論文の内容の要旨

論文題目

Hydrogen in the core

（地球中心核の水素）

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Birch[1] was the first to report that the Earth’s core seems to be lighter than pure iron. The density difference between pure iron at the core conditions and the seismically observed values is around 5–10% at the outer core and 3–5% at the inner core. This suggests that a certain amount of light elements should be contained in the Earth’s core. However, even though the significant effort has been spent for more than 65 years, the kind and amount of the light elements are still an open question. Based on observations from high-pressure mineral physics and cosmochemical / geochemical studies, H, C, O, Si, and S have been proposed for the candidates[2,3].

Hydrogen has recently attracted heightened attention, but the Fe-H alloys have been least investigated among the various alloys due to the experimental challenges. This is mainly because hydrogen quickly intrudes into diamond anvils during heating and then shatters them, and hydrogen escapes from iron under ambient conditions, which makes chemical analysis impossible. I overcame the difficulties by using technical improvements and thus performed the present work, in order to ascertain whether or not hydrogen is a major light element in the core. If hydrogen is the sole light element in the core, its amount is up to ~ 1 wt.%, corresponding to ~120 times the amount of seawater. Therefore, the hydrogen content in the core is key to understanding the building blocks of the Earth and its volatile content. This work comprises the following three viewpoints: partitioning experiments of hydrogen between liquid metal and liquid silicate under the core formation (*i.e.,* metal-silicate distribution) conditions (Chapter 2); phase relations of the Fe-H binary system (Chapter 3); and the compressibility of the *hcp* Fe-H-Si system (Chapter 4).

In Chapter 2, I investigated the partitioning experiments of hydrogen between molten iron and silicate melt under the Earth's core formation conditions. The highly siderophile nature of hydrogen was challenged by the most recent experiments[4,5]. High-pressure and -temperature experiments using a laser-heated diamond anvil cell (LH-DAC) was performed at 30–60 gigapascals (GPa) and 3100–4600 kelvin (K), corresponding to the conditions of single-core formation models. *In situ* X-ray diffraction (XRD) measurements and secondary ion mass spectrometry (SIMS) analyses demonstrate the high siderophile (iron-loving) nature of hydrogen even under such high pressures and temperatures (Figure 1). The hydrogen concentration in liquid metal was obtained based on the lattice volume of *fcc* FeHx, which is found after thermal quenching, and the proportions of FeHx and ε-FeOOH were estimated from electron microprobe analyses (EPMA). If core-forming metals were in equilibrium with the magma ocean, containing about 700 ppm H_2O before degassing the water that later formed oceans[6], the core might include 2900–5300 ppm H; this explains ~30–50% of the density deficit and the velocity excess of the outer core relative to pure iron. It also suggests that 25–66 times of the ocean's mass of water was delivered to the Earth by the time of core formation.

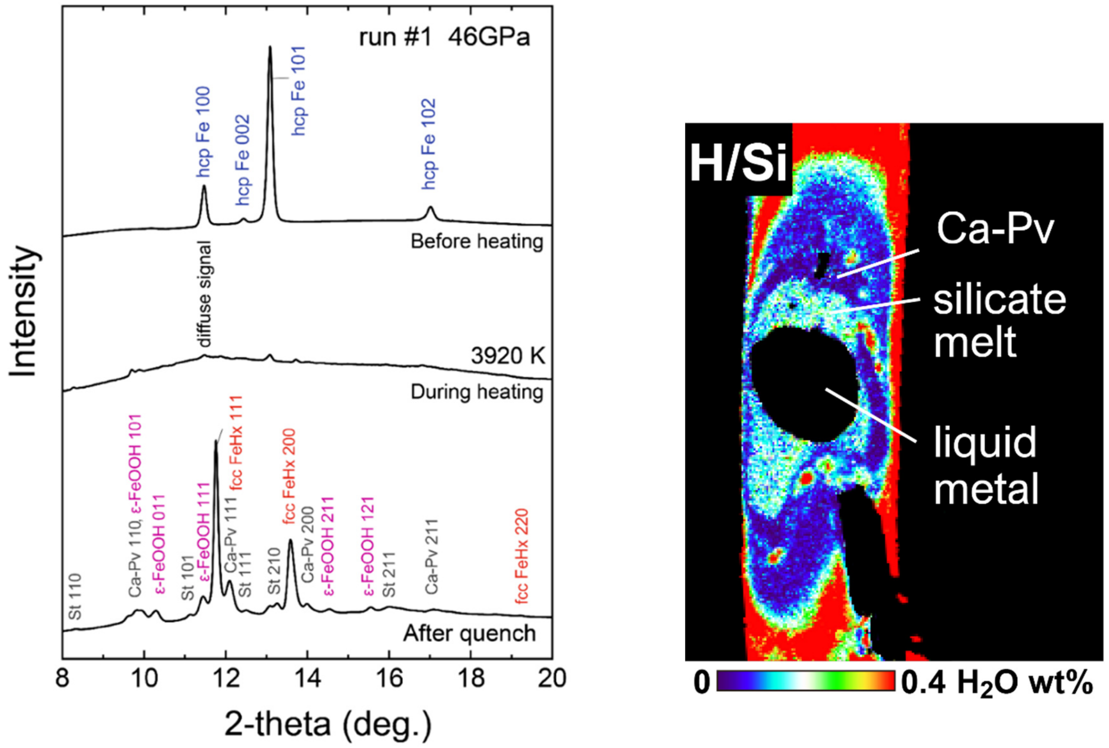
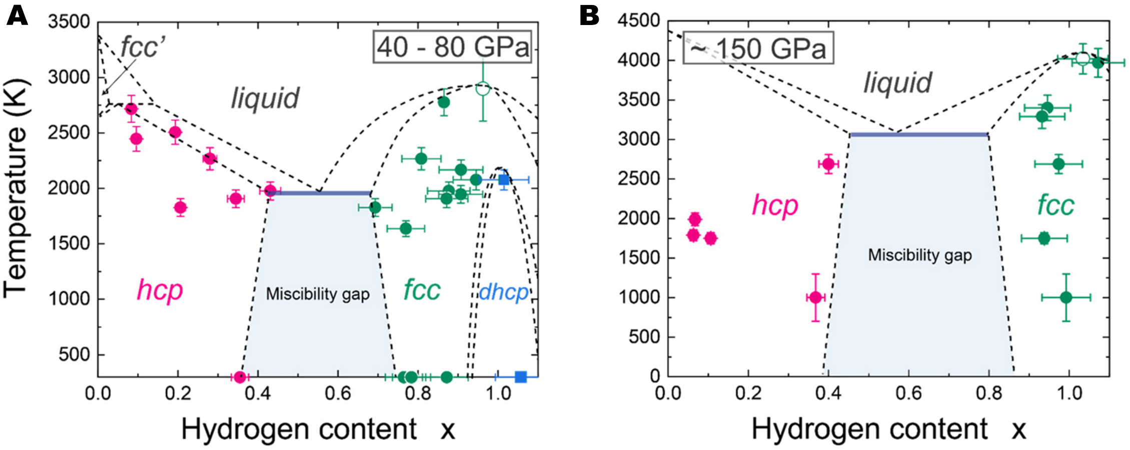


Figure 1. Analysis of hydrogen contents in metal and silicate. Left: XRD patterns collected before/during/after an experiment, which indicates that FeHx was synthesized in the partitioning experiment. Right: Distribution map of water in silicates. The hydrogen contents in metal and quenched silicate melt were 9390 ppm and 201 ppm, respectively. Combining these results, we found the partitioning coefficient of hydrogen was 47 ± 4 in this run, which shows the strong siderophile nature of hydrogen under the core formation conditions.

In Chapter 3, I reported the phase relations of the Fe-FeH binary system up to 173 GPa and 4020 K using an LH-DAC. Despite its importance, the phase diagram of Fe-FeH at over 20 GPa has not been clarified. It is widely accepted that the Fe-FeH system has a solid solution in the full region between Fe and FeH[7]. The concentration of hydrogen was denoted as a molar ratio of H/Fe, which is the definition of "x." I combined three cell assemblies: a sub-stoichiometric (x<1) experiment, a stoichiometric experiment (x=1), and an experiment in which hydrogen diffused in a Fe-H sample. I performed high-pressure and -temperature experiments for 11 runs. Then I determined the melting temperatures of stoichiometric FeH and sub-stoichiometric FeHx, and the stability field of each crystal structure. The resulting phase diagrams are shown in Figure 2. I found that the Fe-FeH system has a eutectic-type phase diagram, and the eutectic temperature would be sufficiently low to explain the low core-mantle boundary temperature inferred from the solidus temperature of pyrolite, although end-member *fcc* FeH had a high melting temperature. The miscibility gap of hydrogen contents between the subsolidus phases exists at least for $0.44 < x < 0.69$, and it implies that *hcp* FeHx is feasible as the inner core crystal structure if hydrogen is the dominant light element. Features of the phase diagram of the Fe-FeH system do not rule out the hydrogen in the core up to ~1 wt.%, which is almost the maximum estimated by the density of the FeHx under the outer core condition[8].



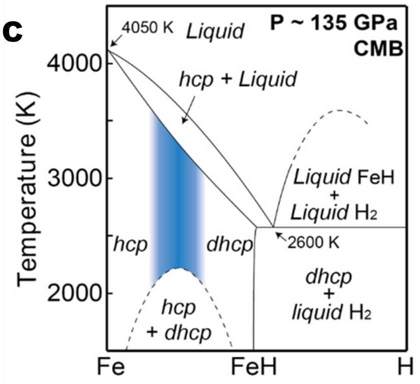


Figure 2. Temperature-x (hydrogen concentration) phase diagrams of the Fe-FeH binary system determined in this study (A, 40 – 80 GPa; B, around at 150 GPa) and expected in the previous study (C)[7]. Each plot indicates the stable phase observed at the conditions in the present work. The Fe-FeH binary system has a eutectic-type phase diagram, which is different from the complete solid solution type conventionally accepted.

In Chapter 4, I examined the compression behavior of hexagonal-close-packed (*hcp*) $(Fe_{0.88}Si_{0.12})_1H_{0.71}$ and $(Fe_{0.88}Si_{0.12})_1H_{0.97}$ (in the atomic ratio) alloys up to 130 GPa in a diamond-anvil cell (DAC). While contradicting experimental results were previously reported on the compression curve of *double-hcp* (*dhcp*) $FeH_{x\approx1}$, this study showed that the compressibility of *hcp* $Fe_{0.88}Si_{0.12}H_x$ alloys is very similar to those of *hcp* Fe and $Fe_{0.88}Si_{0.12}$, indicating that the incorporation of hydrogen into iron does not change its compression behavior remarkably. This data is also applicable to estimating the compressibility of *hcp* FeH_x. The calculated density profile of $Fe_{0.88}Si_{0.12}H_{0.26}$ matches the seismological observations of the outer core, supporting that hydrogen is a significant core light element (Figure 3). Besides, *hcp* $FeH_{0.30–0.37}$ well reconciles the density profile in the inner core.

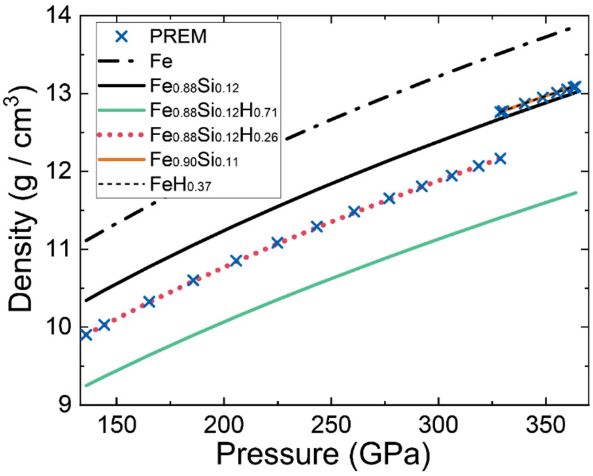


Figure 3. Comparison of the density of $Fe_{0.88}Si_{0.12}H_{0.26}$ alloy (red dotted curve) and related alloys along the isentropic temperature profile ($T_{ICB} = 5000$ K) with the PREM density (cross marks).

The present study enables us to sustain a comprehensive discussion about the feasibility of hydrogen in the core; this information was limited before this work. In the final chapter, I discuss the possible amount of hydrogen in the Earth's core. According to studies on other light element systems and this work, the core is likely to contain around 0.4 wt.% H, which explains ~40% of the outer core's density deficit. It is also consistent with geochemically-constrained core formation models. The hydrogen amount is comparable to 50 times the amount of seawater, and some recent planetary formation theories show that this is plausible. Although further investigation is needed, it is feasible that hydrogen is a major light element in the Earth's core.

References

[1]Birch, 1952. *J. Geophys. Res.*; [2]Hirose et al., 2013. *Annu. Rev. Earth Planet. Sci.*; [3]Li & Fei, 2014. *Treatise on Geochemistry*; [4] Clesi et al., 2018. *Sci. Adv.*; [5]Malavergne et al., 2019. *Icarus*; [6]Hirschmann, 2016. *Am. Mineral.*; [7]Fukai, 1992. *Geophysical Monograph Series.;* [8]Umemoto and Hirose, 2019. *Earth Planet. Sci. Lett.*