

## Melting experiments on Fe–Fe<sub>3</sub>S system to 254 GPa

Sulfur has been considered to be an important light element in the Earth's core because of the low melting temperature of Fe–S alloys and its wide presence in iron meteorites [1]. Previous density measurements of liquid Fe–S alloys under high pressure demonstrated that the outer core density profile is explained by Fe containing 10 wt.% S. The melting phase relations in the Fe–FeS system, in particular at 330 GPa corresponding to the pressure at the solid/liquid core boundary, are of great importance, because the outer core liquid composition must be on the iron-rich side of the eutectic if sulfur is a predominant impurity element.

Fe and FeS exhibit a simple eutectic system at 1 bar, while intermediate compounds are formed at high pressures; Fe<sub>3</sub>S<sub>2</sub> above 14 GPa and Fe<sub>2</sub>S and Fe<sub>3</sub>S above 21 GPa [2]. Based on *in situ* X-ray diffraction (XRD) measurements in a laser-heated DAC, the eutectic temperature and composition in the Fe–Fe<sub>3</sub>S system have been previously determined up to 123 GPa [3]. However, they have not been examined at the core pressure range above 136 GPa yet.

Melting experiments were performed on the Fe–Fe<sub>3</sub>S binary system at high pressures between 34 and 254 GPa in a laser-heated diamond-anvil cell (DAC). We used starting materials of fine-grained homogeneous mixtures of Fe and FeS (<500 nm) prepared by induction melting and rapid quenching techniques. Melting phase relations and the liquid/solid partitioning of sulfur were examined on the basis of a combination between X-ray diffraction measurements at SPring-8 BL10XU and electron microprobe analyses on recovered samples. Angle-dispersive XRD spectra were collected on a flat panel detector (FPD) (Perkin Elmer) with typical exposure time of 1 s. Visible fluorescence light induced by X-rays in a diamond was used to precisely align the laser-heated spot with an X-ray beam.

First, we have examined subsolidus phase relations by XRD measurements before exploring melting phase relations. Using Fe + 5.9 wt% S starting material, four new peaks from the B2 (CsCl-type) structure appeared on heating to 2370 K at 270 GPa, in addition to the hexagonal-close-packed (hcp) phase (Fig. 1). The B2 structure indicates the ordering of sulfur atoms. When we further increased the temperature to 3570 K at 278 GPa, the Debye rings of both hcp Fe and B2 phases became spotty, indicating the grain growth and thus the stability of hcp + B2 at this *P-T* condition. The peaks from the B2 phase diminished, consistent with

an increase in sulfur concentration in solid Fe with increasing temperature under subsolidus conditions. The coexistence of the hcp and B2 phases suggests that the solubility of sulfur in hcp Fe is lower than the starting composition (5.9 ± 0.2 wt% S) at 278 GPa. These indicate that the system we examined in the present experiments is Fe–Fe<sub>3</sub>S binary only up to 254 GPa (see below).

Next, we performed ten separate melting experiments in a pressure range from 34 to 278 GPa. Melting of a sample was confirmed by a characteristic texture. A homogeneous portion with a non-stoichiometric composition was found at the center, the hottest part of a laser-heated sample, representing quenched liquid. Either solid Fe or Fe<sub>3</sub>S in direct contact with liquid alloys should represent a liquidus phase. Interestingly, we sometimes observed both Fe and Fe<sub>3</sub>S solids (see Fig. 2 for experiment at 254 GPa) in contact with liquid, indicating that it represents a eutectic liquid. Based on liquid compositions and coexisting solid phases, we constrain the eutectic liquid composition in the Fe–Fe<sub>3</sub>S binary system to 254 GPa (Fig. 3). The sulfur concentration in the eutectic liquid decreases substantially with increasing pressure; it contains only 5.7 wt.% S at 254 GPa. Our data also demonstrate that solubility of sulfur in solid

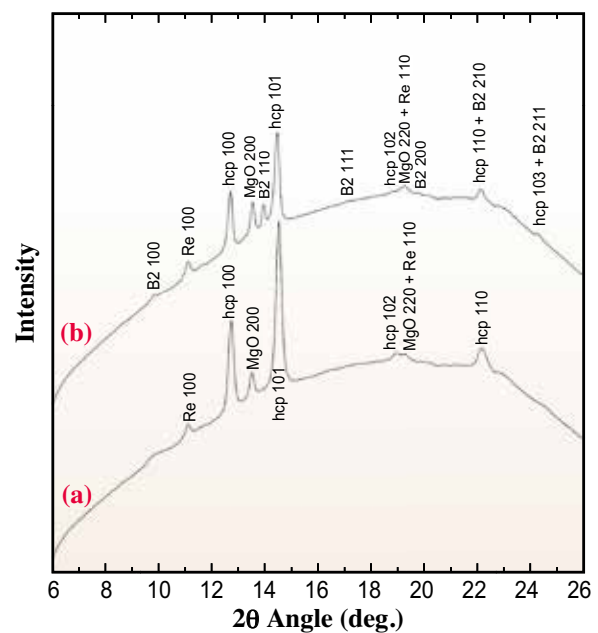
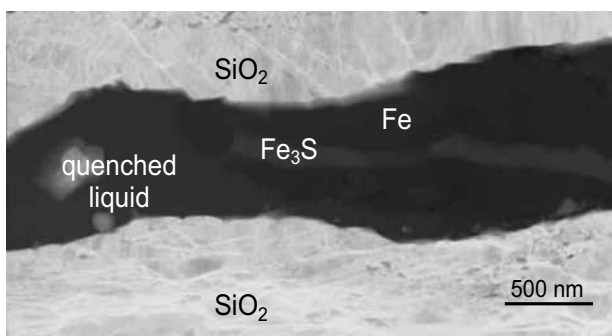


Fig. 1. XRD patterns of Fe + 5.9 wt% S (a) at 270 GPa and 300 K before heating and (b) during heating at 270 GPa and 2370 K.

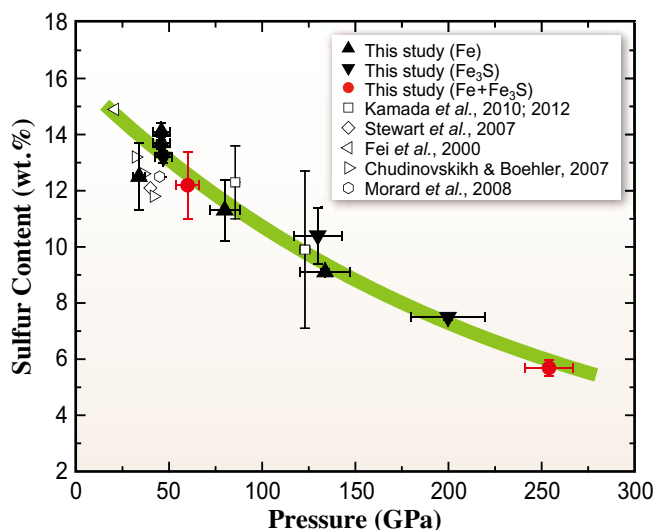


**Fig. 2.** STEM bright field image of the Fe+5.9 wt% S sample recovered from 254 GPa and 3550 K, showing the coexistence of liquid, solid Fe and Fe<sub>3</sub>S. The presence of SiO<sub>2</sub> crystals indicates that the liquid part was molten.

with that of Fe containing 10 to 14 wt.% S at relevant conditions. On the other hand, the present study demonstrates that the eutectic liquid in the Fe–Fe<sub>3</sub>S binary system includes only less than 6 wt.% S at 254 GPa, which should not be much different at 330 GPa, indicating that the liquid Fe with ≥10 wt.% S previously proposed for the outer core composition crystallizes the S-rich phase, Fe<sub>3</sub>S at least to 254 GPa and the CsCl (B2)-type phase at higher pressure including solid/liquid core boundary conditions. It suggests that crystallizing solid is less dense than coexisting liquid at the ICB, which is not consistent with seismic observations. Our experiments also show that liquid Fe + 5.7 wt.% S coexisted with hcp Fe containing 3.9 wt.% S at 254 GPa, showing a relatively small difference in sulfur concentration between coexisting liquid and solid at mid-outer core conditions. The sulfur contents in coexisting liquid and solid will be even closer at the solid/liquid core boundary. The density jump across the solid/liquid core boundary is not reconciled with such a small difference in impurity concentration in addition to the difference in density between solid and liquid. These indicate that sulfur is not a predominant light element in the core, although it could still be one of the alloying components.

iron is enhanced at higher pressures. It increases from <2 wt% S below 50 GPa to 3.4 ± 0.4 wt% S at 80 GPa. The present experiments further show that solid iron coexisting with eutectic liquid includes 3.9 ± 0.4 wt% S at 254 GPa.

Previous studies suggested that seismologically-deduced liquid outer core density profile is consistent



**Fig. 3.** Liquid compositions plotted as a function of pressure. Sulfur concentrations in eutectic liquids should be more or less than those when coexisting with Fe or Fe<sub>3</sub>S, respectively. The change in eutectic composition in the Fe–Fe<sub>3</sub>S system is shown by green curve. Liquid compositions obtained in this study are shown by triangles when coexisting with solid Fe, inverse triangles when in contact with Fe<sub>3</sub>S, and red circles when both were found.

Kei Hirose<sup>a,b</sup>

<sup>a</sup> Earth-Life Science Institute, Tokyo Institute of Technology

<sup>b</sup> Department of Earth and Planetary Science, The University of Tokyo

Email: kei@elsi.jp

**References**

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