Pre-print Statement for

“Fe₅S₂ identified as a host for sulfur in Earth’s core”

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Sincerely,

Claire Zurkowski
Fe$_5$S$_2$ 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 in 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, Fe$_5$S$_2$, crystallizing in equilibrium with iron at Earth’s outer core pressures and high temperatures. Using single-crystal X-ray diffraction techniques, Fe$_5$S$_2$ was determined to adopt the complex Ni$_5$As$_2$-type structure ($P6_3mc$, $Z = 6$). These results conclude that Fe$_5$S$_2$ 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 over time. The increased metal-metal bonding measured in Fe$_5$S$_2$ compared to the other high $P$-$T$ iron sulfides may contribute to signatures of higher conductivity from regions of Fe$_5$S$_2$ is crystallization. Fe$_5$S$_2$ could serve as a host for Ni and Si as has been
observed in the related meteoritic phase, perryite, \((\text{Fe, Ni})_8(P, \text{Si})_3\), adding intricacies to elemental partitioning during inner core crystallization. The stability of \(\text{Fe}_3\text{S}_2\) 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. Buffet, 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 \(\text{Si, O, S, C, and H}\), 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 \(\text{Fe}_3\text{S}\) (\(\text{Fe}_3\text{P}\)-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 \(\text{Fe}_2\text{S}\) (\(\text{Co}_2\text{Si}\)-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 \(\text{Fe}_2\text{(S, Si)}\) chemistry over \(\text{Fe}_3\text{S}\) 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, \(\text{Co}_2\text{P}\)-type \(\text{Fe}_2\text{S}\) (\(Pnma, Z = 4\)) 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: \( a = 5.979(3) \) Å, 11.088(6) Å 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 \( P6_{3}cm \) space group, and structural solution and positional and displacement parameter refinement converged to the \( Ni_{5}As_{2} \)-type \( Fe_{5}S_{2} \) (\( Z=6 \)) (Table S2, S3; Figure 2) (Oryshchyn et al. 2011). The \( Ni_{5}As_{2} \)-type \( Fe_{5}S_{2} \) is derived from the \( Pb_{5}Sb_{2} \) 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 \( Fe_{5}S_{2} \) 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 \( Pb_{5}Sb_{2} \) (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 Fe$_5$S$_2$ 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 Fe$_3$P-type Fe$_3$S ($I-4, Z = 8$) 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 C23 Fe$_2$S (Co$_2$P-type, $Pnma, Z = 4$) phase, and the C37 Fe$_2$S (Co$_2$Si-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 Fe$_5$S$_2$ and Fe$_3$S in these Fe-saturated experiments clarifies that Fe$_5$S$_2$, not Fe$_3$S 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 Fe$_5$S$_2$ as particularly unique among them. Within an interatomic distance of 2.7 Å (Table S4, Appendix A1-A4), C23 and C37 Fe$_2$S consist of Fe sites coordinated only by S, Fe$_3$S marks an increase in Fe-Fe bonding with Fe surrounded by up to 9 Fe sites, and Fe$_5$S$_2$ exhibits Fe surrounded by up to 9 Fe sites with Fe-Fe bond lengths up to 25% shorter in Fe$_5$S$_2$ compared to Fe$_3$S (Table S4). Following previous descriptions of related MsX$_2$ phases (e.g. (Kjekshus et al. 1973; Oryshchyn et al. 2011), Fe$_5$S$_2$ 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$_5$S$_2$ will eventually crystallize over a large depth range up to the CMB. Tetragonal Fe$_3$S has been confirmed up to 120 GPa (Figure 4) (Seagle et al. 2006; Morard et al. 2008; Thompson et al., 2020), constraining the Fe$_3$S + Fe → Fe$_5$S$_2$ + 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$_3$S at the CMB, while Fe$_5$S$_2$ will be crystallizing over much of the core’s depth. C$_{37}$ Fe$_2$S is reported to be stable on the solidus above 306 GPa in Fe-rich systems (Tateno et al. 2019), suggesting a Fe$_5$S$_2$ + Fe → Fe$_2$S + Fe transition in the 200–300 GPa range. C$_{37}$ Fe$_2$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$_5$S$_2$ may instead be the relevant Fe-rich sulfide, necessitating experimental determination of the Fe$_5$S$_2$ → Fe$_2$S + 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$_5$S$_2$ exhibits a complex crystalline arrangement with significant metal-metal bonding compared to Fe$_2$S and Fe$_3$S at core pressures, the significant depth over which Fe$_5$S$_2$ 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 (Fe, Ni)$_8$(Si, P)$_3$ structure in (Fe, Ni) – (Si, 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$_5$As$_2$-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$_5$S$_2$ 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$_5$S$_2$ 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 (Fe, Ni)$_5$(S, Si)$_2$ and (Fe, Ni, 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+%, <10μm, Alfa Aesar) and iron sulfide (FeS, 99.99%, Alfa Aesar) in Fe+12.5 wt% S (Fe$_{80}$S$_{20}$), Fe + 23 wt% S (Fe$_{67}$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 of cubic-boron nitride (cBN) seats. Diamond culets ranged from 150-50 μm in diameter. Foils of Fe$_{80}$S$_{20}$ or Fe$_{67}$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-indentated rhenium gaskets. Samples were dried at 100ºC 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 μm² 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 ±30° 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).

Acknowledgments

Portions of this work were performed at GeoSoilEnviroCARS (The University of Chicago, Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation - Earth Sciences (EAR-1634415). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. Use of the COMPRES-GSECARS gas loading system was supported by COMPRES under NSF Cooperative Agreement EAR-1606856 and by GSECARS through NSF grant EAR-1634415.
and DOE grant DE-FG02-94ER14466. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. This material is based upon work supported by a National Science Foundation Graduate Research Fellowship to C.C.Z. This work was also supported by the National Science Foundation by grant EAR-1651017 to A.J.C.
Figure 1. Fe$_5$S$_2$ diffraction in equilibrium with iron

a) View of a crystallite of the high-temperature Fe$_5$S$_2$ 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 Fe$_{80}$S$_{20}$ composition quenched from 140(2) GPa and 3070(140) K. The reciprocal lattice, colored in black, is associated with a Fe$_5$S$_2$ grain whose lattice parameters are provided in the top left.
Figure 2. Crystal structure of Ni₅As₂-type Fe₅S₂

Crystal structure of Fe₅S₂ 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.
Figure 3. Crystal structures of Fe₃S and Fe₂S observed in this study

a) Fe₃S (Fe₃P-type, I-4, Z = 8) adopts the Fe₃P-type structure that is composed of three tetrahedrally coordinated Fe-sites, each with increasing Fe–Fe bonding. b) The C23 Fe₂S structure (Co₂P-type, Pnma, Z = 4) is made up of columns of FeS₄ tetrahedra and columns of FeS₅ square pyramids linked along edges in the b direction. c) The C37 Fe₂S structure (Co₂Si-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.
At moderate temperatures up to 130 GPa, \( \text{C}_{23} \text{Fe}_2\text{S} \) is observed. At moderate temperatures, tetragonal \( \text{Fe}_3\text{S} \) (Fe\(_5\)P-type) is observed below 120 GPa. At moderate temperatures between 130 and 200 GPa, \( \text{C}_{37} \text{Fe}_2\text{S} \) is observed, and on the liquidus between \(~115–200\) GPa, \( \text{Fe}_5\text{S}_2 \) 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 \( \text{Fe}_5\text{S}_2 \) was observed. The closed squares represent experiments conducted on the \( \text{Fe}_{80}\text{S}_{20} \) starting material, and the open squares represent experiments conducted on the \( \text{Fe}_{67}\text{S}_{33} \) starting material. Both show compatible results, likely indicating that Fe-rich regions of the \( \text{Fe}_{67}\text{S}_{33} \) foils were probed.
References


Fe$_5$S$_2$ identified as a host for sulfur in Earth’s core

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Supplementary Information

The Supplementary Information includes:

- Supplementary Information Text
- Table S1
- Table S2
- Table S3
- Table S4
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Supplementary Information Text

Synthesis of Fe$_5$S$_2$ to 200 GPa

Fe$_5$S$_2$ was synthesized between 119(2) and 193(4) GPa with heating to temperatures between 2400–3300 K. The formation of Fe$_5$S$_2$ phase was first recognized in the diffraction patterns by the onset of diffuse streaks and sets of closely spaced reciprocal nodes in the powder diffraction images, suggesting a complex atomic arrangement (Figure 1, S1). With sustained high temperatures in the samples loaded in more hydrostatic pressure media (e.g. KCl vs. SiO$_2$), large grain growth (3 – 6 μm) was observed and the diffuse streaks became less apparent. Further experiments are required to assess the role of hydrostaticity, kinetics, pressure, and temperature on the disorder of this phase.

Recrystallization of hcp-Fe with the Fe$_5$S$_2$ crystallites at high temperatures was observed in all experiments using the Fe$_{80}$S$_{20}$ and Fe$_{67}$S$_{33}$ starting powders as evidenced by the spotty (100) and (101) hcp-Fe rings in Figure 1a. Fe-recrystallization with this high-temperature Fe-sulfide establishes that the probed sample locations were in a Fe-saturated phase-field (Figure 1a) and this phase is important to consider further in the context of Fe-rich planetary cores.

Upon temperature quenching, rotational single-crystal X-ray diffraction scans were performed across a 37–60º omega range, depending on the DAC configuration, and grains were indexed in the reciprocal space to a hexagonal unit cell compatible with an Fe$_5$S$_2$ volume (Table S1, Figure 1b). Three unit-cell polytypes were observed and indexed in our experiments and are listed in Table S1. All indexed grains exhibit an $a$ axial length of ~ 6 Å, while 3 differing $c$ axial lengths are observed: ~ 11, 26, and 73 Å. Diffraction mappings show that the polytypism is accompanied by diffuse scattering suggesting positional disorder as the atomic arrangement along the $c$ axis configures at high temperatures (Figure S1). Analogous polytypism has also
been observed in the transition metal binary phase Pb₅As₂ (Saini et al. 1964). Decreased diffuse
scattering from the Fe₅S₂ grains was observed after continued heating in the KCl pressure media,
and grains with $a \sim 6 \, \text{Å}, \, c \sim 11 \, \text{Å}$ were indexed, indicating that this configuration is the most
positionally ordered arrangement relevant to these high $P$-$T$ conditions. These measured unit cell
parameters are compatible with 6 formula units per cell volume of Fe₅S₂.

The structure of a grain Fe₅S₂ synthesized at 140(2) GPa and 3070(180) K was
determined based on 159 observed reflections at these extreme conditions (Table S2).

Assessment of the systematic absences for the structure factors reduced for Fe₅S₂ suggests a
$P6_3cm$ space group. Structural solution and positional and displacement parameter refinement
converged on the Ni₅As₂ structure type (Table S2, 3; Figure 2) (Oryshchyn et al. 2011). The
Ni₅As₂ structure is a slight modification of the Pb₅Sb₂ 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 (Figure 2) (Oryshchyn et al. 2011). This structural modification was initiated
based on the large $U_{22}$ parameter observed on the $M_6$ site ($M =$ metal) in Ni₅As₂ when
anisotropic displacement parameters were refined using a Pb₅As₂ starting model (Figure S2). In
the current dataset, a comparably large $U_{22}$ value was observed on the Fe₆ site resulting in an
oblong displacement ellipse when refining the data against the initial Pb₅As₂ structure model.
The Fe₆ site was positionally disordered following Oryshchyn et al. (2011), and the resultant R₁
value was improved by around ~5%, rendering the Ni₅As₂ structure model more compatible with
the current Fe₅S₂ data (Table S2). Isotropic displacement parameters showing errors > 3σ were
fixed to a value equal to approximately the average displacement parameter value for Fe or S
(Table S2). The isotropic displacement parameter for the disordered Fe site was also fixed at an
average Fe$U_{\text{iso}}$ value (Table S2). The number of reflections collected at these extreme pressures
limits the number of statistically meaningful parameters to refine, and fixing displacement
to reasonable values precludes overinterpretation of the current dataset. The high
isotropic displacement parameter observed on the Fe4 site may represent some vacancies on this
site, but the dataset is again deficient to precisely describe the site occupancy.

The experimental details for the solution and refinement of Fe$_5$S$_2$ to the Ni$_5$As$_2$ solution
model are provided in Table S2 and the atomic coordinates of Fe$_5$S$_2$ synthesized at 140(2) GPa
and 3070(180) K are provided in Table S3. In accordance with previous descriptions of related
$M_5X_2$ transitional-metal binary phases (e.g. (Kjekshus et al. 1973; Oryshchyn et al. 2011), Fe$_5$S$_2$
can be viewed as an arrangement of 6 Fe sites and 3 S sites with the Fe1, Fe2, Fe4, and Fe6 sites
are in 13-fold coordination, the Fe3 and Fe5 sites are in 12-fold coordination, and the S sites are
in 10-fold coordination (Figure 2c). The measured bond lengths for the Fe-coordinated polyhedra
are provided in Table S4. All sites are coordinated by both Fe and S sites. A CIF file for Fe$_5$S$_2$
is provided in Appendix A1.

Final $R_1$ values $\approx 10\%$ attest to the less-than ideal quality of the multigrain dataset as a
possible result of the 1-2 megabar synthesis conditions and observed c axial disorder and
stacking complexities in Fe$_5$S$_2$ (Table S2). Previous studies of isomorphic Ni$_5$As$_2$ and related
Pb$_5$As$_2$ at ambient conditions have also reported similar quality of refinements despite obtaining
significantly more reflections in the absence of a DAC (e.g. Saini et al. 1964; El-Boragy et al.
1970; Kjekshus et al. 1973). Notable challenges regarding the refinement of the Fe$_5$S$_2$ structure
model at these extreme conditions are discussed here and compared with similar difficulties
reported in previous characterizations of this structure.

Thirteen violations of the $P6_3cm$ systematic absence condition: $l = 2n$ for $(0kl)$, were
flagged during the refinement of Fe$_5$S$_2$. The reflections associated with these systematic absence
violations were examined in the raw diffraction images and all show low, diffuse intensity.

Discrepancy over the presence or absence of weak reflections with \((0kl), l=2n+1\) has been reported in previous investigations of Ni\(_5\)As\(_2\) and Pb\(_5\)As\(_2\) (e.g. Saini et al. 1964; El-Boragy et al. 1970; Kjekshus et al. 1973), suggesting that these studies may have also faced difficulties with space group determination. Observations of these low-intensity reflections may be a result of residual disorder in the stacking arrangement along the \(c\) direction, and longer heating cycles may be required for the atoms to arrange into equilibrium positions. It is likewise possible that varying synthesis methods for Ni\(_5\)As\(_2\) and Pb\(_5\)As\(_2\) in previous ambient condition studies affected the \(c\) axial atomic arrangement. Ni\(_5\)As\(_2\) and isomorphic Ni\(_5\)P\(_2\) also exhibits a homogeneity range of \(\sim71.25-72.7\) atomic % As (Kjekshus et al. 1973; Litasov et al., 2019), and slight modifications of this structure based on varying stacking arrangements result in structures such as Ni\(_{31}\)Si\(_{12}\) (Frank and Schubert 1971) and (Fe, Ni)\(_6\)(Si, P)\(_3\) (perryite) (Okada et al. 1991).

Attempts to refine the current Fe-sulfide phase with the Ni\(_{31}\)Si\(_{12}\) or perryite structure models did not improve the refinement results. Based on the presence of disorder, polytypism, anisotropic vibrational motion, and nonstoichiometry in the related \(M_5X_2\) phases, additional nuances to the Fe\(_5\)S\(_2\) structure model may be developed in future studies; however, the identification and characterization of the Fe\(_5\)S\(_2\) crystal structure determined here to 200 GPa is novel, and the observations and challenges reported in this study align with that of previous analyses of Ni\(_5\)As\(_2\) and Pb\(_5\)Sb\(_2\) that were not limited by microdiffraction in a DAC at extreme conditions.

Other sulfides observed during heating to 200 GPa

Three experiments and 7 heating cycles were performed in this study between 100 and 200 GPa and to 3400 K, and the X-ray diffraction patterns collected upon heating provide insight
into the Fe-rich Fe-S phase relations at outer core pressures and to high temperatures. In each heating experiment, near melting temperatures were targeted and grains of Fe$_5$S$_2$ were identified upon quenching. Additional Fe-sulfides were also observed across the thermal gradient of the heated spot, providing information on the lower temperature Fe-saturated phase relations in each heating cycle. Upon quenching from high-temperature synthesis at 119(2) GPa, the other grains in the sample were identified and indexed to a tetragonal cell with $a = 8.094(3)$ Å, $c = 3.990(2)$ Å, compatible with 8 formula units of Fe$_3$S (Table S1). The structure was then solved and refined to the Fe$_3$P-type structure ($I-4, Z = 8$) (referred to herein as $I$-4 Fe$_3$S) in agreement with previous studies (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 resultant structure model for Fe$_3$S at these conditions is shown in Figure (3a), a CIF file for Fe$_3$S is provided in Appendix A2, and the refinement details are given in Table S2. The structure can be viewed as containing 3 tetrahedrally coordinated Fe sites (Blanchard et al. 2008): one Fe-site is coordinated only by S atoms with an average bond length of 2.083(9) Å, another Fe site is coordinated by 3 S atoms and 1 Fe atom with an average bond length of 2.146(8) Å, and the third Fe site is coordinated by 2 S and 2 Fe atoms with an average bond length of 2.137(8) Å (Figure 3). The measured interatomic distances are comparable to reports on other transition metal $M_3X$ structures (e.g. Aronnson 1955; Rundqvist 1979).

After temperature quenching from 131(2) GPa and 3050(140) K, grains of Fe$_3$S were not observed across the heated spot. Instead, orthorhombic lattices were also identified with parameters $a = 4.869(2)$ Å, $b = 3.256(2)$ Å, $c = 6.139(2)$ Å, compatible with 4 formula units of Fe$_2$S. Structural solution and refinement indicate that the Fe$_2$S grains adopt the $C23$ structure (Co$_2$P type, $Pnma$, $Z = 4$) in agreement with previous structural analyses at lower pressures.
(Zurkowski et al. in press). Refinement details for the structure model are given in Table S2 and a CIF file for C23 Fe2S is provided in Appendix A3. The structure is composed of columns of FeS₄ tetrahedra and columns of FeS₅ square pyramids linked along edges in the b direction (Figure 3b). The average Fe–S bond lengths are 2.213(8) Å and 2.011(2) Å in the square pyramids and tetrahedra, respectively. These values are comparable with that observed in C23 Fe₂S at 90 GPa (Zurkowski et al. in press).

Upon compression and heating at 140(2) GPa and 3070(180) K, orthorhombic grains were identified in the sample chamber with a = 4.667(2) Å, 3.289(1) Å, 6.186(4) Å. This unit cell is similar to the C23 Fe₂S observed at 130 GPa, but exhibits a 4% contraction of the a axial length, a 1% extension of the b and c axial lengths, and a 2% volume decrease. Structural solution and refinement using the measured structure factors establish that Fe₂S adopts the C37 structure (Co₂Si-type, Pnma, Z=4) at these conditions (Figure 3c). A CIF file for C37 Fe₂S is provided in Appendix A4 and the analysis details are given in Table S2. In agreement with the proposed C23–C37 Fe₂S phase transition around 140 GPa that is accompanied 1.6% volume decrease (Zurkowski et al., in press), this work confirms that the C23–C37 transition in Fe₂S occurs between 130 and 140 GPa with a similar volume change. Inherent to the C23–C37 transition is coordination change from the 4-fold Fe1 coordination polyhedra in the C23 structure to the 5-fold dipyramid polyhedra in the C37 structure (Figure 3b, c). Comparing the C23 and C37 structure models determined at 130 and 140 GPa, respectively, a 10% contraction of the interatomic distance involved in the coordination change is observed (Figure S3). The average Fe–S bond lengths measured in C37 Fe₂S are 2.196(2) Å and 2.165(3) Å in the square pyramids and dipyramids, respectively. These values are comparable with C23 Fe₂S.
Fe-rich sulfide phase relations at core-mantle boundary pressures

The presented single-crystal derived structures of Fe₅S₂, Fe₃S, C23 Fe₂S and C37 Fe₂S were then used to inform the changes in diffraction patterns collected during heating between 110 and 200 GPa and to ~3300 K. Beginning at 112 GPa, diffraction signal from C23 Fe₂S coexisting with Fe was first identified upon heating of the Fe₈₀S₂₀ starting material to ~2000 K. With continued heating, peaks associated with tetragonal Fe₃S were observed over a limited temperature range (≤ 2400 K) until diffuse scattering signal and Bragg reflections from Fe₅S₂ first appeared. Crystallization of the Fe₅S₂ grains with iron occurred with continued heating to 119(2) GPa and 2840(180) K. Upon heating beginning at 120 GPa, C23 Fe₂S was observed coexisting with Fe to 122(1) GPa and 2290(120) K, above which the onset of diffraction from the Fe₅S₂ phase was identified and Fe₅S₂ crystallites formed coexisting with hcp-Fe to 131(2) GPa and 3050(140) K. I-4 Fe₃S was not observed. With continued heating cycles between 133(1) GPa and 194(2) GPa and up to 3300 K, C37 Fe₂S coexists with Fe at moderate temperatures and a phase transition to Fe₅S₂ occurs at high temperatures. A phase diagram satisfying these observations is proposed in Figure 4, and integrated XRD patterns for the heating cycles at 119(2) and 184(3) GPa and to 3300 K are shown in Figure S4 to demonstrate the identification of C23 Fe₂S, Fe₃S, C37 Fe₂S, and Fe₅S₂ coexisting with hcp-Fe. The peak intensities from the Fe₅S₂ lattices vary during heating up at high temperatures as a result of disorder, polytypism, and the formation of large crystallites at high temperatures (Figure 1, S1). These structural complexities render the powder diffraction patterns difficult to characterize without incorporating single-crystal XRD techniques.
Transitional metal binary compounds with metal-to-nonmetal ratios ranging from 2.33–2.66 (~70–73 atm% metal) predominantly adopt complex trigonal or hexagonal structures with considerable metal-metal bonding (Chen and Whitmire 2018 and references therein). Our observations of the disorder, polytypism, and complex coordination environments inherent to Fe$_5$S$_2$ demonstrate that it aligns with this systematic characterization. Interestingly, the Fe$_5$S$_2$ atomic arrangement is thermodynamically favored at the extreme conditions of Earth’s outer core over that of I-4 Fe$_3$S. These results are contrary to previous reports of Fe$_3$S stability on to high temperatures in Fe-rich systems to 250 GPa (Kamada et al. 2010; Kamada et al. 2012; Ozawa et al. 2013; Mori et al. 2017). Few lines of reasoning may account for these discrepancies. Interpretation of Fe$_5$S$_2$ in the integrated powder diffraction patterns is difficult due to the variation in diffraction signal obtained from the Fe$_5$S$_2$ polytypes and the low intensity scattering from the disordered sites during its formation. Fe$_5$S$_2$ also forms large crystallites, limiting the orientations of the phase and rendering indexation of all diffraction angles for Fe$_5$S$_2$ quite challenging without rotating the sample. The implementation of single-crystal X-ray diffraction techniques at high pressures was critical in the current study to accurately characterize the hexagonal unit cell geometry and complex structure of the Ni$_5$As$_2$-like Fe$_5$S$_2$.

Several studies have also reported chemically analyzed Fe$_3$S grains in samples recovered from high temperatures in the 200–250 GPa range (Mori et al. 2017; Yokoo et al. 2019; Ozawa et al. 2013), but the difference in Fe content between Fe$_3$S and Fe$_5$S$_2$ may be as few as 3%. This value is generally within 3 sigma of the atomic percent error reported for chemical analyses of samples recovered from these extreme conditions, posing another challenge for distinguishing between the synthesis of Fe$_3$S and Fe$_5$S$_2$. Furthermore, based on characterizations of the
isomorphic Ni₅As₂ and Ni₅P₂, these structures exhibit a homogeneity range with up to ~73 atm%
metal (Kjekshus et al. 1973; Litasov et al., 2019). For example, TEM analysis of a Fe–S sample
recovered from 236 GPa and 2980 K reveals sulfide grains with on average ~73 atm% Fe
(Ozawa et al. 2013). This value is within 0.3–1.25 atomic percent of the possible range of Fe₅S₂
stoichiometries and 2 atomic percent less than an Fe₃S composition. The results from this
previous work as well as other chemical analyses of samples recovered from outer core pressures
and high temperatures therefore do not contradict the current results (Mori et al. 2017; Yokoo et
al. 2019; Ozawa et al. 2013) and may reveal a previous misinterpretation of Fe₅S₂ as Fe₃S based
on measured chemistries.
Table S1. Unit cell parameters of FeS$_2$, Fe$_3$S, and Fe$_2$S measured upon quenching from high $P$-$T$ synthesis in this study. Each cell was indexed in the reciprocal space, and the DAC opening, and number of reflections obtained for each lattice are listed. For select experiments, high-temperature synthesis was conducted without collecting X-ray diffraction data, and the synthesis conditions for these experiments are listed as “high $T$, not measured.”

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<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>DAC opening (°)</th>
<th>no. of reflections</th>
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<th>$T$ (K)</th>
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Table S2. Select experimental details for crystal structure synthesis and analysis of Fe₅S₂, Fe₃S, and the Fe₂S polymorphs.

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Table S3. Atomic coordinates of the Fe$_5$S$_2$ refinement model for the data collected at 140(2) GPa and quenched from 3070(180) K.

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*indicates half occupancy
Table S4. Selected interatomic distances for the Fe sites measured in Fe$_5$S$_2$ at 140 GPa.

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Figure S1. Unwarped diffraction mappings of the (1kl), (0kl), and (-1kl) directions for an Fe₅S₂ crystallite exemplifying the diffuse scattering signal collected at 119(2) and 2840(180) K. The (1kl) and (-1kl) mappings also show the presence of a polytype with more closely spaced reflections oriented ~51° from the mapped crystallite.
Figure S2. Fe$_5$As$_2$ structure model shown with anisotropic displacement ellipsoids using the starting Pb$_5$As$_2$ structure model. In accordance with the Ni$_5$As$_2$ structural characterization (Oryshchyn et al. 2011), these sites were disordered about their position and ascribed half occupancy.
Figure S3. Comparison of the C23 and C37 structure models refined at 130 and 140 GPa, respectively. In the C23 Fe$_2$S structure, the next nearest sulfur site to the Fe1 tetrahedral site is at a 2.963(1) Å distance at 130 GPa (dotted line). A 10% contraction of this interatomic distance and a coordination change is observed in the formation of C37 Fe$_2$S at 140 GPa (right).
Figure S4. X-ray diffraction patterns collected upon heating in an Fe\textsubscript{80}S\textsubscript{20} starting composition at a) 119(2) GPa and b) 184(3) GPa. The miller indices for C23 Fe\textsubscript{2}S (blue), Fe\textsubscript{3}S (burgundy), and C37 Fe\textsubscript{2}S (green) are provided, and the red “H” symbols represent the observations of the formation of Fe\textsubscript{5}S\textsubscript{2}. The growth of large crystallites, along with the disorder and polytypism of this phase make for challenging powder diffraction indexing, but the lattice parameters of Fe\textsubscript{5}S\textsubscript{2} indexed in the reciprocal space after quenching from these high \textit{P}-\textit{T} conditions are provided.
Supplementary Information References

Aronsson, B. (1955) The crystal structure of Ni₃P. (Fe₃P-Type). Acta Chemica Scandinavica, 9, 137-140.


