

Decomposition of Fe₃S above 250 GPa

The Earth's core includes substantial amounts of light elements in addition to iron and nickel. Sulfur is one of the candidates for such a light element. A phase diagram of the Fe–FeS system, particularly for the high-pressure and high-temperature (*P-T*) conditions of the core, is needed to understand the composition and state of the Earth's core. Fe and FeS exhibit a simple binary eutectic system at ambient pressure. Previous experimental studies revealed the formation of the intermediate compounds Fe₃S₂, Fe₂S, and Fe₃S at high pressures [1]. Earlier experiments showed that tetragonal Fe₃S, known as the most iron-rich Fe–S compound, is stable at least up to 220 GPa and 3300 K [2]. In contrast, theoretical calculations predicted a continuous solid solution between Fe and FeS under inner core boundary (ICB) conditions [3]. In this study [4], we examine the subsolidus phase relations of iron–sulfur alloys up to 271 GPa by a combination of *in situ* synchrotron X-ray diffraction (XRD) measurements and chemical analyses on recovered samples.

All high *P-T* experiments were conducted at beamline **BL10XU**. High *P-T* conditions were generated in a laser-heated diamond-anvil cell (DAC). We prepared the starting materials by mixing FeS powder and metallic iron. In addition, the high-pressure Fe₃S phase was used as the starting material in run #2. The samples were heated with a couple of 100 W single-mode Yb fiber lasers by a double-side heating technique. The temperature was measured by using a spectroradiometric method. Angle-dispersive XRD spectra were collected on a charge-coupled device or an imaging plate detector. A monochromatic incident X-ray beam with a wavelength of 0.41332–0.42342 Å was collimated to approximately 6 μm (full width at half maximum). In addition to the XRD measurements, chemical analyses were also carried out on samples recovered from runs #1 and #2, using an analytical transmission electron microscope.

Five separate sets of experiments were conducted at pressures between 226 and 271 GPa and temperatures up to 3100 K. In the first set of experiments with Fe (+20 atm% S), the starting material was initially compressed to 238 GPa at room temperature. Broad diffraction peaks from hcp Fe, B2-FeS, and rhenium were observed before heating (Fig. 1(a)). We subsequently heated the sample to 2510 K at 241 GPa and observed the appearance of Fe₃S diffraction peaks [1] (Fig. 1(b)). The Fe₃S peak intensities increased at 2130 K and 226 GPa,

indicating its stability under these *P-T* conditions. Chemical analyses also indicated the presence of Fe₃S in the recovered sample. In the second run, we used the tetragonal Fe₃S phase as the starting material. It was compressed in the DAC and heated to 2530 K at 271 GPa for 3 h. The XRD pattern obtained before heating showed only MgO peaks; however, two weak reflections appeared at *d* = 1.70 and 1.65 Å, which can be attributed to the B2 110 and hcp 101 peaks. The chemical analysis suggests the coexistence of sulfur-rich and sulfur-poor particles (Fig. 2), which most likely correspond to the B2 and hcp phases, respectively, as observed in the XRD pattern. Point analyses suggest

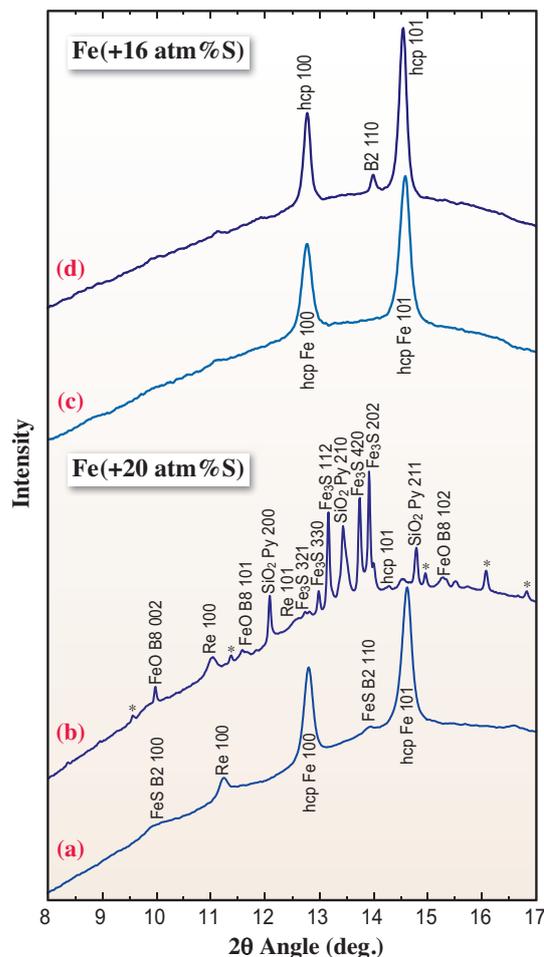


Fig. 1. XRD patterns (a) at 238 GPa and 300 K before heating and (b) after heating at 236 GPa and 2980 K in the first run, and at (c) 259 GPa and 300 K before heating and (d) 269 GPa and 2700 K in the fourth run. Peak broadening due to nonhydrostatic stress before heating and the smaller amount of FeS likely resulted in the absence of peaks from FeS in (c). SiO₂ Py stands for the pyrite-type SiO₂ insulation material and Re for the rhenium gasket. The peaks marked with an asterisk are likely from the Fe₂S phase.

a lower limit of 33.5 atm% S for the S-rich phase and an upper limit of 12.4 atm% S for the S-poor phase. These results clearly indicate the decomposition of Fe₃S into two phases. In run #3, the Fe (+20 atm% S) sample was squeezed to 255 GPa and subsequently heated. Whereas only diffraction peaks of hcp Fe were observed before heating, two new peaks appeared upon heating to 3100 K at 251 GPa and were assigned to the 100 and 110 lines of the B2 structure. In addition, the spots appeared on the Debye rings of hcp iron, indicating grain growth and thus the stability of hcp under this *P-T* condition. In the fourth set of experiments with the Fe (+16 atm% S), the sample was first compressed to 259 GPa at 300 K (Fig. 1(c)). On subsequent heating, the diffraction lines from hcp became sharper, and the B2 110 peak appeared at 2540 K and 264 GPa and further grew at 2700 K and 269 GPa (Fig. 1(d)). Similarly, in the fifth run using the Fe (+10 atm% S) sample, we originally compressed it to 268 GPa at 300 K. The B2 110 peak appeared during heating to 1630 K at 267 GPa. These results are summarized in Fig. 3.

The coexistence of hcp Fe and Fe₃P-type Fe₃S was previously reported at 220 GPa and 3300 K [2]. In agreement with the earlier experiments, we observed the formation of Fe₃S from a mixture of Fe and FeS up to 241 GPa and 2510 K (Fig. 3). On the other hand, the Fe₃S starting material decomposed into Fe-rich and Fe-poor phases at 271 GPa and 2530 K (Fig. 2). Furthermore, the XRD measurements in this study repeatedly confirmed that tetragonal Fe₃S did not form, and alternatively, hcp Fe and B2 coexisted above 251 GPa and 3000 K (Fig. 3). Previous first-principles calculations [3] predicted that Fe and FeS exhibit a continuous solid solution at ICB pressures, and that coexisting solid and liquid contain very similar

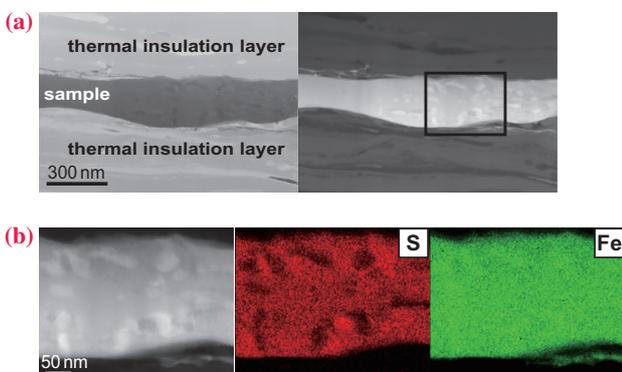


Fig. 2. (a) STEM bright-field (left) and dark-field (right) images of the recovered sample in the second run. In the bright-field image, the light domains represent the thermal insulation layers, which consist of SiO₂ and MgO, and the dark region shows the assemblage of the iron-sulfur alloys. The dark-field image gives the atomic number contrast (*Z*); the bright areas correspond to high *Z* values. (b) Magnified image of the boxed area in (a) (left). Sulfur (middle) and iron (right) maps in the same area.

amounts of sulfur. This suggests that the observed density jump across the ICB cannot be reconciled with the difference in sulfur content between the inner and outer core; therefore, sulfur is not likely the predominant light element in the core. However, we have demonstrated that the compositional range of the solid solution is limited at 271 GPa and 2530 K, where Fe₃S decomposes into mixed phases. Recent laser-heated DAC experiments have revealed that both Fe and Fe (+10% Ni) alloy adopt the hcp structure under inner core *P-T* conditions. However, theoretical calculations suggested that a small amount of sulfur impurity in iron stabilizes the bcc rather than the hcp structure under the inner core conditions. The present experimental results suggest that the hcp phase forms in the S-bearing system at 2700 K and 269 GPa.

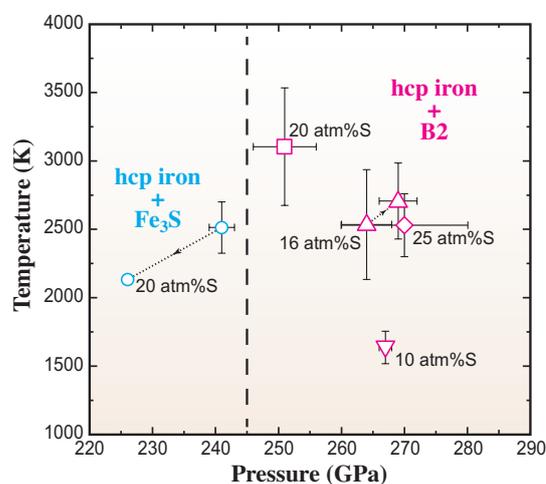


Fig. 3. Experimental conditions and results. Blue and red symbols represent the stabilities of the hcp and Fe₃S, and hcp and B2 phases, respectively. The sequential changes in *P-T* conditions are illustrated by the arrows. The starting bulk compositions are indicated by the numbers: run #1 (circles); run #2 (diamonds); run #3 (squares); run #4 (triangles); and run #5 (downward triangle).

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