Fe₂S: the most iron-rich Fe-S compound at pressures of the inner core

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Sulfur is considered to be one of the light elements in the Earth's core as iron sulfides are universally found in iron meteorites. The phase diagram of the Fe–FeS system at the high-pressure and high-temperature (P-T) conditions of the core has particular importance to understand the composition and state of the Earth's core. Because Fe3S is known as the most iron-rich Fe–S compound at > 20 GPa, the iron-sulfur core model has been discussed considering Fe and Fe₃S in the solid core. However, our previous experiment reveals that Fe₃S decomposes into S-bearing hcp-Fe and CsCl (B2)-type phase above \sim 250 GPa from X-ray diffraction measurements (XRD) (Ozawa et al., 2013 GRL). Furthermore, TEM analysis on the recovered sample exhibits that S-poor phase, likely to be a former hcp-Fe, coexisted with S-rich phase with >33.5 atm% S. Hence, the S-rich end-member compound has not been constrained under pressure more than 250 GPa. In order to re-investigated the phase relations in Fe-FeS system, we studied phase relations in Fe₂S at multi-megabar pressure range.

High P-T conditions were generated in a laser-heated diamond-anvil cell (DAC) using double-beveled diamond anvils with 40 or 60 μ m culets. We used the Fe₂S phase as the starting material, which was synthesized beforehand at high pressures in a multianvil apparatus and confirmed by microprobe analysis. SiO₂ glass and MgO were used for thermal insulation and pressure calibration. We loaded such sample assembly as MgO/SiO₂-glass/Fe₂S/SiO₂-glass so that MgO was detached from an iron sample, in order to avoid possible chemical reaction at high temperature. Angle-dispersive XRD measurements were conducted at BL10XU, SPring-8. Heating was performed from both sides of the sample by employing a pair of 100 W Yb fiber lasers.

We performed three separate sets of experiments at pressures between from 120-310 GPa and temperature up to 3000 K. When we heated the Fe_2S sample being mostly amorphous by compression to 300 GPa at 300 K, the 20 new peaks appeared in a few minutes and became spotty with further heating. All peaks are assigned to the orthorhombic structure, which agrees well with Pnma symmetry phase proposed by the theoretical prediction (Bazhanova et al., 2017). This observation indicates that Fe_2S composition crystallizes as a single phase. In the following decompression and re-heating the sample, its stability was confirmed to be 150-310 GPa.

Our previous study (Mori et al., 2017 EPSL) reported that hcp-Fe and B2 phase crystallizes in Fe-6wt% S bulk composition at 270 GPa and 2400 K. Then, the peaks from the B2 phase become weak at further hearting. We re-analyzed the series of XRD datum, and found that such apparent weakening was caused due to the appearance of Fe₂S phase. Indeed, in the XRD patten collected at 3500 K, we confirmed that additional weak peaks from Pnma-Fe₂S were clearly visible and the reflection from the coexisting hcp-Fe phase became intense simultaneously. This indicates that stable phase assemblage in Fe-6wt% S bulk composition changes from hcp-Fe + B2-FeS into hcp-Fe + Pnma-Fe₂S. Hence, Fe₂S is the sulfur-rich end-member compound after the decomposition of Fe₃S at 250 GPa. The slope of eutectic melting curve should have kink at the decomposition of Fe₃S. Also, pressure evolution of the eutectic composition should change as well. Since the extrapolation from lower pressure data <250 GPa is not available, higher P-T experiments are necessary to establish the phase diagram at the pressure of inner core boundary.

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