

DENSITY MEASUREMENTS OF IRON-SULFUR COMPOUNDS AT HIGH PRESSURES AND TEMPERATURES: IMPLICATIONS FOR THE CORES OF TERRESTRIAL PLANETS. Mark R. Frank¹, Yingwei Fei¹, Heather C. Watson^{1,2} and Vitali Prakapenka³ (Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd., Washington DC, 20015; m.frank@gl.ciw.edu), ²(Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, 110 Eighth St., Troy NY, 12180), ³(Argonne National Lab Building 434A, APS, 9700 S.Cass Ave, Argonne, IL 60439)

Introduction: It has long been hypothesized that iron and sulfur are important contributors to the cores of terrestrial planets such as Earth and Mars [1, 2]. Compositional models, based on elemental trends observed in SNC meteorites, suggest that the core of Mars may contain a significant component of sulfur (> 10 wt.%; [3]). Further, the dearth of high-pressure data in the Fe-S system required that Fe and FeS be considered end-member compositions. Recent high-pressure experiments conducted using a multi-anvil apparatus were able to determine the presence of high-pressure iron-sulfur compounds at 14 and 21 GPa, respectively [4, 5]. The melting relations and bulk mineralogy in the Fe-FeS system at 21 GPa were outlined for temperatures ranging from 950-1400°C (Fei et al., 2000). These high-pressure experiments revealed that at least three new iron-sulfur compounds, Fe₃S₂, Fe₂S, and Fe₃S, were formed at high pressures.

The possible presence of light elements in the cores of terrestrial planets requires that the properties of high-pressure Fe-S compounds be well understood [6]. Specifically, Fe₃S is important because it is the sulfur-bearing component that will be in equilibrium with metallic Fe for cores with sulfur concentrations <16.1 wt.%. To date, only the structure and pressure-density relation of Fe₃S have been determined at 300 K [5]. A recent study noted that Fe₃S is the only quenchable phase in the system, whereas Fe₃S₂ and Fe₂S were unstable at ambient conditions [7]. The absence of structure and pressure-density data for the Fe₃S₂ and Fe₂S phases, plus the lack of any data for the three phases at elevated temperatures and pressures limits the ability to model accurately the density profile of a sulfur-bearing iron core. Therefore, it is essential to determine the properties of these phases at elevated temperatures and pressures to place constraints on models of terrestrial core formation.

Experimental Procedures: Although Fe₃S₂ and Fe₂S are not quenchable, samples with their bulk mineralogy were synthesized in a multi-anvil apparatus at 25 GPa and 1220 and 1370 K, respectively. The synthesized starting compositions were compressed in a Mao-Bell type diamond anvil cell with flat anvils (300 microns). Rhenium gaskets were pre-indented to ~25 GPa and 70-150 micron holes were drilled in the compressed regions by using an erosion drill. The Fe-S starting material and gold (internal pressure calibrant) were loaded into the sample chamber.

High temperatures were obtained using a small Mo-wire resistance heater placed around the diamond anvils in addition to a Ni_{0.8}Cr_{0.2} heater placed around the body of the cell. The temperature of the experiment was monitored by placing a Pt-Pt_{0.9}Rh_{0.1} thermocouple between the diamond anvil and Re-gasket, directly against the surface of the diamond. Temperatures were kept constant to ±3 K during data collection, whereas the uncertainty associated with the thermocouple itself is ±2 K over the range of temperatures in this study.

Synchrotron radiation was used to monitor the unit cells of Fe₃S₂, Fe₂S, Fe₃S and gold. The experiments were conducted at the Advanced Photon Source, GSECARS 13-ID-D beamline, by using the on-line imaging plate system. Data were analyzed using the FIT2D software [8]. CeO₂ was used to calibrate the sample to detector distance, coordinates of the directed beam on the detector, and the angle and tilt of the detector. The unit cell of gold determined from the diffraction lines was used in conjunction with a previously established *PVT* equation of state [9] to calculate the experimental pressure.

Results: X-ray diffraction data were collected from 300 to 1000 K at pressures > 16 GPa. Table 1 lists the experimental pressures and temperatures at which the diffraction data were collected for Fe₃S and Fe₂S. The data presented here will concentrate on the properties of Fe₃S.

Table 1. Pressures, temperatures and phases present in the experiments.

Temperature (K)	Pressure (GPa)	Phases
300	19	Fe ₃ S + Fe ₂ S
300	23	Fe ₃ S + Fe ₂ S
300	30	Fe ₃ S + Fe ₂ S
450	26	Fe ₃ S + Fe ₂ S
700	21	Fe ₃ S + Fe ₂ S
700	28	Fe ₃ S + Fe ₂ S
800	20	Fe ₃ S + Fe ₂ S
850	21	Fe ₃ S + Fe ₂ S
900	16	Fe ₃ S + Fe ₂ S
900	28	Fe ₃ S + Fe ₂ S
950	16	Fe ₃ S + Fe ₂ S
950	22	Fe ₃ S + Fe ₂ S
1000	19	Fe ₃ S + Fe ₂ S

Some typical X-ray data, presented as a function of 2 theta, are displayed in Figure 1. Generally, the spectra would sharpen as temperature was increased, however, no new phases were observed over the range of conditions in this study. Fe₃S was found to be isostructural with Fe₃P (space group $I\bar{4}$) confirming the work of others [5, 7].

The unit cell dimensions of Fe₃S were calculated from the 321, 330, 141, and 420 diffraction lines. Our results are generally consistent with those of previous studies [5, 7] at 300 K. Preliminary data analysis indicates that thermal expansion of the Fe₃S phase is broadly consistent with that of similar compounds. Our results suggest that the volume of Fe₃S at 1000 and 19 GPa is ~6% greater than the volume at 300 K and equivalent pressure.

An extensive data set on the density-temperature-pressure relations of the Fe₃S phase will be presented. Previous models of sulfur-bearing cores used FeS as an end-member to estimate the density of the Martian core [6]. The density of the Martian core should be modeled using Fe₃S as an end-member in light of the finding of these new Fe-S compounds at high pressures. Our results present the first data on Fe₃S at elevated pressures and temperatures and should provide for more accurate density models for the Martian core.

Conclusions: We conducted experiments in the Fe-S system at elevated pressures and temperatures to evaluate the pressure-temperature-volume relations of Fe₃S. Fe₃S is the sulfur-bearing end-member phase in the iron-rich regime of the Fe-S system at high pressures. We provided new density data of Fe₃S that are applicable to density models of the Martian core. Thus, previous models of core formation that used FeS as an end-member should be reevaluated using the data presented here.

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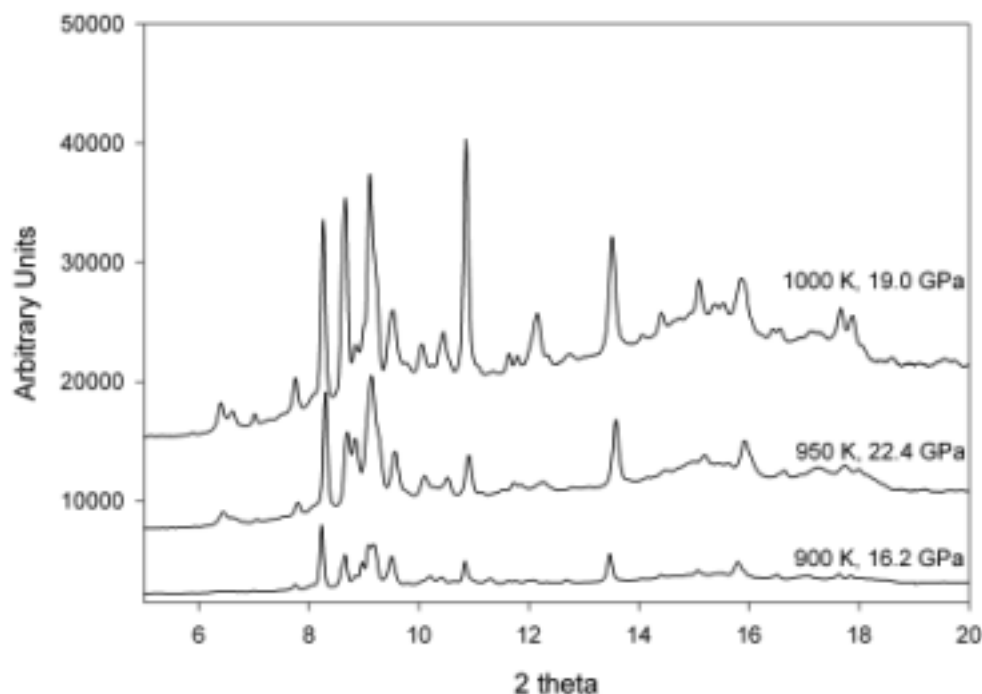


Figure 1. Representative X-ray diffraction patterns of Fe₃S + Fe₂S samples with gold as an internal pressure calibrant.