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Fe₅S₂ identified as a host for sulfur in Earth's core

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Abstract

Planetary habitability, as we experience on Earth, is linked to a functioning geodynamo which is in part driven by the crystallization of the liquid iron-nickel-alloy core as a planet cools over time. Cosmochemical considerations suggest that sulfur is a candidate light alloying element in rocky planetary cores of varying sizes and oxidation states; such that, iron sulfide phase relations at extreme conditions contribute to outer core thermochemical convection and inner core crystallization of a wide range of planetary bodies. Here we experimentally investigate the structural properties of the Fe-S system and report the discovery of the sulfide, Fe₅S₂, crystallizing in equilibrium with iron at Earth's outer core pressures and high temperatures. Using single-crystal X-ray diffraction techniques, Fe₅S₂ was determined to adopt the complex Ni₅As₂-type structure ($P6_3cm$, $Z = 6$). These results conclude that Fe₅S₂ is likely to crystallize at the interface of Earth's core and mantle and will begin to crystallize during the freezing out of Earth and Venus' core overtime. The increased metal-metal bonding measured in Fe₅S₂ compared to the other high P - T iron sulfides may contribute to signatures of higher conductivity from regions of Fe₅S₂ is crystallization. Fe₅S₂ could serve as a host for Ni and Si as has been

observed in the related meteoritic phase, perryite, $(\text{Fe, Ni})_8(\text{P, Si})_3$, adding intricacies to elemental partitioning during inner core crystallization. The stability of Fe_5S_2 presented here is key to understanding the role of sulfur in the multicomponent crystallization sequences that drive the geodynamics and dictate the structures of Earth and rocky planetary cores.

Introduction

Earth and the other terrestrial planets along with rocky exoplanets that continue to be discovered are composed of silicate mantles and iron-rich metallic cores (e.g. Birch 1952; Scott and Wasson 1975; Jephcoat and Olsen 1987; McDonough and Sun 1995; Rubie et al. 2011). The likelihood of planetary habitability as we know it demands the presence of a geomagnetic field, sustained by a convecting metallic liquid core, that protects the planet from harmful cosmic rays (e.g. Buffett, 2000). In Earth's liquid outer core, the presence of light alloying elements introduces complex pressure-temperature-dependent melting and crystallization thermodynamics that drives core convection (Fearn and Loper, 1981; Stevenson 1981; 1988; Nimmo 2015). While there remains no method to directly sample Earth's or any terrestrial planetary core, iron meteorites are recognized as relics of the cores of planetesimal building blocks of terrestrial planets, and have long provided insight into the cosmochemically abundant light elements contributing to planetary core dynamics (e.g. Scott and Wasson 1975; Malvin et al. 1984). Of the candidate core-alloying elements such as Si, O, S, C, and H, sulfur is present in nearly all iron meteorites, suggesting that sulfur is a core alloying element in rocky planets with varying sizes, oxidation states, and formation histories (Scott and Wasson 1975; Jones and Drake, 1983; Kruijer et al. 2014). Examination of the structural properties of iron sulfides at high pressures

and temperatures (P - T) is therefore critical to ascertaining the chemistry and thermodynamics of Earth, terrestrial and exoplanetary cores.

At present, the crystallographic assessment of iron sulfides at Earth and planetary core conditions remains limited, even though properties such as density and elasticity are directly related to the atomic arrangement of core-crystallizing phases and are critical for assessing the seismic and dynamic observations of planetary cores. Previous work on Fe-rich systems indicate that tetragonal Fe_3S (Fe_3P -type structure) is stable from Martian core conditions to Earth's outer core conditions (Fei et al. 2000; Kamada et al. 2010; Ozawa et al. 2013; Mori et al. 2017), and an orthorhombic Fe_2S (Co_2Si -type structure) phase becomes stable near Earth's inner-core boundary (ICB) conditions (Tateno et al. 2019). The presence of Si has also been observed to stabilize the $\text{Fe}_2(\text{S}, \text{Si})$ chemistry over Fe_3S at Mercurian core-mantle-boundary (CMB) conditions (Tao and Fei 2021). These reports were predominantly based powder X-ray diffraction studies at high pressures and temperatures and chemical analyses of recovered samples. However, recent work has demonstrated that the iron-sulfur phase diagram is more complex at high P - T , but that this complexity requires a superior method for accurately characterizing crystal structures at extreme conditions. Using single-crystal X-ray diffraction techniques on multigrain samples, Co_2P -type Fe_2S ($Pnma$, $Z = 4$) was recently identified and characterized at 90 GPa (Zurkowski et al. *in press*). It remains, however, that these methods have not been applied to iron-sulfide phases synthesized at high temperatures above 90 GPa, leaving the role of sulfur in the crystallization sequences occurring in Venus, Earth and larger rocky exoplanets open to further discovery.

Results and Discussion

In the current study, Fe-rich Fe-S compositions were probed using both single-crystal and powder X-ray diffraction techniques in a laser-heated diamond anvil cell to 200 GPa and 3300 K. At high temperatures between 120 and 200 GPa, spanning Earth's CMB to mid-outer-core conditions, crystallization of hcp-Fe (Figure 1a) is observed in the diffraction patterns along with diffuse streaks and sets of closely spaced reciprocal nodes (Figure 1a, Figure S1), suggesting a complex atomic arrangement of the coexisting sulfide. Upon temperature quenching in this pressure range, diffraction images were collected while rotating the DAC across a +/- 17–30° range (depending on the DAC configuration). Grains of a hexagonal lattice were identified in the reciprocal space with indexed parameters: $a = 5.979(3) \text{ \AA}$, $11.088(6) \text{ \AA}$ at 140(2) GPa and 3070(180) K (Table S1). Assessment of the systematic absences for the structure factors reduced for this hexagonal sulfide suggests a $P6_3cm$ space group, and structural solution and positional and displacement parameter refinement converged to the Ni_5As_2 -type Fe_5S_2 ($Z=6$) (Table S2, S3; Figure 2) (Oryshchyn et al. 2011). The Ni_5As_2 -type Fe_5S_2 is derived from the Pb_5Sb_2 structure (El-Boragy et al. 1970) where the Fe6 site (Table S3) is split about its position and given half occupancy, changing its Wyckoff site from $6c$ to $12d$ (Oryshchyn et al. 2011) (Figure 2, Table S3, Appendix A1). Within error, all sites are fully occupied, except the Fe6 site that is ascribed half occupancy (Oryshchyn et al. 2011).

Additionally, two polytypes associated with stacking variations along the c direction were measured at lower temperatures and in stiff pressure media (Table S1). The Fe_5S_2 polytypism is accompanied by observations of diffuse scattering between reciprocal nodes along the c direction (Figure S1), indicating positional disorder as the atoms configure at high temperatures. Analogous polytypes have been reported in related phases such as Pb_5Sb_2 (Saini et al. 1964).

X-ray diffraction from seven heating cycles performed between 100 and 200 GPa and to 3300 K provide insight into the Fe-rich Fe-S phase relations at outer core pressures and to high temperatures. In each heating experiment, temperatures near melting were attained, and lattices of Fe₅S₂ were indexed in the reciprocal space upon quenching. By further probing locations across the thermal gradient of the laser heated spots, additional Fe-sulfides were characterized, offering information on the lower temperature Fe-saturated sulfide crystal chemistries (Table S1, S2). These include the Fe₃P-type Fe₃S (*I*-4, *Z* = 8) phase (Fei et al. 2000; Seagle et al. 2006; Morard et al. 2007; Kamada et al. 2010; Kamada et al. 2012; Thompson et al. 2020), the *C*23 Fe₂S (Co₂P-type, *Pnma*, *Z* = 4) phase, and the *C*37 Fe₂S (Co₂Si-type, *Pnma*, *Z*=4) phase, in lower temperature regions at 119 GPa, 131 GPa, and 140 GPa, respectively (Figure 3; Table S1, S2). Notably, identification and crystal-structure analysis of Fe₅S₂ and Fe₃S in these Fe-saturated experiments clarifies that Fe₅S₂, not Fe₃S is stable on the solidus above 120 GPa, despite reports from previous powder diffraction studies (e.g. Kamada et al. 2010; Kamada et al. 2012; Ozawa et al. 2013; Mori et al. 2017).

Comparison of the interatomic distances and coordination environments in the Fe-sulfides observed in this study separates Fe₅S₂ as particularly unique among them. Within an interatomic distance of 2.7 Å (Table S4, Appendix A1-A4), *C*23 and *C*37 Fe₂S consist of Fe sites coordinated only by S, Fe₃S marks an increase in Fe-Fe bonding with Fe surrounded by up to 9 Fe sites, and Fe₅S₂ exhibits Fe surrounded by up to 9 Fe sites with Fe-Fe bond lengths up to 25% shorter in Fe₅S₂ compared to Fe₃S (Table S4). Following previous descriptions of related *M*₅*X*₂ phases (e.g. (Kjekshus et al. 1973; Oryshchyn et al. 2011), Fe₅S₂ can be viewed as an arrangement of 6 Fe sites and 3 S sites with the Fe1, Fe2, Fe4, and Fe6 sites in 13-fold

coordination, the Fe3 and Fe5 sites in 12-fold coordination, and the S sites in 10-fold coordination (Figure 2c, Table S4). All sites are coordinated by both Fe and S sites.

The presented single-crystal derived structures of Fe₅S₂, Fe₃S, *C23* Fe₂S, and *C37* Fe₂S were then used to interpret the changes in powder X-ray diffraction patterns collected during heating between 110 and 200 GPa and to ~3300 K (Figure 4, Figure S4). *C23* Fe₂S is observed coexisting with Fe to ~125 GPa and up to ~2300 K. In combination with previous studies, *C23* Fe₂S is stable at moderate temperatures between 25 and 125 GPa (Zurkowski et al. *in press*, Zurkowski et al. submitted). A pressure-induced *C23*–*C37* Fe₂S transition is constrained between 125 and 135 GPa, in agreement with previous investigations of Fe₂S (Zurkowski et al. submitted). *C37* Fe₂S is stable between 130–200 GPa and to ~3000 K in this study, and previous work suggests that *C37* Fe₂S may remain stable to 306 GPa at high temperatures (Tateno et al. 2019). Tetragonal Fe₃S forms from the reaction of *C23* Fe₂S + Fe between 2000–2400 K at ~115 GPa. The stability of tetragonal Fe₃S is constrained to pressures below ~120 GPa at high temperatures in Fe-rich systems (Figure 4) (Seagle et al. 2006; Morard et al. 2008; Kamada et al. 2010; Kamada et al. 2012; Thompson et al, 2020). Fe₅S₂ is observed coexisting with iron between ~120–200 GPa and in the 2400–3300 K range, making it the relevant sulfide in the melting and crystallization properties of Fe-rich metallic cores at these pressures (Figure 4).

Sulfur in Earth and planetary cores

The stability of Fe₅S₂ and the phase relations observed in this study present novel constraints on the material properties of Fe-sulfides at conditions relevant to Earth’s outer core, Venus’ core, and exoplanetary cores of similar size and core-mass fraction (CMF). Namely, at pressures ≥ 120 GPa, Ni₅As₂-type Fe₅S₂, not tetragonal Fe₃S as previously believed, is the

relevant Fe-rich sulfide. As Earth's outer core crystallizes over time, Fe_5S_2 will eventually crystallize over a large depth range up to the CMB. Tetragonal Fe_3S has been confirmed up to 120 GPa (Figure 4) (Seagle et al. 2006; Morard et al. 2008; Thompson et al., 2020), constraining the $\text{Fe}_3\text{S} + \text{Fe} \rightarrow \text{Fe}_5\text{S}_2 + \text{Fe}$ transition to ~ 120 GPa. Rocky planetary bodies with sizes and CMFs like that of Venus (CMB = 114 GPa) (Aitta 2012) would likely crystallize Fe_3S at the CMB, while Fe_5S_2 will be crystallizing over much of the core's depth. $C37 \text{ Fe}_2\text{S}$ is reported to be stable on the solidus above 306 GPa in Fe-rich systems (Tateno et al. 2019), suggesting a $\text{Fe}_5\text{S}_2 + \text{Fe} \rightarrow \text{Fe}_2\text{S} + \text{Fe}$ transition in the 200–300 GPa range. $C37 \text{ Fe}_2\text{S}$ remains the candidate Fe-rich sulfide at Earth's ICB, but for planets like Venus with a central pressure of 274 GPa (Aitta 2012), Fe_5S_2 may instead be the relevant Fe-rich sulfide, necessitating experimental determination of the $\text{Fe}_5\text{S}_2 \rightarrow \text{Fe}_2\text{S} + \text{Fe}$ decomposition P - T boundary. Additional assessment of the volume and melting-temperature changes across these newly determined sulfide transitions are critical for matching the density and seismic profiles of Earth and rocky planetary cores. Furthermore, as Fe_5S_2 exhibits a complex crystalline arrangement with significant metal-metal bonding compared to Fe_2S and Fe_3S at core pressures, the significant depth over which Fe_5S_2 crystallizes in and Venus- to Earth-sized planetary cores is likely to contribute to higher conductivity signatures in these regions.

Terrestrial core chemistries are multicomponent; Si and Ni are also important core-alloying elements in planets such as Earth, drawing attention to the potential stability of the perryite $(\text{Fe}, \text{Ni})_8(\text{Si}, \text{P})_3$ structure in $(\text{Fe}, \text{Ni}) - (\text{Si}, \text{S})$ -rich cores. Perryite, is a mineral observed in enstatite chondrites and aubrites that adopts a structure that is trigonal stacking variant of the Ni_5As_2 -type structure (Wasson and Wai, 1970; Okada et al. 1991) and iron phosphides tend to adopt analogous structures to that observed in iron sulfides (i.e., Fei et al. 2000; Dera et al. 2008;

Gu et al. 2014; Gu et al. 2016; Zurkowski et al., in press). Fe_5S_2 could potentially serve as a host for nickel and silicon in the perryite structure at Earth's outer core conditions. Further, Si has recently been shown to dissolve into iron-sulfide phases and expand their stability fields with pressure (Tao and Fei, 2021). The dissolution of silicon into Fe_5S_2 may expand its stability to higher pressures, making it potentially relevant at Earth's ICB conditions. If this is the case, the partitioning of Si and Ni between $(\text{Fe}, \text{Ni})_5(\text{S}, \text{Si})_2$ and $(\text{Fe}, \text{Ni}, \text{Si})$ and the density difference between the inner-core-crystallizing phase and remaining light-element-rich liquid will be crucial to investigations of the inner-core-density deficit and inner core seismic morphology.

Materials and Methods

Experiments targeting multigrain synthesis in the Fe-S system consisted of mixtures of Fe (99.9+%, $<10\mu\text{m}$, Alfa Aesar) and iron sulfide (FeS , 99.99%, Alfa Aesar) in Fe+12.5 wt% S ($\text{Fe}_{80}\text{S}_{20}$), Fe + 23 wt% S ($\text{Fe}_{67}\text{S}_{33}$) compositions. The Fe-FeS compositions were ground in ethanol in a pestle and mortar for 1 hour then mixed dry for a short interval to homogenize any density settling during alcohol evaporation.

Pressure was generated using BX-90-type (Kantor et al. 2012) diamond anvil cells (DAC) with type 1 Boehler-Almax conical diamonds and seats, and Mao symmetric-type DACs with Type 1 standard cut diamonds mounted on tungsten carbide or cubic-boron nitride (cBN) seats. Diamond culets ranged from 150-50 μm in diameter. Foils of $\text{Fe}_{80}\text{S}_{20}$ or $\text{Fe}_{67}\text{S}_{33}$ were produced by pressing the Fe-S starting powders between two ungasketed diamond anvils, then loaded between pellets of KCl or SiO_2 . Sample chambers ranged from 180-25 μm in diameter and were drilled from pre-indented rhenium gaskets. Samples were dried at 100°C for 30 minutes prior to pressurization.

Angle dispersive X-ray diffraction (XRD) experiments were conducted at Argonne National Laboratory, sector 13 ID-D, of the Advanced Photon Source. At Sector 13 ID-D, a 2.5 μm x 3.54 μm full width, half maximum (FWHM) monochromatic X-ray beam tuned to 37 or 42 keV was utilized, and diffracted X-rays were collected with a CdTe 1M Pilatus detector. Sample-to-detector geometries were calibrated using a LaB₆ NIST standard and a single crystal of enstatite was used for calibration of the rotational geometry of the X-ray beam and detector.

Double-sided laser heating and *in-situ* XRD collection took place at Sector 13 ID-D. Fibers lasers shaped with ~ 10 μm radius flat tops were aligned with the X-ray beam using the X-ray fluorescence of the sample pressure media or the gasket (Prakapenka et al., 2008). During heating, thermal emission from a 6 μm central region of the laser-heated spot was measured spectroradiometrically and fit to a gray body approximation (Heinz and Jeanloz, 1987). A 3% temperature correction was then applied to correct for axial gradients through the sample (Campbell et al., 2007; 2009). The laser power on each side of the sample was adjusted to maintain uniform double-sided heating and X-Ray diffraction and temperature measurements were collected every ~ 200 K with 1s exposure times. Samples were typically quenched at high temperatures within 30-45 minutes of heating or after a phase transition and suitable grain growth was observed. Powder diffraction patterns were processed using Dioptas (Prescher and Prakapenka, 2015) and CrysAlisPro (Rigaku OD, 2018). Pressure was determined using the equation of state of hcp-Fe (Dewaele et al. 2006).

Upon quenching, X-ray diffraction maps of the heated spot were collected across a 100 μm^2 square region in 3 μm steps. Map locations showing high intensity, spotty diffraction patterns were chosen for multigrain single-crystal type X-ray diffraction collection approach, as these features indicate high-temperature induced crystallite growth. At chosen map locations, X-

ray diffraction images were collected across ± 17 to $\pm 30^\circ$ rotational scans in 0.25° – 0.5° steps with 1–4 s exposure times. The diffraction reflections were then mapped in the reciprocal space and target grains were identified and separated from reflections associated with the pressure media, iron, and diamond (Rigaku OD, 2018).

Target Fe-S lattices were then indexed and the peak intensities were integrated and reduced using CrysAlisPro (Rigaku OD, 2018). Absorption corrections and scaling factors were applied to the structure factors in CrysAlisPro using the multi-scan method via the Scale3 Abspack program (Rigaku OD, 2018). The final structure factors and lattice geometries were then refined to known structure models (El-Boragy et al. 1970; Oryshchyn et al. 2011) using SHELXL2014/7 (Sheldrick 2015). Reflections showing anomalous calculated versus measured structure factors; likely due to overlap with diamond and other phases in the multigrain sample, resolution limitations, and volume of crystal illuminated by the X-ray beam, were omitted. Structure models were visualized using Vesta during the refinement procedure (Momma and Izumi 2011).

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Figure 1. FeS₂ diffraction in equilibrium with iron

a) View of a crystallite of the high-temperature FeS₂ coexisting with recrystallized hcp-Fe after synthesis at 159(2) GPa and 3230(130) K (inset). The spotty rings corresponding to the hcp-Fe (100) and (101) planes demonstrate that iron equilibrated at 159(2) GPa and 3230(130) K. b) View of the reciprocal space for reflections detected in an experiment on the Fe₈₀S₂₀ composition quenched from 140(2) GPa and 3070(140) K. The reciprocal lattice, colored in black, is associated with a FeS₂ grain whose lattice parameters are provided in the top left.

Figure 2. Crystal structure of Ni_5As_2 -type Fe_5S_2

Crystal structure of Fe_5S_2 viewed along the a) c axis and the b) (100) plane. c) The Fe-coordination polyhedra observed in this atomic arrangement are provided. Fe1, Fe2, Fe4, and Fe6 are coordinated by 13 sites and Fe3 and Fe5 are coordinated by 12 sites. Each coordination polyhedron consists of Fe and S sites.

a) Fe_3S (Fe_3P -type, $I-4$, $Z = 8$)

b) $\text{C23 Fe}_2\text{S}$ (Co_2P -type, $Pnma$, $Z = 4$)

c) $\text{C37 Fe}_2\text{S}$ (Co_2Si -type, $Pnma$, $Z = 4$)

Figure 3. Crystal structures of Fe_3S and Fe_2S observed in this study

a) Fe_3S adopts the Fe_3P -type structure ($I-4$, $Z = 8$) that is composed of three tetrahedrally coordinated Fe-sites, each with increasing Fe–Fe bonding. b) The $\text{C23 Fe}_2\text{S}$ structure (Co_2P -type, $Pnma$, $Z = 4$) is made up of columns of FeS_4 tetrahedra and columns of FeS_5 square pyramids linked along edges in the b direction. c) The $\text{C37 Fe}_2\text{S}$ structure (Co_2Si -type, $Pnma$, $Z = 4$) has the same site symmetries as the C23 structure, but is marked by a shortened a axis and elongated b and c axes accompanied by the formation of a 5-fold dipyramid.

Figure 4. Iron-rich sulfide phase diagram to Earth's outer core pressures

At moderate temperatures up to 130 GPa, C23 Fe₂S is observed. At moderate temperatures, tetragonal Fe₃S (Fe₃P-type) is observed below 120 GPa. At moderate temperatures between 130 and 200 GPa, C37 Fe₂S is observed, and on the liquidus between ~115–200 GPa, Fe₅S₂ is the liquidus phase. A kink the Fe-S solidus curve (Mori et al. 2017), is presented to account for the change in phase relations and the high temperatures at which Fe₅S₂ was observed. The closed squares represent experiments conducted on the Fe₈₀S₂₀ starting material, and the open squares represent experiments conducted on the Fe₆₇S₃₃ starting material. Both show compatible results, likely indicating that Fe-rich regions of the Fe₆₇S₃₃ foils were probed.

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