Pressure-induced $C23–C37$ transition and compression behavior of orthorhombic Fe$_2$S to Earth’s core pressures and high temperatures

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ABSTRACT

The phase stability of orthorhombic Fe$_2$S was explored to 194 GPa and 2500 K using powder and multigrain synchrotron X-ray diffraction techniques. Between 30 and 120 GPa, a $C23$-like (Co$_2$P, $Pnma$, $Z$=4) Fe$_2$S unit cell is observed and determined to exhibit a highly compressible $a$ axis. A softening of the $a$ axis occurs between 120 and 150 GPa and a relative stiffening of the $b$ and $c$ axes accompanies this compressibility change. Above 150 GPa, the $a$ axis stiffens as the $b$ and $c$ axes soften and a $C37$-like (Co$_2$Si, $Pnma$, $Z$=4) Fe$_2$S unit cell is measured. On the basis of these changes in unit-cell geometry, a pressure-induced $C23–C37$ Fe$_2$S phase transition is inferred between 120–150 GPa. The $C23$ and $C37$ ($Pnma$, $Z$=4) structures are closely related and share the same site symmetries. Forming the $C37$ structure from the $C23$ structure requires a shortening of the $a$ axis and lengthening of the $b$ and $c$ axes.
accompanied by a 4- to 5-fold coordination change. The softening of the $a$ axis above 120 GPa may therefore indicate the onset of a coordination change, and the final compressibility change above 150 GPa may mark the completion of this phase transition. The presented pressure-temperature ($P$-$T$) stabilities of $C_{23}$ and $C_{37}$ structures of $Fe_2S$ are in agreement with and resolve the differing observations of two previous studies (Tateno et al. 2019; Zurkowski et al. in press). As $C_{37} Fe_2S$ is observed to core-mantle boundary pressures and high temperatures, the $C_{37} Fe_2S$ density profile through Earth’s outer core was determined by fitting the $C_{23} Fe_2S$ equation of state ($<120$ GPa) and applying a 1.6 % volume reduction based on the $C_{37} Fe_2S$ volume residuals to this fit. Comparing the density of liquid $C_{37} Fe_2S$ with that of liquid hcp-Fe (Dewaele et al. 2006) and the seismologically determined density deficit of Earth’s core (Irving et al. 2018), 13.9±1.5 wt% and 8.6±0.8 wt% sulfur is required to match the density at the CMB and ICB, respectively, for a purely Fe–S core.

INTRODUCTION

Earth’s seismologically determined density profile and geomagnetic field indicate that its core is likely iron rich, and chemical analysis of mantle materials compared to meteorite compositions suggest that the density deficit measured in Earth’s core compared to iron is a result of a light element component (e.g. Birch, 1952; Jephcoat and Olsen, 1987; McDonough and Sun, 1995; Scott and Wasson, 1975). Earth’s core is a complex, natural system, and cosmochemically abundant elements such as S, O, Si, C and H are primary core alloying candidates. Investigating the densities of these core-relevant Fe-alloys at high pressures and temperatures is critical for assessing the multicomponent composition of Earth’s liquid outer and solid inner core (Birch, 1952, McDonough and Sun, 1995). Fe–S alloys are of particular
importance because sulfur is a significant component of the iron-rich meteorites thought to originate in the cores of planetesimals. As Earth likely formed from collision and aggregation of planetesimals, iron meteorites may be relict of the building blocks of terrestrial planets like Earth. Sulfur also significantly lowers the melting point of pure iron (e.g. Campbell et al. 2007; Chen et al. 2008; Fei et al. 1997; Fei et al. 2000; Morard et al. 2008), and during Earth’s differentiation, the presence of sulfur would have facilitated metal melt formation and core segregation (e.g. Murthy and Hall, 1970; Shannon and Agee, 1996; Stevenson, 1988; Yoshino et al. 2003).

The Fe–S system is characterized by intricate phase and melting relations. Several high P-T sulfide phases have been reported in Fe-rich systems. At low pressures, Fe and FeS form a binary eutectic with Fe$_3$S$_2$ stabilizing as an intermediate compound above 14 GPa. Fe$_3$S$_2$ melts at a peritectic to FeS plus liquid at 14 GPa (Fei et al. 1997), and a non-ideal Fe-rich liquidus curve is observed between 14 and 21 GPa (Chen et al. 2008; Tao and Fei, 2021). Above 21 GPa, several other sulfides have been identified: Fe$_3$S is observed to melt incongruently to Fe$_3$S$_2$ plus liquid, and Fe$_2$S is observed over a limited subsolidus temperature and composition range (Fei et al. 2000). The structures of Fe$_3$S$_2$ (exhibiting nonstoichiometry close to Fe$_{3.2}$S$_2$) and Fe$_2$S were preliminarily investigated by TEM after synthesis at 21 GPa and 1900 K and were reported to both adopt hexagonal lattices (Koch-Müller et al. 2002). Fe$_3$S adopts a tetragonal unit cell with the Fe$_{3}$P-type structure (I-4, Z=8) is reported to be the Fe-rich sulfide to 250 GPa at high temperatures (Fei et al. 2000; Kamada et al. 2010; Mori et al. 2017; Ozawa et al. 2013; Seagle et al. 2006; Thompson et al. 2020). Above 250 GPa, tetragonal Fe$_3$S breaks down into $B_8$ FeS+Fe at moderate temperatures, and at high temperatures above 250 GPa, $B_8$ FeS and Fe react to form an orthorhombic Fe$_2$S on the liquidus in Fe-rich compositions (Mori et al. 2017; Ozawa et al.
2013; Tateno et al. 2019). The orthorhombic Fe\textsubscript{2}S observed at these conditions adopts a unit-cell compatible with the C\textsubscript{37} structure (Co\textsubscript{2}Si-type, Pnma, Z=4) (Tateno et al. 2019).

As Fe\textsubscript{2}S is observed coexisting with Fe on the liquidus at pressures related to Earth’s outer core (136–360 GPa), investigating its material properties has become the focus of recent investigations (Tateno et al. 2019; Zurkowski et al. in press). Tateno et al. (2019) measured the volume of Fe\textsubscript{2}S between 190 and 306 GPa and determined that its unit-cell parameters and diffraction angles are compatible with an orthorhombic lattice with space group Pnma. In particular, the c/a ratio measured for Fe\textsubscript{2}S is similar to that of the Co\textsubscript{2}Si structure type (C\textsubscript{37}, Pnma, Z=4) (Geller and Wolontis, 1955) (Figure 1). The recent crystallographic analyses of Fe\textsubscript{2}S synthesized at ~90 GPa and 2400 K established that Fe\textsubscript{2}S assumes a C\textsubscript{23} structure at these conditions (Co\textsubscript{2}P-type, Pnma, Z=4) (Zurkowski et al. in press) (Figure 1). To resolve the differences in observations between these two recent studies, a C\textsubscript{23}–C\textsubscript{37} transition in Fe\textsubscript{2}S must occur in the 90–190 GPa pressure range. Furthermore, a C\textsubscript{23}–C\textsubscript{37} pressure-induced transition has been recently reported in Fe\textsubscript{2}P around 42 GPa (Nakajima et al. 2020), supporting that pressure plays a role in shaping the Co\textsubscript{2}P structure type into the Co\textsubscript{2}Si structure type, as the Fe–P system has been shown to be a low-pressure analog to the Fe–S system (e.g. Gu et al. 2016).

Comparing the C\textsubscript{23} and C\textsubscript{37} structures may provide insight into the plausible mechanism for a pressure-induced C\textsubscript{23}–C\textsubscript{37} transition. These structures are routinely compared on the basis of their relative unit cells and coordination environments (e.g. Rundqvist 1960; Shoemaker and Shoemaker, 1965; Rundqvist and Nawapong, 1966; Jeitschko and Altmeyer, 1990; Nakajima et al. 2020). The C\textsubscript{23} and C\textsubscript{37} structures have the same site symmetries, space group, and formula units per cell, but the C\textsubscript{37} structure is distinct from the C\textsubscript{23} structure based on its relatively larger b and c axes and shorter a axis (Figure 1). The C\textsubscript{23} structure is composed of MX\textsubscript{4}}
tetrahedra and $MX_5$ square pyramids while the $C_{37}$ structure is composed of $MX_5$ dipyramids and $MX_5$ square pyramids (Figure 1). The additional $M-X$ bond in the $C_{37} MX_5$ dipyramid compared to the $C_{23} MX_4$ tetrahedra is oriented along the $a$ direction. The $C_{37}$ structure can therefore be seen as a distortion of the $C_{23}$ structure: the $C_{37}$ structure forms from the $C_{23}$ structure by shortening the $a$ axis and lengthening the $b$ and $c$ axes, resulting in a 4- to 5-fold coordination change with the next nearest $X$ site along the $a$ direction.

This work investigates the compression behavior of orthorhombic $Fe_2S$ using powder and multigrain X-ray diffraction techniques between 29 and 194 GPa and to 2500 K. A $C_{23}$-like $Fe_2S$ phase is observed between 30 and 120 GPa and at high temperatures. Between 120 and 150 GPa, a softening of the $a$ axis and relative stiffening of the $b$ and $c$ axes is measured, and, above 150 GPa, a $C_{37}$-like unit-cell of $Fe_2S$ is observed. A sharp $C_{23}$–$C_{37}$ transition is not observed; instead, the $C_{23}$ $Fe_2S$ unit-cell evolves towards a $C_{37}$ structure with pressure and this behavior intensifies in the 120-150 GPa pressure range, likely as a result of the onset of a 4- to 5-fold coordination change on the FeS$_4$ tetrahedral sites. $Fe_2S$ is observed in this study to coexist with hcp-Fe, and, as the $C_{23}$–$C_{37}$ $Fe_2S$ transition occurs around core-mantle boundary pressures and high temperatures, this transition in $Fe_2S$ is important to consider in the context of Earth’s core chemistry and dynamics. A thermal equation of state (EoS) is presented for $C_{23} Fe_2S$ to 120 GPa and a volume reduction is applied to characterize the $P-V-T$ behavior of $C_{37} Fe_2S$ above 150 GPa. Comparing the calculated density of $C_{37} Fe_2S$ with that of hcp-Fe (Dewaele et al. 2006) and the seismologically determined densities at CMB and ICB conditions (Dziewonski and Anderson, 1981; Irving et al. 2018), the sulfur content of a purely Fe–S core is presented.
MATERIALS AND METHODS

In this study, Fe$_2$S was observed in experiments on Fe-rich Fe–S and also Fe–S–O compositions. Previous single crystal analyses of Fe$_2$S at 90 GPa and 2400 K (Zurkowski et al. in press) indicate that Fe$_2$S forms in an oxygen-free system with all sites occupied by sulfur. Observations of Fe$_2$S in FeO saturated compositions are therefore included in this study, as differences in measured Fe$_2$S volumes are not discernable between the Fe–S and Fe–S–O compositions. Starting powders for these experiments consisted of Fe (99.9+%, <10μm, Alfa Aesar), iron sulfide (FeS, 99.99%, Alfa Aesar) and iron oxide (FeO, 99.5%, Alfa Aesar) powders. Two Fe-FeS compositions were weighed: Fe–12.5S, Fe–23S (dashed notation indicates wt%). The Fe-FeS compositions were homogenized in a mortar and pestle for 1 hour in alcohol, dried and then mixed dry for a short duration to reset any density settling during alcohol evaporation. Fe-S-O mixtures were homogenized in alcohol in a ball mill for 1.5-3 hours at 20 Hz, dried and then ball milled dry for a short duration to reset any density segregation. The final Fe–S–O starting compositions were measured by SEM: Fe–13S–5O, Fe–17S–5O, Fe–6S–12O, Fe–3O–7S, and Fe– 4O–8S.

The starting material was compressed into foils between two ungasketed diamond anvils prior to loading into the diamond anvil cell (DAC). Type I diamonds and tungsten carbide or cBN seats as well as Boehler-Almax conical diamonds and seats were used for the high-pressure experiments. The culet sizes ranged from 300-50 μm. Sample foils were loaded into rhenium gaskets preindentated to 28-40 GPa with 120-25 μm diameter sample chambers. Samples were loaded in KCl, KBr, NaCl, SiO$_2$, or Ne pressure media and were dried at 100ºC for 30 minutes prior to gas loading or pressurization.
Angle dispersive X-ray diffraction (XRD) experiments took place at Argonne National Laboratory, Sector 13 ID-D (GeoSoilEnviroCars) of the Advanced Photon Source. Data was collected with a 2 μm x 3 μm full width at half maximum incident X-ray beam with energy of 37 or 42 keV. Diffracted X-rays were collected using a CdTe 1M Pilatus detector or a MarCCD detector with a typical exposure time of 1-2 s. The sample to detector geometry was calibrated using the diffraction of LaB$_6$ NIST standard at 1 bar.

Double-sided laser heating was conducted using fiber lasers shaped with a flat top ~10 μm radius spot size. The X-ray beam and laser were aligned using the X-ray induced fluorescence of the alkali halide pressure media and sample, ruby or the gasket (Prakapenka et al. 2008). Temperature was measured spectroradiometrically (Heinz and Jeanloz, 1987) during XRD collection using a gray body approximation of the thermal emission from a 6 μm diameter region at the center of the laser heated spot. A 3% correction was applied to account for axial temperature gradients through the sample (Campbell et al. 2007; 2009). Samples were typically heated for 15-30 minutes.

Rotational scans of the sample chamber were collected upon quench during select experiments. Upon quenching from target temperatures, rotation XRD images were collected spanning ±17 to ±30º depending on the angular opening of the cell. During rotation, diffraction images were collected in 0.25º-0.5º steps with exposure times of 1–2 s at each step. Grains of the target Fe$_2$S phase were then identified in reciprocal space (Rigaku OD, 2018).

Powder diffraction data were integrated using Dioptas (Prescher and Prakapenka, 2015). Peaks were fitted using Fityk (Wojdyr, 2010) and lattice parameters from each measurement were obtained on the basis of an orthorhombic Fe$_2$S cell. For runs where rotational scans were
performed, data from individual grains of Fe₂S were indexed using Crysallis Pro (Rigaku OD, 2018).

RESULTS AND DISCUSSION

Evidence for a C23–C37 transition in Fe₂S

Between 30 and 194 GPa and upon heating to subsolidus temperatures, in all compositions examined, hcp-Fe (and FeO, if oxygen was present) was observed in the diffraction patterns coexisting with a set of diffraction angles that cannot be accounted for by the tetragonal Fe₂S phase that is reported to be stable at higher temperatures in this pressure range (e.g. Ozawa et al. 2013; Seagle et al. 2006; Thompson et al. 2020) (Figure 2). The peaks were instead indexed to an orthorhombic lattice with a volume equal to 4 formula units of Fe₂S. As shown in the example provided in Figure 2a, the diffraction angles measured for Fe₂S at 74(1) GPa and 1750(110) K fit to an orthorhombic unit-cell with parameters: 

\[ a = 5.253(2) \text{ Å}, \quad b = 3.328(2) \text{ Å}, \quad c = 6.222(3) \text{ Å}. \]

This cell is compatible with that reported for C23 Fe₂S at 90 GPa (Zurkowski et al. in press). In contrast, at 169(1) GPa and 2100(120) K (Figure 2b), Fe₂S is observed with unit cell parameters: 

\[ a = 4.561(3) \text{ Å}, \quad b = 3.281(3) \text{ Å}, \quad c = 6.145(5) \text{ Å}, \]

in agreement with the C37-like Fe₂S unit-cell geometry reported by Tateno et al. (2019) at ~190 GPa.

The high temperature observations of Fe₂S in P-T space are shown in Figure 3 and all data associated with these measurements are given in Appendix A1. The light blue data indicate the stability of a C23-like Fe₂S, including the data from Zurkowski et al. (in press), and the emerald green data indicate the stability of C37 Fe₂S, including the data from Tateno et al. (2019). The
split blue-green data points represent the region where the measured Fe$_2$S unit-cell is transitional between the C23 and C37 structures. The observed C23 and C37 unit cells suggest that the structural evolution of Fe$_2$S is more sensitive to pressure than temperature (Figure 3). The C23, transitional, and C37 Fe$_2$S phase fields plotted in Figure 3 were determined based on the evolution of the measured unit cell parameters with pressure (Figure 4, including the data by Zurkowski et al. *in press* and Tateno et al. 2019). Between 29 and 306 GPa, Fe$_2$S exhibits pronounced anisotropic compression, wherein the $a$ axis is more compressible than the $b$ and $c$ axes (Figure 4a). A more rapid softening of the $a$ axis and relative stiffening of the $b$ and $c$ axes is observed above $\sim$120 GPa, indicating a change in compressibility of the structure. Stiffening of the $a$ axis and softening of the $b$ and $c$ axis is further observed above $\sim$150 GPa, marking another structural change in Fe$_2$S (Figure 4a). The Fe$_2$S unit-cell geometries reported by Zurkowski et al. (in press) and Tateno et al. (2019) support the trend observed in Figure 4a; namely a C23 Fe$_2$S cell between 30 and $\sim$120 GPa and a C37 Fe$_2$S unit cell above $\sim$150 GPa. Between these pressures, the unit cell geometry is transitional between the C23 and C37 lattices.

The compressional behavior of Fe$_2$S can also be viewed in terms of the $c/a$ ratio trend and systematically compared to the $c/a$ ratio of the Co$_2$P and Co$_2$Si structure types (Figure 4b). The relative unit cells of $M_2X$ and $MX_2$ structures with these site symmetries have been routinely compared and grouped into Co$_2$P- and Co$_2$Si-branches of the PbCl$_2$ family in previous studies (e.g. Rundqvist 1960; Shoemaker and Shoemaker, 1965; Rundqvist and Nawapong, 1966; Jeitschko and Altmeyer, 1990; Nakajima et al. 2020). At ambient conditions, Co$_2$P and Co$_2$Si have $c/a$ ratios of 1.19 and 1.44 respectively (dashed horizontal lines in Figure 4b), and here we take these values as characteristic of their two structure types and associated with the difference in their cation coordinations. Up to 112 GPa, the Fe$_2$S $c/a$ ratio shows a nearly linear trend.
increasing from around 1.14 at 29 GPa to 1.22 at 112 GPa, similar to that of the Co$_2$P structure type (Figure 4b). Between 159 GPa and 306 GPa, the Fe$_2$S $c/a$ ratios show an approximately linearly increasing trend with $c/a$ ratios ranging from 1.34–1.40, more like that of the Co$_2$Si structure type (Figure 4b). Across the pressure range of this study (30-194 GPa), the data trend along an S-shaped curve where Fe$_2$S is more rapidly evolving from a C23- to a C37-like unit cell in the 120–150 GPa transitional pressure range. The inflection point in this trend occurs around 142 GPa, marking the possible cut-off pressure between the C23 and C37 structural stabilities (Figure 4).

Based on the systematic comparison between the C23 and C37 structures (Figure 1), a highly compressible $a$ axis and the onset of bonding between Fe and the next nearest S site along the $a$ direction is necessary for a C23–C37 pressure-induced transition. The unit-cell compression of Fe$_2$S shown in Figure 4 demonstrates this pronounced anisotropic compression behavior. The softening of the $a$ axis above 120 GPa may also indicate the onset of a coordination change, and the final compressibility change above 150 GPa may mark its completion. Further crystallographic analysis is required to better characterize the details of the Fe$_2$S atomic arrangement across this transition, but it is clear that Fe$_2$S exhibits distinct structural changes in this pressure range that are supportive of the requisite behavior of a pressure-induced C23–C37 transition.

Previous studies have reported analogous C23–C37 transitions in other $M_2X$ compounds, including PbF$_2$ at 10 GPa and Fe$_2$P at 42 GPa (Haines et al. 1998; Nakajima et al. 2020). These lower pressure studies observe the C23–C37 $M_2X$ transition to occur over a few GPa, whereas changes in compressibility of Fe$_2$S bracket a C23–C37 Fe$_2$S transition across ~30 GPa pressure range above 120 GPa. The difference in chemistry and the higher transition pressures observed
in Fe$_2$S compared to PbF$_2$ and Fe$_2$P may play a role in the difference in behavior across the transition, but further compression experiments are needed to better characterize the structural changes in these phases during the respective C23–C37 transitions.

**Equation of state of C23 and C37 Fe$_2$S**

The measured volumes of Fe$_2$S between 29 and 194 GPa are plotted in Figure 5 along with the Fe$_2$S volumes reported by Zurkowski et al. (in press) and Tateno et al. (2019). As Fe$_2$S is observed to undergo a change in compressibility above 120 GPa and again above 150 GPa (Figure 4), a thermal equation of state was fit only to the C23 Fe$_2$S volumes measured below the first compressibility change (<120 GPa, Figure 4). The C23 Fe$_2$S P-V data were fitted to a Mie-Grüneisen EoS given in Equation 1. The $P_{300}(V)$ term in Equation 1 (expanded in Equation 2) is a third-order Birch-Murnaghan EoS (Birch, 1952) fit to the room temperature P-V data via the isothermal bulk modulus, $K_0$; pressure derivative, $K'$; and zero-pressure volume, $V_0$. High temperature data were fitted using the Grüneisen parameter ($\gamma$, Equation 3) and the Debye model of vibrational energy relating thermal energy $E$ with $\gamma$ and Debye temperature ($\theta_D$, Equation 4). To decrease the number of fitted parameters, anharmonic and electronic contributions to thermal pressure were not included, and the one bar Grüneisen parameter, $\gamma_0$, was fit to our high temperature data with $\theta_0$ and q fixed to 400 K and 1, respectively.

1. $P(V, T) = P_{300}(V) + (\gamma/V)[E(\theta_D, T) - E_{300}(\theta_D, 300)]$

2. $P_{300}(V) = 3K_0f(1 + 2f)^{2.5} \cdot (1 + 1.5(K' - 4)f), f = 0.5 * ((V/V_0)^{(2/3)} - 1)$

3. $\gamma = \gamma_0 (V/V_0)^q$

4. $\theta_D = \theta_0 \exp[\gamma_0(1 - (V/V_0)^q)/q]$
The fitted C23 Fe\(_2\)S equation of state is listed in Table 1 and the covariance in the EoS parameters are plotted in Figure S1. The room temperature, 1000 K, 2000 K and 3000 K isotherms calculated from this EoS fit are plotted in Figure 5. Pressure residuals for the C23 Fe\(_2\)S data (<120 GPa) show a root mean square value of ~1.5 GPa (Figure 5b). The pressure residuals for the Fe\(_2\)S measurements in the 120–194 GPa range (triangles, Figure 5) and those reported by Tateno et al. (2019) were calculated based on the EoS and plotted in Figure 5b. These data are not well described by the C23 Fe\(_2\)S equation of state, supporting the observed structural changes in Fe\(_2\)S above 120 GPa.

As C37 Fe\(_2\)S is only observed above 150 GPa, the low pressure data necessary for adequately describing its EoS parameters are lacking. To characterize the \(P-V-T\) behavior of C37 Fe\(_2\)S, we assume here that its compressional and thermal behavior are identical to the C23 phase, with only a different volume \(V_0\). The high-temperature volume residuals observed for C37 Fe\(_2\)S above 150 GPa show an average 1.6% decrease in volume compared to the C23 Fe\(_2\)S thermal EoS (Figure S2). As the C23 and C37 structure types are closely related and low pressure (<150 GPa) data for C37 Fe\(_2\)S is not available, a C37 Fe\(_2\)S EoS was constructed by applying this volume change to the C23 Fe\(_2\)S thermal equation of state, while keeping the \(K_0, K',\) and \(\gamma_0\) parameters fixed. The resulting modified thermal equation of state is plotted with the high temperature C37 data (>150 GPa) in Figure 6. The 120–150 GPa pressure range was not included in this volume change calculation, as a phase transition is likely occurring.

The 300 K C37 Fe\(_2\)S data reported in the Tateno et al. (2019) study show anomalously high volumes compared to the high temperature C37 Fe\(_2\)S volumes measured in this study (Figure 5). In the Tateno et al. (2019) study, Fe\(_2\)S was synthesized at high pressures and temperatures, quenched, and decompressed at 300 K in an MgO pressure medium, a significantly harder
medium compared to Ne or NaCl mediums used to collect the room temperature data reported in this study. The greater room temperature Fe\(_2\)S volumes measured in the Tateno et al. (2019) study may be a consequence of the more nonhydrostatic nature of the ceramic medium compared to alkali halide and noble gas media, and future room temperature decompression measurements on C\(_{37}\) Fe\(_2\)S synthesized in neon would benefit the EoS fitting presented here and resolve the difference in volume of Fe\(_2\)S reported in this study compared to that of Tateno et al. (2019).

**IMPLICATIONS**

The C\(_{23}\)–C\(_{37}\) Fe\(_2\)S transitional pressure range (120-150 GPa) encompasses core-mantle boundary pressures. As Fe\(_2\)S is observed in this study coexisting with hcp-Fe at moderate temperatures, further experimental work is required to understand how the C\(_{23}\)–C\(_{37}\) Fe\(_2\)S transition affects the thermodynamics and phase relations in Fe-rich systems at core-mantle boundary conditions. Furthermore, at pressure beyond the C\(_{23}\)–C\(_{37}\) transition in Fe\(_2\)S, anisotropic compression of C\(_{37}\) Fe\(_2\)S is observed to still higher pressures, where the \(a\) axis continues to compress more rapidly than the \(b\) and \(c\) axes (this study, Tateno et al. 2019). As C\(_{37}\)-like Fe\(_2\)S is observed in Fe-rich systems on the liquidus to at least 306 GPa (Tateno et al. 2019), any further structural transitions in C\(_{37}\) Fe\(_2\)S may be addressed in future experiments as this phase, or a high-pressure polymorph of it, may be relevant to the thermodynamics ofsolidification at Earth’s inner core boundary.

To constrain the possible sulfur contribution to the density of Earth’s multicomponent core, the density profile of Fe\(_2\)S was calculated using the C\(_{37}\) Fe\(_2\)S EoS and extrapolated throughout the core. As the C\(_{37}\) Fe\(_2\)S phase is stable at core mantle boundary pressures and high temperatures, the C\(_{37}\) Fe\(_2\)S density profile extrapolated through the core provides an important

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addition to previous Fe-sulfide EoS studies (e.g. Fei et al. 2000; Kamada et al. 2014; Seagle et al. 2006; Tateno et al. 2019). The densities of \( \text{Fe}_2\text{S} \) calculated at CMB and ICB conditions were then combined with that of hcp-Fe (Dewaele et al. 2006) and compared to the seismologically determined CMB density reported by Irving et al. (2018) and the ICB density reported by the PREM model (Dziewonski and Anderson, 1981). Results from the Irving et al. (2018) study of the outer core is used for the CMB density calculations in this study, as this work reported elastic parameters that better predict the observed normal mode frequencies and body wave models for the outer core. A CMB density and pressure of 10.05 g/cm\(^3\) and 135.8 GPa (Irving et al. 2018) and an ICB density and pressure of 12.8 g/cm\(^3\) and 328.9 GPa (Dziewonski and Anderson, 1981) was implemented into our calculations, respectively. An adiabatic temperature profile for the outer core (Birch, 1952), a 1% volume increase from solid to liquid iron alloy (Anderson, 2003), and a CMB temperature set at 4000 ± 500 K (Anderson, 2003) was assumed. The inner core boundary temperature, calculated along the hcp-Fe adiabat, was determined to be 5200 ± 500 K.

Figure 7 shows the adiabatic density profiles of \( C37 \text{ Fe}_2\text{S} \) (this study) (blue) and hcp-Fe (Dewaele et al. 2006) (red), compared to the density profile for the outer core and inner core (Dziewonski and Anderson, 1981; Irving et al. 2018). Comparing these density trends, 13.9 ± 1.5% S is required to match CMB density and 8.6 ± 0.8 wt% S is required to match the ICB density. Previous iron sulfide equations of state studies conclude that 11-16 wt% S is required to match the density deficit at the CMB (e.g., Seagle et al. 2006; Thompson et al. 2016; Thompson et al. 2020) and 6.9 ± 0.9 wt% S is required to match the ICB density deficit (Kamada et al. 2014). Within error, the calculated CMB and ICB sulfur concentrations reported in this study are in good agreement with these previous works.
Earth’s core is likely a multicomponent system with significant compositional contributions from cosmochemically abundant light elements such as S, Si, O, C, and H (McDonough 2003). From the density extrapolations presented here, it is apparent that the curvature of the liquid Fe$_2$S and Fe and the liquid outer core density profiles do not match, indicating that the density and sound velocities of a purely Fe–S core would not satisfy geophysical constraints. Furthermore, melting studies of the Fe-Fe$_2$S system report 5.7 ± 0.3 wt% S in the eutectic liquid at 250 GPa, and the eutectic liquid composition is likely more Fe-rich at ICB conditions (Mori et al. 2017; Tateno et al. 2019). Results from this work combined with that of Kamada et al. (2014) predict 6.9–8.6 wt% S to match the density at the inner core boundary, suggesting that the sulfur content of a purely Fe-S core may be on the S-rich side of the Fe-liquidus field, violating the observed presence of a denser inner core (Mori et al. 2017; Tateno et al. 2019). The novel equation of state for C37 Fe$_2$S reported here agrees with previous iron-sulfide EoS studies (e.g., Seagle et al. 2006; Thompson et al. 2016; Thompson et al. 2020; Kamada et al. 2014) and improves quantification of the density and elasticity of Fe-S alloys by presenting $P$-$V$ data at outer core pressures and high temperatures. In comparison to geophysical constraints on the density, melting, and crystallization sequences of Earth’s iron-rich core, this work also supports that sulfur is likely not the sole core-alloying light element, but rather a contributor to the chemistry and dynamics occurring in Earth’s complex core.
ACKNOWLEDGMENTS

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Tao, R. and Fei, Y. (2021) High-pressure experimental constraints of partitioning behavior of Si


FIGURE CAPTIONS

Figure 1. Comparison between the a) C23, Co2P-type and b) C37, Co2Si type structures (Geller and Wolontis, 1955; Rundvist, 1960) that are inferred in this Fe2S study. The C23 structure is composed of CoP₅ square pyramid (green) and CoP₄ tetrahedral (blue) building blocks. The C37 structure is composed of CoP₅ square pyramid (green) and CoP₅ dipyramid (blue) building blocks. The C23 and C37 structures are closely related: both structures have the same symmetry, are orthorhombic and adopt the Pnma (Z=4) space group. The C37 structure can be seen as a distortion of the C23 structure; namely, the Co2Si structure can be formed from the Co2P structure by shortening the a axis and lengthening the b and c axes and inducing a coordination change from a 4-fold tetrahedral site (blue polyhedra) in Co2P to a 5-fold dipyramid site (blue polyhedra) in Co2Si.

Figure 2. Integrated X-ray diffraction patterns exemplifying the observations of Fe2S at high P-T. a) At 74(1) GPa and 1750(110) K, Fe2S is observed coexisting with hcp-Fe and B1 FeO in a KCl medium. The Fe–12S–5O (wt%) starting composition is shown by the star in the ternary. The fitted lattice parameters of Fe2S support a C23 unit cell. The calculated diffraction angles based on this fit are plotted as the red dashed vertical lines, and prominent peaks of C23 Fe2S are labeled with their corresponding Miller indices in light blue. Two low intensity unidentified
peaks are marked by the question mark (?) and may represent the initial peaks of the higher
temperature Fe$_3$S phase. b) At 169(1) GPa and 2100(120) K, Fe$_2$S is observed coexisting with
hcp-Fe in a SiO$_2$ pressure medium. The starting composition is Fe–12.5S (wt%) and given by the
star in the ternary. The fitted lattice parameters of Fe$_2$S support a C37-like unit cell. The
calculated diffraction angles based on this fit are plotted as the red dashed vertical lines and
prominent peaks of C37 Fe$_2$S are labeled with their corresponding Miller indices in emerald
green. One unidentified peak at around 17.5º 2Θ is distinguishable from the background and
marked by the question mark.

**Figure 3.** The phase stability of C23 and C37 Fe$_2$S in pressure-temperature space. The blue
circles indicate observations of a C23-like unit cell of Fe$_2$S in this study. The blue star at 89 GPa
and 2380 K refers to the single crystal study by Zurkowski et al. (in press) in which the structure
of Fe$_2$S was determined to be C23 after temperature quenching from these conditions. The
emerald circles represent observations of a C37-like unit cell of Fe$_2$S in this study. The emerald
squares refer to the Tateno et al. (2019) study, where a C37 Fe$_2$S unit cell was measured above
190 GPa. The split blue/green data between 110 and 150 GPa indicate the observations of a
transitional C23–C37 Fe$_2$S unit-cell.

**Figure 4. a)** Relative lattice parameters measured for Fe$_2$S in this study (circles) along with the
data reported by Tateno et al. (2019) (squares) and Zurkowski et al. (in press) (stars). The shaded
regions encompass the data that is more compatible with a Co$_2$P-like unit-cell (light blue
shading) and data more compatible with a Co$_2$Si-like unit-cell (green shading). The shaded
regions overlap where the relative lattice parameters measured along the $a$ axis soften as the $b$
and $c$ axes stiffen between ~110-150 GPa, indicating a potential transitional pressure range between these two structure types. The red, vertical dashed line represents this $C23–C37$ cut-off.

b) $C/a$ ratio measured for Fe$_2$S in this study (circles) along with the data reported by Tateno et al. (2019) (squares) and Zurkowski et al. (in press) (star). The horizontal dashed lines indicate the $c/a$ ratio determined for Co$_2$P (light blue) (Rundqvist, 1960) and Co$_2$Si (emerald green) (Geller and Wolontis, 1955). The shaded regions encompass the data that is more compatible with a Co$_2$P-like $c/a$ ratio (light blue shading) and data more compatible with a Co$_2$Si-like $c/a$ ratio (green shading). As the $c/a$ ratios measured evolve smoothly from Co$_2$P-like to Co$_2$Si-like, the shaded regions overlap in the potentially transitional pressure range. The inflection point in this S-shaped $c/a$ ratio trend occurs around 142 GPa, differentiating the more $C23$-like and $C37$-like unit-cells of Fe$_2$S. The red, vertical dashed line represents this $C23–C37$ cut-off.

Figure 5. a) $P-V$ data for Fe$_2$S (color coded for temperature) collected in this study (circles, triangles), Zurkowski et al. (in press) (stars), and Tateno et al. (2019) (squares). The 300 K (black), 1000 K (green), 2000 K (orange) and 3000 K (red) isotherms (solid lines) were calculated based on the thermal EoS fit to $C23$ Fe$_2$S data collected up to 120 GPa in this study and the study by Zurkowski et al. (in press) (~90 GPa, stars) (Table 1). The dashed line and label brackets the Fe$_2$S volumes included in the fit. The Fe$_2$S volumes measured above 120 GP are not included in the EoS fit as the lattice parameters indicate a change in compressibility and phase transition to the $C37$ structure. For comparison, the Bazhanova et al. (2017) calculated 300 K EoS for $Pnma$ Fe$_2$S (dashed-dot line) is included. The shaded regions represent the pressure ranges where $C23$-like (light blue), transitional (blue green), and $C37$-like (light green) Fe$_2$S structures are observed. The red, vertical dashed line represents this $C23–C37$ cut-off determined...
in Figure 4. b) Residuals to the EoS fit 1 are plotted with an r.m.s. of ~1.5 for the fitted C23 Fe$_2$S data (<120 GPa) (filled circles). The plotted open triangles depict the difference in pressure calculated from this EoS versus measured pressure for the Fe$_2$S data in the transitional and C37 Fe$_2$S pressure range. The black squares show the same comparison for the data reported by Tateno et al. (2019).

Figure 6. P-V data collected on C23 Fe$_2$S (<120 GPa, light blue shaded region), C37 Fe$_2$S (>150 GPa, green shaded region) and the transitional cell (120-150 GPa, blue-green shaded region) in this study up to 194 GPa and to 2500 K. The equation of state fit to the C23 Fe$_2$S data is plotted up to 120 GPa and is color coded for temperature. The C37 Fe$_2$S volume residuals for this equation of state show an average 1.6% volume reduction in Fe$_2$S above 150 GPa. This volume reduction was applied to the C23 Fe$_2$S equation of state, keeping $K_0$, $K'$, and $\gamma_0$ fixed, and plotted above 150 GPa. The overlap in the C23 (blue) and C37 (green) shaded regions in the 120-150 GPa pressure range indicates the pressure range where C23-like Fe$_2$S transitions to the C37-like structure. This pressure range was not included in the volume reduction calculation. The red, vertical dashed line represents the C23–C37 cut-off determined in Figure 4.

Figure 7. Calculated adiabatic density curves for liquid C37 Fe$_2$S (blue) and liquid hcp-Fe (red) (Dewaele et al. 2006) plotted with the density profiles of the outer core based on the PREM model (Dziewonski and Anderson, 1981) (solid black line) and Irving et al. (2018) (dashed black line).
Table 1. EoS parameters for Fe$_2$S calculated based on the volumes measured in this study.

<table>
<thead>
<tr>
<th>$V_0$ (cm$^3$/mol)</th>
<th>$K_0$ (GPa)</th>
<th>$K'$</th>
<th>$\gamma_0$</th>
<th>$q$</th>
<th>$T_0$ (K)</th>
<th>Dataset</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.6(3)</td>
<td>138(22)</td>
<td>5.6(7)</td>
<td>2.59(8)</td>
<td>1</td>
<td>400</td>
<td>C23 Fe$_2$S EoS fitted to the C23 Fe$_2$S volumes measured in this study (&lt; 120 GPa) and combined with the Fe$_2$S data from Zurkowski et al. 2021</td>
</tr>
</tbody>
</table>
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Figure 1, Revision 1

a) C23 Co₂P

b) C37 Co₂Si
Figure 3, Revision 1

Color
- C23 Fe\(_2\)S
- C37 Fe\(_2\)S

Symbol
- This Study
- Tateno et al. 2019
- Zurkowski et al. in press

Temperature (K)

Pressure (GPa)

C23 Fe\(_2\)S

C37 Fe\(_2\)S
Revision 1

Figure 5, Revision 1

(a) Rackly, Revision 1

Color
- >2500 K
- 1500-2500 K
- 500-1500 K
- 300 K

Symbol
- C23-like Fe₂S
- Żurkowski et al. in press
- transitional/C37-like Fe₂S
- Tateno et al. 2019

(b) Rackly, Revision 1

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Figure 7, Revision 1

- PREM
- Irving et al. 2018
- hcp-Fe, Dewaele et al. 2006
- C37 Fe2S

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