

Behavior of light elements in iron-silicate-water system under high pressure and high temperature condition (Proposal No. 2017B0064)

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1. Introduction

The Earth's outer core is considered to consist of Fe-Ni alloy and some light elements (O, S, Si, H, C). Hydrogen is the most abundant element in the solar system and one of the promising candidates existing in the Earth's core. However, the amount of hydrogen dissolved in the core and its process are still unknown because hydrogen cannot be detected by X-ray and it easily escapes from iron by the release of pressure. Recently, hydrogen content in *fcc*-Fe at high pressure and high temperature (high-PT) has been determined using *in-situ* neutron diffraction measurements at J-PARC [1,2]. It is suggested that the possibility that hydrogen had preferentially dissolved into iron before any other light elements have dissolved in the very early stage of Earth's evolution. It is important to further study the partitioning of the other light elements between iron hydride and silicates. In this proposal, we have focused on sulfur and investigated its effect on hydrogenation of iron by determining the amount of hydrogen in iron hydride using *in-situ* high-PT neutron diffraction observation techniques. The ultimate aim of this study is to clarify the effects of light elements on the core-mantle segregation in the Earth's formation.

[1] A. Machida, H. Saitoh, H. Sugimoto, T. Hattori, A. Sano-Furukawa, N. Endo, Y. Katayama, R. Iizuka, T. Sato, M. Matsuo, S. Orimo, K. Aoki, Nature Commun. 5, 5063 (2014).

[2] R. Iizuka-Oku, T. Yagi, H. Gotou, T. Okuchi, T. Hattori, A. Sano-Furukawa, Nature Commun. 8, 14096 (2017).

2. Experiment

As a starting material, Fe rod and powder mixture of quartz (SiO_2), brucite $\text{Mg}(\text{OH})_2$ (or MgO) and S (2:1:1 of molar ratio and 5wt.%S) were used. The sample composition simulates an ideal condition of the primitive Earth, Fe-enstatite silicate (MgSiO_3) system with/without water. High-PT experiments were carried out using a six-axis multi-anvil press "Atsuhime", which was installed at MLF, PLANET (BL11). A multi-anvil 6-6 type (MA6-6) assembly was used with an improved anvil assembly optimized for the neutron experiments [2]. Samples were pressurized up to 6–7 GPa (corresponding to 1200 kN of the applied load pressure) and then heated up to 700°C step by step. During heating, the reaction processes (dehydration of $\text{Mg}(\text{OH})_2$, phase transformations of Fe (*bcc-fcc*) and FeS, formation of silicates) were carefully check in real time. The diffraction patterns of *fcc*-Fe were measured at 550°C and 700°C for 10–12 hours. Pressures were calculated at intervals from the equation of state of NaCl as a pressure marker, which was placed close to the sample capsule. Temperatures were calculated by the relation between a Pt-Pt13Rh thermo-couple and the electrical power from the preliminary calibration test. The obtained data were analyzed using the Rietveld refinement method to determine structural and atomic parameters. All the recovered samples were examined by X-ray diffractometer with Position Sensitive Proportional Counter (PSPC) and a scanning electron microscope (SEM) - Energy Dispersive X-ray Spectroscopy (EDS) to more precisely identify the products (Fe, FeS, and silicates), their compositions, and the elements partition.

3. Results

In the beam-time, two experimental runs with different sample composition (with/without water) were performed under similar PT conditions. Figure 1 shows a representative neutron diffraction pattern of *fcc*-Fe in the system with water obtained at 6.6 GPa, 700°C. The volume changes in *fcc*-Fe were investigated for each one hour

during the long-time measurements at 550°C and 700°C as shown in Fig. 2. For the sample including water, the unit cell volume of *fcc*-Fe was significantly increased with time at 700°C but not at 550°C, whereas the sample without water showed no change regardless of temperatures. This suggested the deuterium (D) was gradually dissolved into Fe in the existence of water and iron deuteride (FeD_x) formed. However, its D content at 700°C was only $x \sim 0.04$ even after >10 hours, which was quite lower than that ($x \sim 0.17$) obtained by synchrotron XRD experiments, for which the powder sample was used. This D content was further small compared to the value ($x = 0.23$) obtained in our previous study on Fe-silicate- D_2O system [2]. The inhibition of deuteration on Fe-silicate- D_2O -S system was probably caused by the formation of FeS layer surrounding the Fe rod from the SEM images and elemental mapping as shown in Fig. 3. The large grains of Fe-rich olivine (Mg, Fe) $_2\text{SiO}_4$ were observed. On the other hand, the sample without water did not include FeS layer nor Fe-bearing silicates, suggesting that both S and Fe were not mobile and could not react with each other without the existence of water. Determination of x in FeD_x using the Rietveld analysis had some troubles in refining the diffraction intensities indicating that the obtained D content might be partly influenced by the preferred orientation of Fe rod. In the next experiments, Fe powder or heat-treated rods would be required as initial materials.

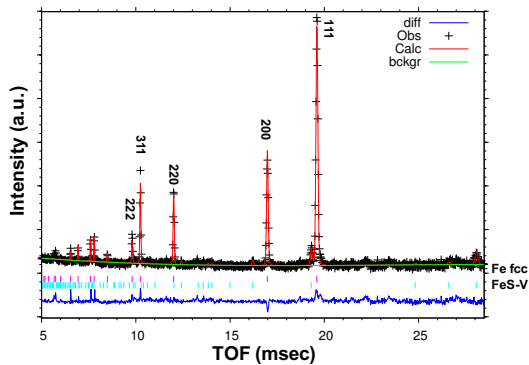
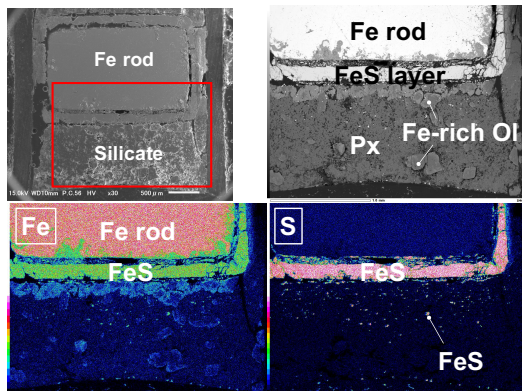


Fig. 1. Representative powder diffraction profile of *fcc*-Fe obtained at 6.6 GPa and 700°C in the run including water. The beam size was adjusted to get diffractions from only Fe rod using a four-quadrant slit (1w x 2h).



←Fig. 3. Results of SEM analysis on the recovered samples with water. Electron images with different magnification and elemental maps on Fe and S. A thin FeS layer was found on the surface of the Fe rod. Several silicates of Fe-rich olivine (Ol) and pyroxene (Px) were observed in the area where the powder mixture of $\text{Mg}(\text{OD})_2$ and SiO_2 , S was initially placed. Olivine containing rich Fe preferentially located close to the Fe rod.

4. Conclusion

The volume expansion of *fcc*-Fe was obviously observed only in the Fe-silicate- D_2O -S system, suggesting the formation of FeD_x and the increased D content even in the existence of the other light element, sulfur. However, the effect of sulfur on hydrogenation might be negative. Further improved study using *in-situ* high-PT neutron diffraction observations on samples with different initial compositions and experimental conditions could determine the amount of hydrogen dissolved into both solid Fe and FeS and reveal the detailed reaction process for the implication of the Earth's evolution. We are now preparing for the next beam-time (2018A).