suggests a much gentler image for the thermal activity of the solid Earth at present than that suggested by previous work.

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