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**Revision 3**

**Density Determination of Liquid Iron–Nickel–Sulfur at High Pressure**

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19

20 **Abstract**

21 The density of liquid iron–nickel–sulfur ( $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$ ) alloy was determined at  
22 pressures up to 74 GPa and an average temperature of 3400 K via pair distribution  
23 function (PDF) analysis of synchrotron X-ray diffraction (XRD) data obtained using  
24 laser-heated diamond anvil cells. The determined density of liquid  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  at 74  
25 GPa and 3400 K is  $8.03(35) \text{ g/cm}^3$ , 15% lower than that of pure liquid Fe. The obtained  
26 density data were fitted to a third-order Vinet equation of state (EoS), and the  
27 determined isothermal bulk modulus and its pressure derivative at 24.6 GPa are  $K_{TP_r} =$   
28  $110.5(250) \text{ GPa}$  and  $K'_{TP_r} = 7.2 (25)$ , respectively, with a fixed density of  $\rho_{Pr} = 6.43$   
29  $\text{g/cm}^3$  at 24.6 GPa. The change in the atomic volume of  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  upon melting was  
30 found to be approximately 10% at the melting temperature, a significantly larger value

31 than that of pure Fe (~3%). Combined with the above EoS parameters and the thermal  
32 dependence reported in the literature, our data were extrapolated to the outer core  
33 conditions of the Earth. Assuming that S is the only light element and considering the  
34 range of suggested Ni content, we estimated a 5.3-6.6wt% S content in the Earth's outer  
35 core.

36 **Keywords:** liquid iron alloy, high pressure, Fe<sub>3</sub>S, Earth's outer core

37

38

## Introduction

39 The liquid outer core of the Earth primarily comprises iron (Fe)–nickel (Ni) alloyed  
40 with lighter elements. Recent measurements of the density contrast between the liquid  
41 outer core and pure liquid Fe were estimated to be 7.6%, assuming an adiabatic  
42 temperature profile with an inner core boundary temperature of 5400 K (Kuwayama et al.  
43 2020). Both the nature and number of light elements in the core have remained to be the  
44 two biggest enigmas in Earth sciences for more than 60 years (Birch, 1961). In this study,  
45 we focus on sulfur (S) as a potential light element in the Earth's core. S has a high

46 solubility in liquid Fe at low pressures (Fei et al. 1997, 2000; Li et al. 2001; Stewart et al.  
47 2007) and is missing in the mantle compared with other volatile elements (Murthy and  
48 Hall, 1970). Owing to its high volatility, S was limited to ~1.7wt% in core composition  
49 models (Dreibus and Palme, 1996). However, recently, high-pressure partitioning  
50 experiments revised this value to greater than 6wt% (Mahan et al. 2017). Therefore,  
51 from a geochemical perspective, S can be the primary light element in the Earth's core.

52 The density and sound velocity of the Earth's liquid outer core can be obtained from  
53 seismic observations such as the Preliminary Reference Earth Model (PREM,  
54 Dziewonski and Anderson, 1981). Recently, we determined the sound velocity of liquid  
55 Fe–Ni–S alloys at pressures up to 52 GPa in diamond anvil cells (DACs) using  
56 high-resolution inelastic X-ray scattering (Kawaguchi et al. 2017). Moreover, we  
57 discussed the S content in the Earth's outer core Earth based on sound velocity data and  
58 concluded the compatibility of seismic data using 5.8wt%–7.5wt% S in the Earth's outer  
59 core, suggesting S as the primary light element in the Earth's core. To complete this  
60 preceding study, we performed density measurements of liquid Fe–S alloys at pressures

61 corresponding to those in the Earth's core.

62 The density of liquid Fe alloys under extreme conditions were successfully  
63 determined using Paris–Edinburgh press and DAC via pair distribution function analysis  
64 of liquid diffuse signals in X-ray diffraction (XRD) patterns (Eggert et al, 2002; Morard  
65 et al. 2013; Morard et al. 2018; Kuwayama et al. 2020). Herein, we use this method to  
66 determine the density of liquid  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  in DAC at pressures up to 70 GPa and an  
67 average temperature of 3400 K. Further, we employ our findings to construct the  
68 isothermal equation of state (EoS).

69

70

## Method

71 We determined the density of liquid  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  via XRD measurements at the  
72 BL10XU beamline at SPring-8 (Hirao et al. 2020).  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  synthesized in a  
73 multianvil apparatus was used as the samples in all runs. The sample composition was  
74 determined using field emission-electron probe microanalysis before loading. The  
75 sample pellets were cut into  $\phi 30\text{--}50\text{-}\mu\text{m}$  pieces and loaded into a sample hole drilled in a

76 rhenium gasket with a pressure medium (a dry potassium chloride (KCl) powder). The  
77 samples were compressed to the pressures of interest using single crystal diamond anvils  
78 with 300- $\mu\text{m}$  culets. Then, they were heated using a double-sided laser-heating system to  
79 minimize the axial temperature gradient. The heating spot sizes on the samples were 25–  
80 40  $\mu\text{m}$ . The temperature was measured using a spectroradiometric method, the variation  
81 of which was approximately 10%. The X-ray was monochromatized to 30 and 50 keV  
82 using liquid nitrogen-cooled silicon (Si)(111) and Si(220) double crystals. The X-ray  
83 compound refractive lenses achieved a focus of approximately  $\sim 8 \mu\text{m}$  (H)  $\times$   $8 \mu\text{m}$  (V)  
84 at 30 keV and  $10 \mu\text{m}$  (H)  $\times$   $12 \mu\text{m}$  (V) at 50 keV (full width at half maximum),  
85 which were sufficiently small compared with the laser beam size. Two-dimensional (2D)  
86 XRD images were captured on a charge-coupled device detector (SMART APEX,  
87 Bruker AX) and X-ray flat-panel detector (XRD0822, PerkinElmer, Inc.) with an  
88 exposure time of 1–10 seconds. We used IPAnalyzer and PDIndexer (Seto et al. 2010)  
89 for the X-ray energy and camera-length calibration and one-dimensional (1D)  
90 integration calculation of 2D XRD images. The pressure was determined using the KCl

91 unit-cell volume with high-temperature thermal EoS proposed in Tateno et al. (2019).  
92 Additionally, we collected powder XRD patterns of  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  at 1 atm in a  
93 temperature range of 100–400 K at the BL02B2 beamline at SPring-8 (Kawaguchi et al.  
94 2017). The X-ray energy was 30 keV using water-cooled Si(111) double crystals; XRD  
95 data were collected using multiple 1D detectors (MYTHEN 1K, Dectris) in the  
96 temperature range of 100–400 K. Note that 24.8 keV X-ray was used for the XRD data  
97 collection for structural refinement. We performed structural refinements by the Rietveld  
98 method using JANA2006 (Petricek et al. 2006).

99

100

## Results

101 We conducted nine separate experiments to collect XRD data of  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  at  
102 pressures up to 70 GPa. Table 1 lists the density, pressure, and temperature, KCl unit-cell  
103 volume, and calculated properties. We obtained XRD data in the temperature range of  
104 2700–3900 K, and the temperature effect was included in the analytical pressure error.  
105 We set the average temperature of 3400 K as the temperature condition in this study (Fig.



106 5). All experiments were performed at temperatures higher than the predicted melting  
107 point of Fe<sub>3</sub>S (Fei et al. 1997, 2000; Morard et al. 2008; Mori et al. 2017). We excluded  
108 liquid data coexisting with major XRD peaks obtained from solid Fe and other  
109 compounds.

110 The density of liquid Fe<sub>46.5</sub>Ni<sub>28.5</sub>S<sub>25</sub> was determined by pair distribution analysis.  
111 More information pertaining to this method is available in the literature (Morard et al.  
112 2013). Figure 1 shows typical 1D and 2D XRD patterns of solid and liquid  
113 Fe<sub>46.5</sub>Ni<sub>28.5</sub>S<sub>25</sub> at 70 GPa (the highest pressure tested in this study) and approximately 30  
114 GPa using 30 keV X-rays. In the analysis, Bragg spots from the diamond anvils were  
115 masked. Figure 1 also shows the results of whole XRD pattern profile fitting using the  
116 Le Bail method of (Fe,Ni)<sub>3</sub>S (space group:  $I\bar{4}$ ) and KCl B2 (space group:  $Pm\bar{3}m$ ). In  
117 the XRD patterns, the liquid sample exhibits broad halos. Both before and after melting,  
118 the signals were fitted using spline curves. The only halo peak intensity of the liquid  
119 sample, which is expressed as a function of the scattering angle  $I_{sample}(\theta)$ , was extracted  
120 from the measured XRD signal function after melting  $I_{mes}(\theta)$  via the subtraction of the

121 background signal function  $I_{bg}(\theta)$ . Herein,  $I_{bg}(\theta)$  was obtained from the solid XRD signal  
122 before melting. The scattering angle  $2\theta$  can be transformed into scattering momentum  
123 ( $Q$ ) with wavelength ( $\lambda$ ) via  $Q = 4\pi\sin\theta/\lambda$ . Then,  $I_{sample}(Q)$  can be written as

$$124 \quad I_{sample}(Q) = I_{mes}(Q) - bI_{bg}(Q), \quad (1)$$

125 where  $b$  is a background factor. In this study, we used Krogh-Moe–Norman  
126 normalization (Krogh-Moe 1956; Norman 1957; Morard et al. 2013) for processing  
127  $I_{sample}(Q)$  to structure factor  $S(Q)$ . Reduced pair distribution function  $G(r)$  and pair  
128 distribution function  $g(r)$  were calculated from  $S(Q)$  using Fourier transform:

$$129 \quad G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^{Q_{Max}} Q \{S(Q) - 1\} \sin(Qr) dQ, \quad (2)$$

$$130 \quad g(r) = G(r)/4\pi r\rho_0 + 1, \quad (3)$$

131 where  $r$ ,  $\rho(r)$ ,  $\rho_0$ , and  $Q_{Max}$  are the radial distance from the atom, atomic density, average  
132 atomic density, and maximum scattering momentum in each data point, respectively.  
133 Figure 2 shows the typical  $S(Q)$ ,  $G(r)$ , and  $g(r)$  functions after completing the analytical  
134 calculations. Owing to the repulsive force of an atom from a reference point ( $r = 0$ ), no  
135 atom should be closer than the first coordination shell  $r_{min}$ . Therefore, in the range  $0 < r$

136  $< r_{min}$ ,  $G(r)$  can be represented as a linear function:

137 
$$G(r) = -4\pi\rho_0r. \quad (4)$$

138 Using the above principle, it is necessary to integrate Eq. (2) from  $Q = 0$  to  $\infty$ , which is

139 not possible using experimental data. Additionally,  $Q = 6-7 \text{ \AA}^{-1}$  is the upper limit when

140 using 30-keV X-rays because of the aperture angle of the DAC. Such a limited  $Q$  range

141 produces ripples (Fig. 2a) in the distribution functions. To minimize these ripples in  $G(r)$ ,

142 which are attributed to the  $Q$  truncation effect, the difference between ideal  $G(r) = -4\pi r$

143 and  $G(r) = G_0(r)$  directly obtained from the raw data (without iteration) was calculated

144 in the range  $0 < r < r_{min}$ :

145 
$$\Delta G_0(r) = -4\pi r - G(r). \quad (5)$$

146 Then, the function was integrated from 0 to  $r_{min}$  as the sum of the squares of the

147 differences:

148 
$$\chi^2(\rho_0, b) = \int_0^{r_{min}} \Delta G_i(r)^2 dr. \quad (6)$$

149 To minimize  $\chi^2$ , background factors  $b$  and  $\rho_0$  were determined.

150 The density of the liquid sample can then be expressed as

151 
$$\rho = \rho_0 \times M, \tag{7}$$

152 where  $M$  is the average atomic weight. We determined the uncertainty of the calculated  
153  $\rho_0$  to be  $\pm 3 \times 10^{-3}$  atoms/Å by considering the  $Q$  truncation effects. Herein, the bulk of  
154 runs for the XRD measurements were operated using 30-keV X-rays. Thus, the  $Q$  range  
155 was limited to  $< 6-7 \text{ \AA}^{-1}$ , implying that only two oscillations could be observed for liquid  
156 Fe alloys. In run #9, using higher-energy X-rays at 50 keV, we successfully obtained  
157 data for a higher  $Q$  range of up to  $10.5 \text{ \AA}^{-1}$  (Fig. 1). Further, we examined the  
158 uncertainty in the  $\rho_0$  determination using two oscillations compared with the data after  
159 the third oscillation, which we calculated to be  $\pm 2.9 \times 10^{-3}$  atoms/Å<sup>3</sup>. This estimated  
160 uncertainty was consistent with that reported by Morard et al. (2013) and was confirmed  
161 via a similar examination using higher  $Q$  range data at lower pressures with Paris–  
162 Edinburgh press. Similar to the method followed by Morard et al. (2013), calculations  
163 were performed by shifting  $r_{\min}$  in steps of  $0.1 \text{ \AA}$ . The  $\rho_0$  fluctuation in  $r = \pm 0.1 \text{ \AA}$  was  
164 approximately  $\pm 1 \times 10^{-3}$  atoms/Å<sup>3</sup>. We estimated the uncertainty of density in the present  
165 study to be  $3.9 \times 10^{-3}$  atoms/Å<sup>3</sup>, i.e.,  $0.349 \text{ g/cm}^3$ , for Fe<sub>46.5</sub>Ni<sub>28.5</sub>S<sub>25</sub>.

166 The obtained density values were fitted using third-order Vinet EoS.

$$167 \quad (P - P_r) = K_{TP_r} x^{2/3} (1 - x^{-1/3}) \times \exp \left[ \frac{3}{2} (K'_{TP_r} - 1) (1 - x^{-1/3}) \right], \quad (8)$$

168 where  $P_r$ ,  $K_{TP_r}$ ,  $K'_{TP_r}$ , and  $x$  are the reference pressure, isothermal bulk modulus, its first

169 pressure derivative at reference pressure and 3400 K, and  $x = \rho/\rho_{Pr, 3400K}$ , respectively. A

170 structural transition at around 20 GPa has been suggested for liquid  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  from

171 sound velocity determination (Kawaguchi et al., 2017). Considering the structural

172 transition below 20 GPa, we performed the fitting based on measured density data at the

173 lowest pressure point. We derived the pressure dependence of the density of liquid

174  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$ . The best fit for the compression curve of the density data yielded  $K_{TP_r} =$

175 110.5(250) GPa and  $K'_{TP_r} = 7.2(25)$  with a fixed  $\rho_{Pr, 3400K} = 6.434 \text{ g/cm}^3$  (Table 2). Figure

176 3 shows the confidence ellipsoid of the determined  $K_{TP_r}$  and  $K'_{TP_r}$ . As reported in Angel

177 (2000), the confidence ellipsoid is expressed as

$$178 \quad \Delta = (K_{TP_r}, K'_{TP_r}) \begin{pmatrix} \sigma_{K_{TP_r}K_{TP_r}} & \sigma_{K_{TP_r}K'_{TP_r}} \\ \sigma_{K'_{TP_r}K_{TP_r}} & \sigma_{K'_{TP_r}K'_{TP_r}} \end{pmatrix}^{-1} \begin{pmatrix} K_{TP_r} \\ K'_{TP_r} \end{pmatrix}, \quad (9)$$

179 with the covariance of  $K_{TP_r}$  and  $K'_{TP_r}$ , where  $\Delta$  is the chi-square distribution (here,  $\Delta =$

180 2.3 for  $1\sigma$ -level confidence with two degrees of freedom).

181 To characterize thermal expansion of  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$ , we performed powder XRD  
182 measurements at 1 atm from 90 to 400 K. Figures 4(a) and (b) show temperature  
183 dependence of XRD pattern and structural refinement results via Rietveld analysis with  
184 high reliability ( $R_{\text{WP}} = 2.79\%$ ,  $R_{\text{I}} = 3.84\%$ ) at room temperature. These data indicate that  
185 the sample had no impurities. Tetragonal  $(\text{Fe,Ni})_3\text{S}$  (space group:  $I\bar{4}$ ) was stable  
186 throughout the temperature range measured.

187

188

## Discussion

189 All density data and fitting results are summarized as a function of pressure in Fig. 5.  
190 In Fig. 5, we show the isothermal density profiles at 2700 K and 3900 K, which are the  
191 minimum and maximum temperatures, respectively. Although the temperature  
192 conditions in the present study were slightly different in each run, the agreement of the  
193 fitting results and the present density data were within the estimated pressure and density  
194 errors. The present data show that the density of liquid  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  increased from  
195  $6.434(349) \text{ g/cm}^3$  at 24.6 GPa and 2700 K to  $8.027(349) \text{ g/cm}^3$  at 74.2 GPa and 3700 K.

196 Figure 5 shows the density profile of pure liquid Fe at 3400 K calculated from the EoS  
197 reported provided by Kuwayama et al. (2020). The difference between the densities of  
198 liquid Fe and liquid  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  was 16% in the pressure range of 20–70 GPa.

199 Morard et al. (2013, 2018) and Terasaki et al. (2019) reported density measurement  
200 results for liquid Fe–(Ni)–S systems. Morard et al. (2013) performed  $\text{Fe}_{76}\text{Ni}_{4}\text{S}_{20}$   
201 measurements using laser-heated DACs, as we used in this study; the average atomic  
202 mass in our study differed from theirs by only 4%. The results reported by Morard et al.  
203 (2013) and the present data are consistent within the margin of error.

204 However, although their temperatures were lower by more than 1300 K, Morard et al.  
205 (2018) and Terasaki et al. (2019) reported high compressibility at lower pressures (<20  
206 GPa) than that obtained in the present study. This observation indicates the existence of  
207 a semimetallic to compact metallic structural transition, as discussed in Kawaguchi et al.  
208 (2017) and other existing studies that treated Fe–S alloys (Nishida et al. 2011; Morard et  
209 al. 2007). Morard et al. (2008) suggested that covalent Fe–S bonds in liquid Fe–S  
210 transformed into an interstitial metallic-like configuration, similar to Fe–Si at high

211 pressures.

212 Figure 5 compares our results with the density profile at 3400 K and densities at 30  
213 GPa and 100 GPa near the melting temperatures of solid Fe<sub>3</sub>S calculated using the EoS  
214 of Thompson et al. (2020). This comparison indicates that melting reduces the density of  
215 (Fe,Ni)<sub>3</sub>S by approximately 9.3% at 30 GPa and 2000 K and 11.5% at 100 GPa at 2500  
216 K, thereby indicating a 12%–15% increase in the atomic volume. Although our sample  
217 included 28at% Ni, it produced only a 3% density difference. When melting pure Fe,  
218 Anderson and Isaak (2002) found that the atomic volume change was 1.2%–1.3% at 330  
219 GPa, a pressure condition that corresponded to the inner core boundary. From recent  
220 compression experiments on pure solid hcp Fe (Dewaele et al. 2006) and pure liquid Fe  
221 (Kuwayama et al. 2020), the atomic volume changes were estimated to be 3% at 100  
222 GPa and near the melting temperature,  $T=3000$  K. The results indicate that S increases  
223 the volume change when Fe alloys are melted. Figure 6 shows the crystal structure of  
224 Fe<sub>46.5</sub>Ni<sub>128.5</sub>S<sub>25</sub> at 1 atm and 300 K with anisotropic displacement ellipsoids at the 80%  
225 probability level drawn using the VESTA (Momma and Izumi, 2011). Figure 7 plots



226 variations of unit-cell parameters  $a$  and  $c$  and unit-cell volume  $V$  as a function of  
227 temperature. Cell parameters increase almost linearly with increasing temperature;  
228 however, the  $c$  axis exhibits a higher expansion rate than the  $a$  axis. Sun and Hoyt (2004)  
229 attributed the anisotropy of melting to that of the crystal structure based on  
230 molecular-dynamics (MD) simulation results. They revealed that bcc Fe has higher  
231 mobility and lower free energy of the solid-liquid interface than those of fcc Fe. In  
232 addition, mobility along the (100) orientation of bcc Fe is larger than those along its  
233 (111) and (110) orientations. Hence, the large atomic volume change related to melting  
234 of  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  was possibly a result of the large anisotropy in thermal vibration of the  
235 bcc  $\text{Fe}_3\text{S}$  structure (space group  $I\bar{4}$ ) compared with face-centered cubic and hexagonal  
236 close-packed Fe. Structural refinement and MD simulation of the solid materials  
237 immediately before their melting and precise structural characterization of the liquid and  
238 amorphous materials via pair distribution analyses using higher-energy X-rays should be  
239 attempted in future work.

240

241 **Implications**

242 The density deficit in the outer core in terms of pure liquid Fe was estimated to be  
243 7.5%–7.6% (Kuwayama et al. 2020). To discuss the density of the Earth’s outer core, we  
244 used a constant  $\alpha K_T$  relationship:

245 
$$P(\rho, T) = P(\rho, T_0) + \Delta P_{th}, \quad (10)$$

246 
$$\Delta P_{th} = \alpha K_T (T - T_0), \quad (11)$$

247 where  $\alpha$ ,  $K_T$ , and  $T_0$  are the thermal expansion coefficient, isothermal bulk modulus, and  
248 reference temperature (3400 K), respectively. Additionally,  $\alpha \times K_T$  can be considered as  
249 constant from reference pressure and temperature to the pressure–temperature ( $P$ – $T$ )  
250 condition of interest ( $\alpha \times K_T = \alpha_{Pr} \times K_{TPr}$ ). Assuming that the temperature effect on the  
251 sound velocities can be negligible, we refitted the sound velocity data of Kawaguchi et  
252 al. (2017) using  $\rho_{Pr,3400\text{ K}}$  determined herein, yielding an adiabatic bulk modulus  $K_{SPr} =$   
253 186.8 GPa at 24.6 GPa and 3400 K. The relation between  $K_{SPr}$  and  $K_{TPr}$  can be expressed  
254 as  $K_{SPr}/K_{TPr} = (1 + \alpha_{Pr} \times \gamma_{Pr} \times T_{Pr})$ , where  $\gamma_{Pr}$  of pure Fe is from Kuwayama et al. (2020).  
255 Combination of  $K_{SPr}$ ,  $K_{TPr}$ , and  $\gamma_{Pr}$  yielded  $\alpha_{Pr} \times K_{TPr} = 1.18 \times 10^{-2}$  GPa/K.

256 We calculated the adiabatic temperature as follows:

257 
$$T = T_{ref} \exp \left[ \gamma_{ref} \left( 1 - \frac{\rho_{ref}}{\rho} \right) \right], \quad (12)$$

258 where  $T_{ref}$  is the reference temperature, and  $\gamma_{ref}$  is the Grüneisen parameter at 24.6 GPa  
259 and  $T_{ref}$ . We calculated  $\gamma_{ref}$  for pure Fe based on the data of Kuwayama et al. (2020). In  
260 Fig. 8, the density of liquid Fe–Ni–S alloys and Fe is plotted along the adiabatic  
261 temperature profiles corresponding to the temperatures at the core–mantle boundary  
262 (CMB), i.e.,  $T_{CMB} = 3600$  and  $4300$  K ( $T_{ref} = 2459$  and  $2812$  K, respectively). The  
263 obtained density profiles appear to differ from previous shock experimental results  
264 (Huang et al. 2013). Conversely, our results are consistent with the density calculated  
265 from the sound velocity data reported by Kawaguchi et al. (2017), which was  
266 recalculated using thermo-elastic parameters of pure Fe (Kuwayama et al. 2020). We  
267 also calculated the density of liquid  $Fe_3S$ , assuming that the effect of Ni has little effect  
268 on the thermal elastic parameters (e.g. Kawaguchi et al. 2017). Finally, assuming ideal  
269 mixing with pure Fe and S as the only light element in the Earth’s core, the density  
270 profile of the outer core is best explained using 5.7-6.6wt% S with Ni and 5.3-6.2wt% S

271 without Ni. This estimation is compatible with our sound velocity measurements, which  
272 suggest a volume of 5.8-7.5wt% S in the Earth's outer core.

273 S is considered a dominant candidate for lighter components in the Martian core. The  
274 S content of Mars is approximately 10.6–16.2 wt%, estimated from Martian-origin  
275 shergottite, nakhlite, and chassignite meteorites (e.g., Dreibus and Wanke 1985). A  
276 (partially) molten Martian core has been reported using observed large Love number  $k_2$   
277 (e.g., Yoder et al. 2003). In Fig. 9, we show the isothermal density profiles of  
278  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  (16wt% S) and pure Fe (0wt% S) at 1500, 1900, and 2300 K in the  
279 pressure range corresponding to that of the Martian core (Tsujino et al. 2013). Mars  
280 exploration lander, InSight, landed on Mars in 2018. Additionally, ExoMars 2022 will be  
281 launched in the denoted year. InSight's rotation and interior structure experiment  
282 (Folkner et al. 2018), seismometer data (Giardini et al. 2020), and ExoMars' lander  
283 radio-science experiment (Péters et al. 2020) will provide additional information about  
284 the interior structure of Mars and its core. Our density and sound velocity data may help  
285 better understand the Martian core and its thermal evolution.

286

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291 2014A0080, 2014A1127, 2016A1846, 2016B1954, 2016B1955, 2017B1977,  
292 2018A2062, 2018B2109, 2019A1381, 2019B2094) and BL02B2 beamlines (proposals  
293 no. 2019B2086) of SPring-8.

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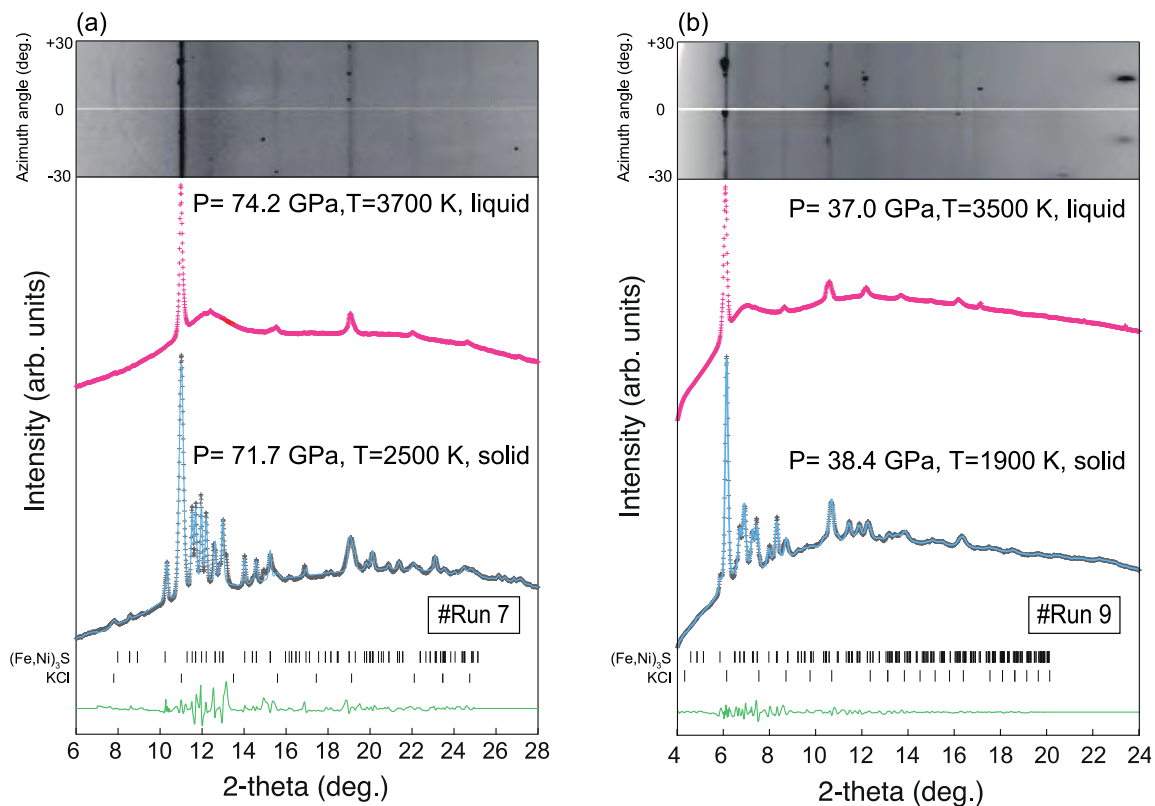
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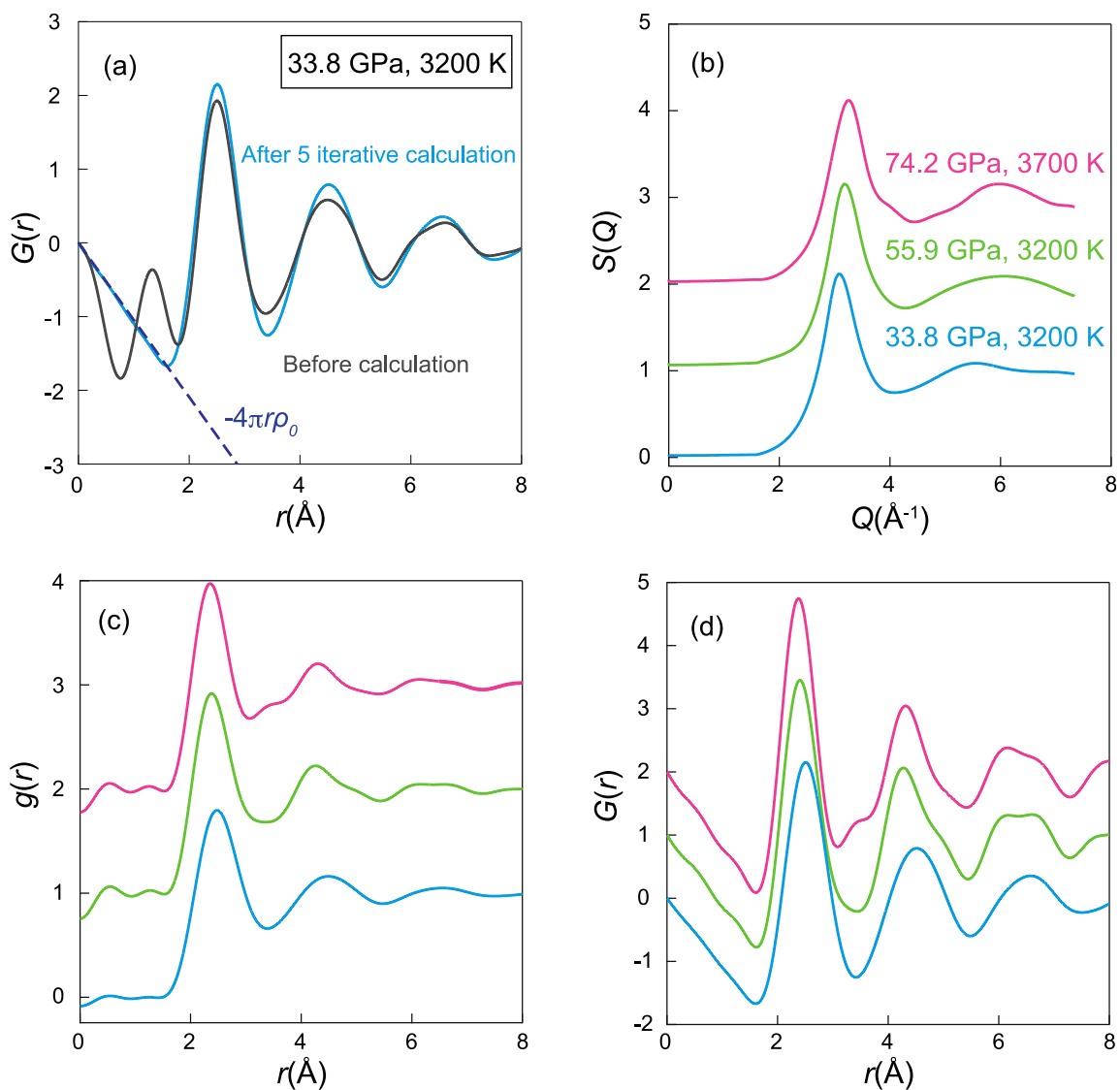
426 **FIGURE 1.** 1D XRD patterns of solid (gray symbols) and liquid (pink symbols)

427  $\text{Fe}_{47}\text{Ni}_{28}\text{S}_{25}$  and 2D XRD patterns of liquid  $\text{Fe}_{47}\text{Ni}_{28}\text{S}_{25}$  obtained at (a) ~74 GPa using a

428 30 keV X-ray and (b) ~37 GPa using a 50 keV X-ray. Blue and green lines indicate the

429 whole pattern profile fitting results of  $(\text{Fe,Ni})_3\text{S}$  (space group:  $I\bar{4}$ ) and KCl B2 (space

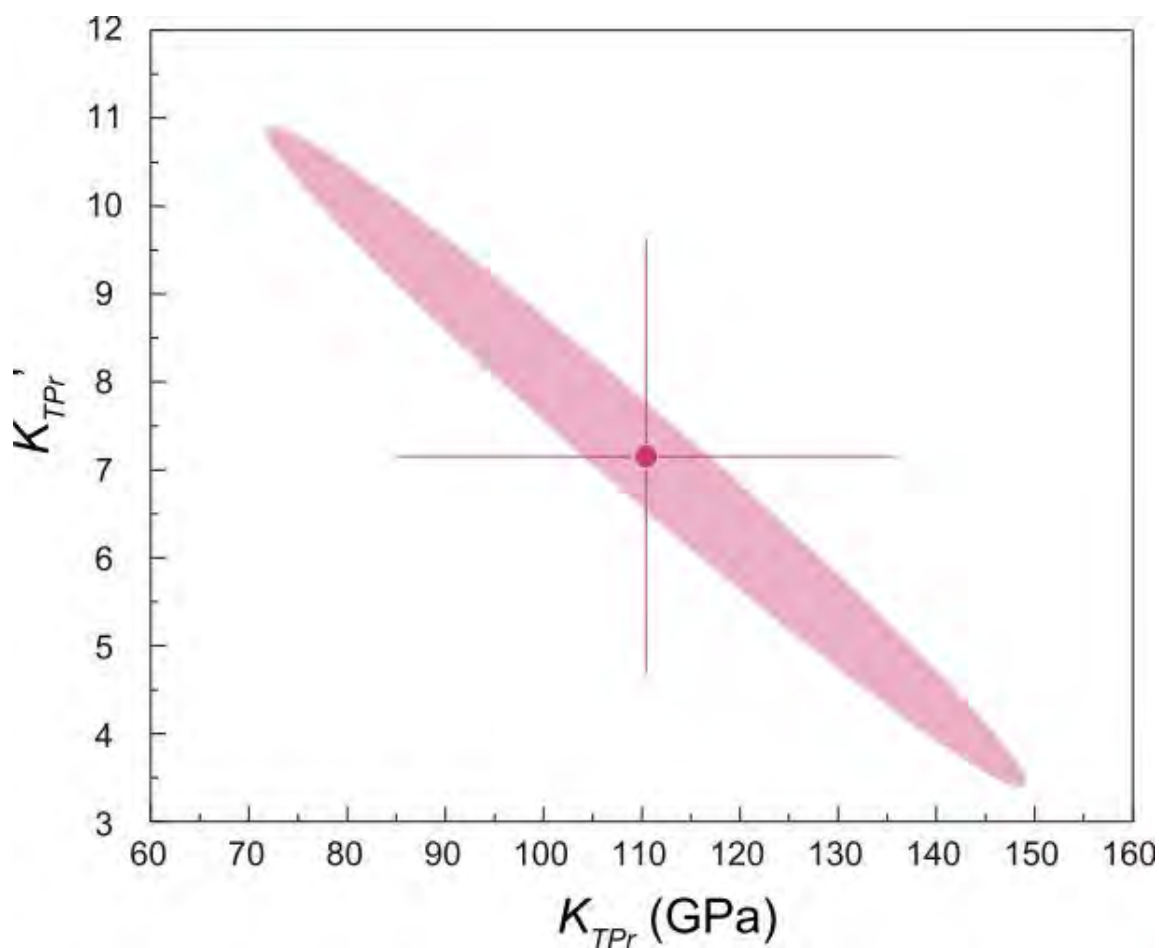
430 group:  $Pm\bar{3}m$ ) using the Le Bail method and the differences between the observed and  
431 calculated profiles, respectively.



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434 **FIGURE 2.** Typical Faber–Ziman structure factor  $S(Q)$ , reduced pair distribution  
435 function  $G(r)$ , and pair distribution function  $g(r)$ . (a) Comparison of  $G(r)$  functions

436 before and after five iterative optimization calculations; (b)–(d) typical  $S(Q)$ ,  $g(r)$ , and  
437  $G(r)$  functions after optimization at 34, 56, and 74 GPa (light blue, light green, and pink  
438 lines, respectively).



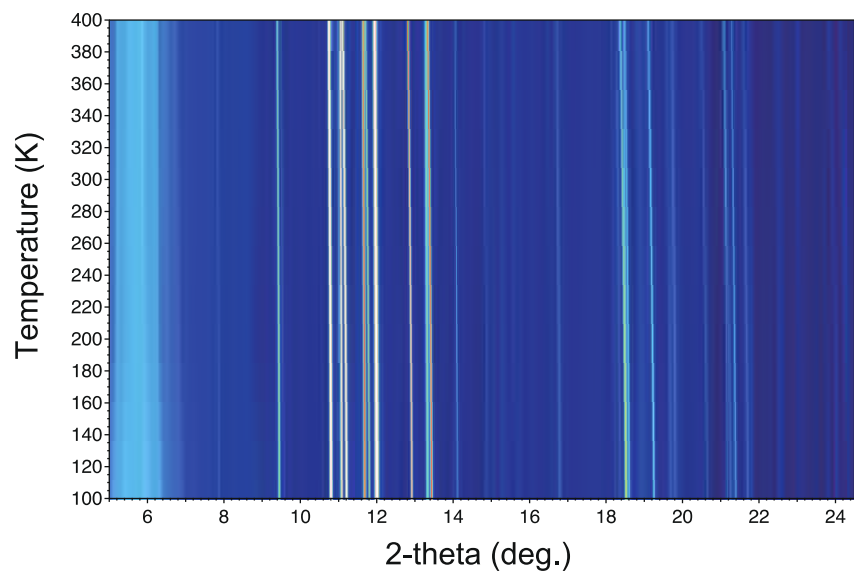
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440 **FIGURE 3.** Confidence ellipsoid in  $K_{TP_r}$  and  $K'_{TP_r}$  for fitting using the third-order  
441 Vinet EoS with a 68.3% confidence level and  $\Delta = 2.3$ . The fitting result is shown as a  
442 circular symbol with errors of  $K_{TP_r} = 110.5(250)$  GPa and  $K'_{TP_r} = 7.2(25)$ .



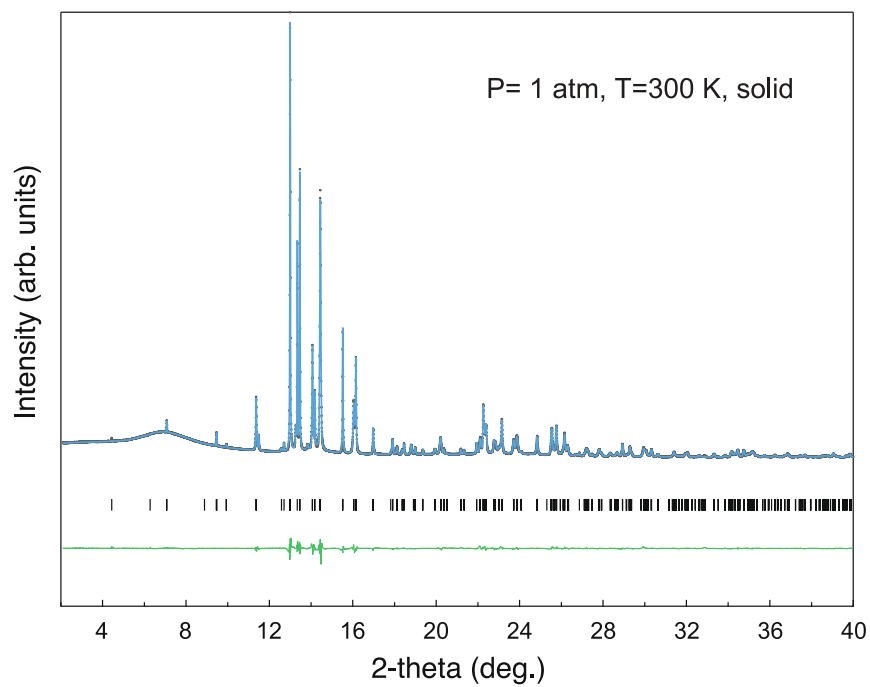
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(a)



(b)



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447 **FIGURE 4.** (a) Temperature dependence of powder XRD pattern of  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  in the

448 temperature range 100–400 K at 1 atm using 30 keV X-ray; (b) XRD pattern of

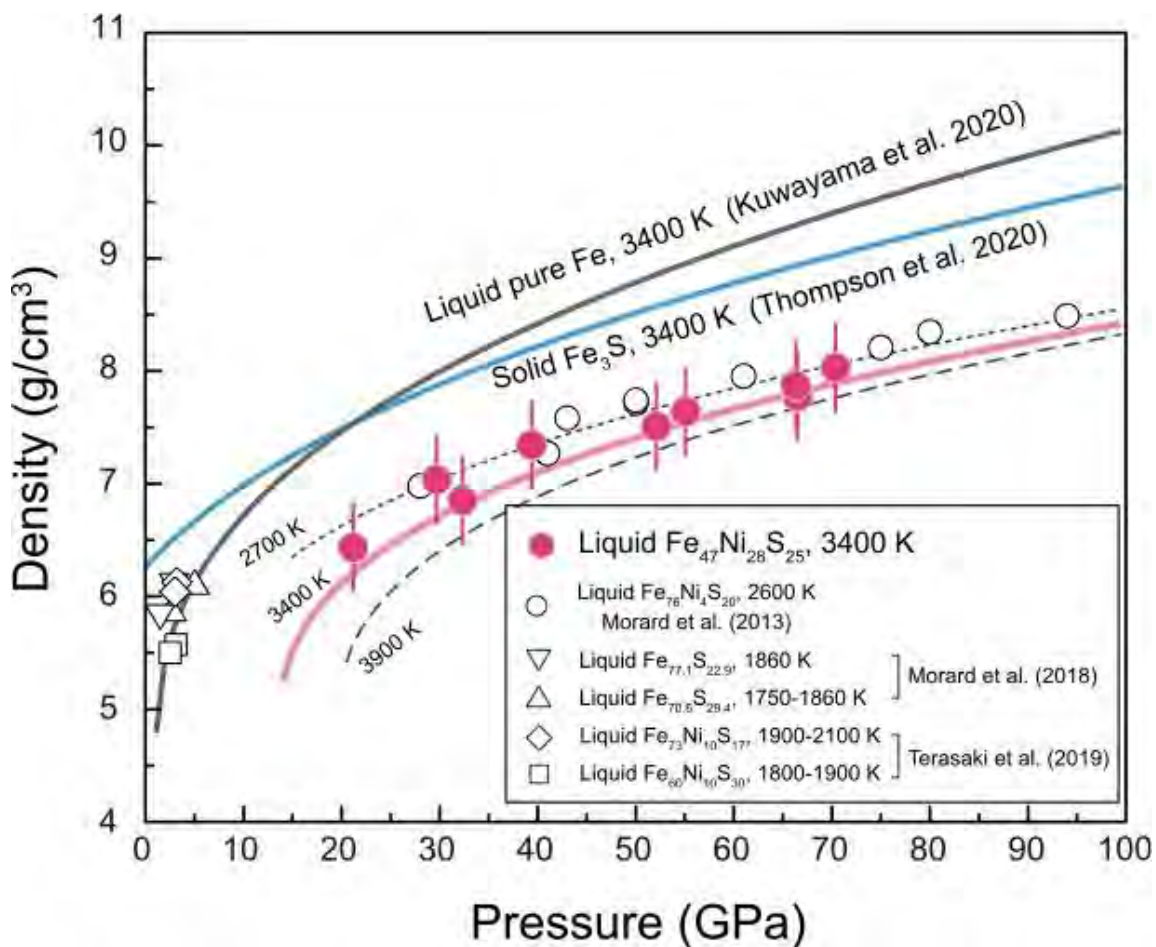
449  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  at room temperature using 24.8 keV X-ray and its Rietveld analysis.

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455 **FIGURE 5.** Densities of liquid and solid Fe–Ni–S and Fe–S alloys and Fe. The data of  
 456  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  obtained in this study are represented by solid pink circles. The pink line  
 457 indicates the fitting result using Vinet EoS. Previous measurements using a similar XRD  
 458 method for liquid  $\text{Fe}_{76}\text{Ni}_4\text{S}_{20}$  (Morard et al. 2013), XRD method in Paris–Edinburgh  
 459 press for liquid  $\text{Fe}_{77.1}\text{S}_{22.9}$  and  $\text{Fe}_{70.6}\text{S}_{29.4}$  (Morard et al. 2018), and X-ray absorption  
 460 method in multianvil press (Terasaki et al. 2019) for liquid  $\text{Fe}_{73}\text{Ni}_{10}\text{S}_{17}$  and  $\text{Fe}_{60}\text{Ni}_{10}\text{S}_{30}$

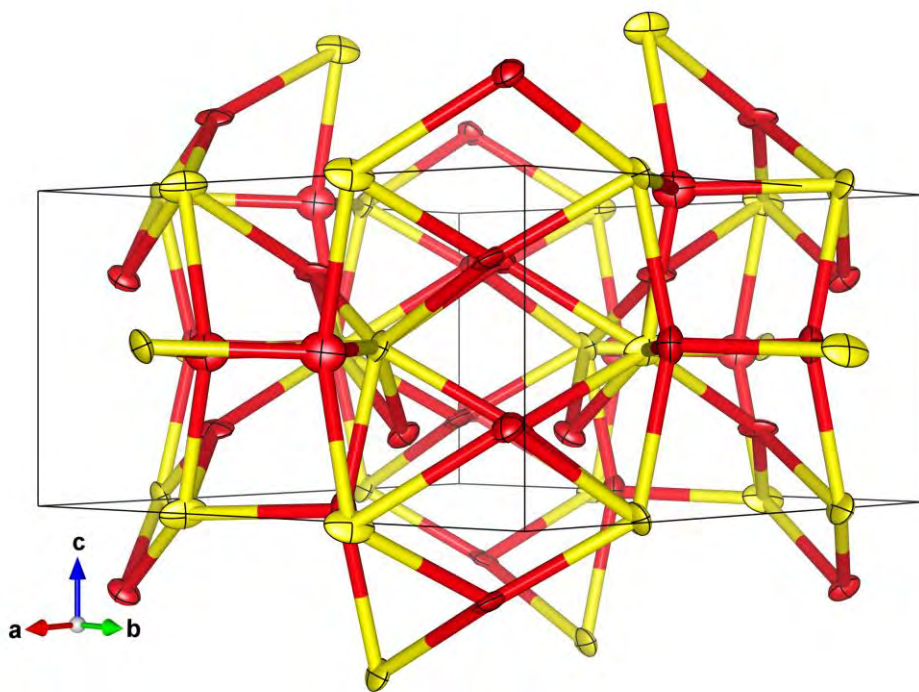
461 are represented by the open diamonds and squares, respectively. The gray and light blue  
462 lines indicate the calculated densities of liquid Fe using the EoS in Kuwayama et al.  
463 (2020) and solid Fe<sub>3</sub>S using the EoS in Thompson et al. (2020), respectively, at 3400 K.  
464 Dotted and broken lines indicate the calculated isothermal density profiles of liquid  
465 Fe<sub>46.5</sub>Ni<sub>28.5</sub>S<sub>25</sub> at 2700 and 3900 K.

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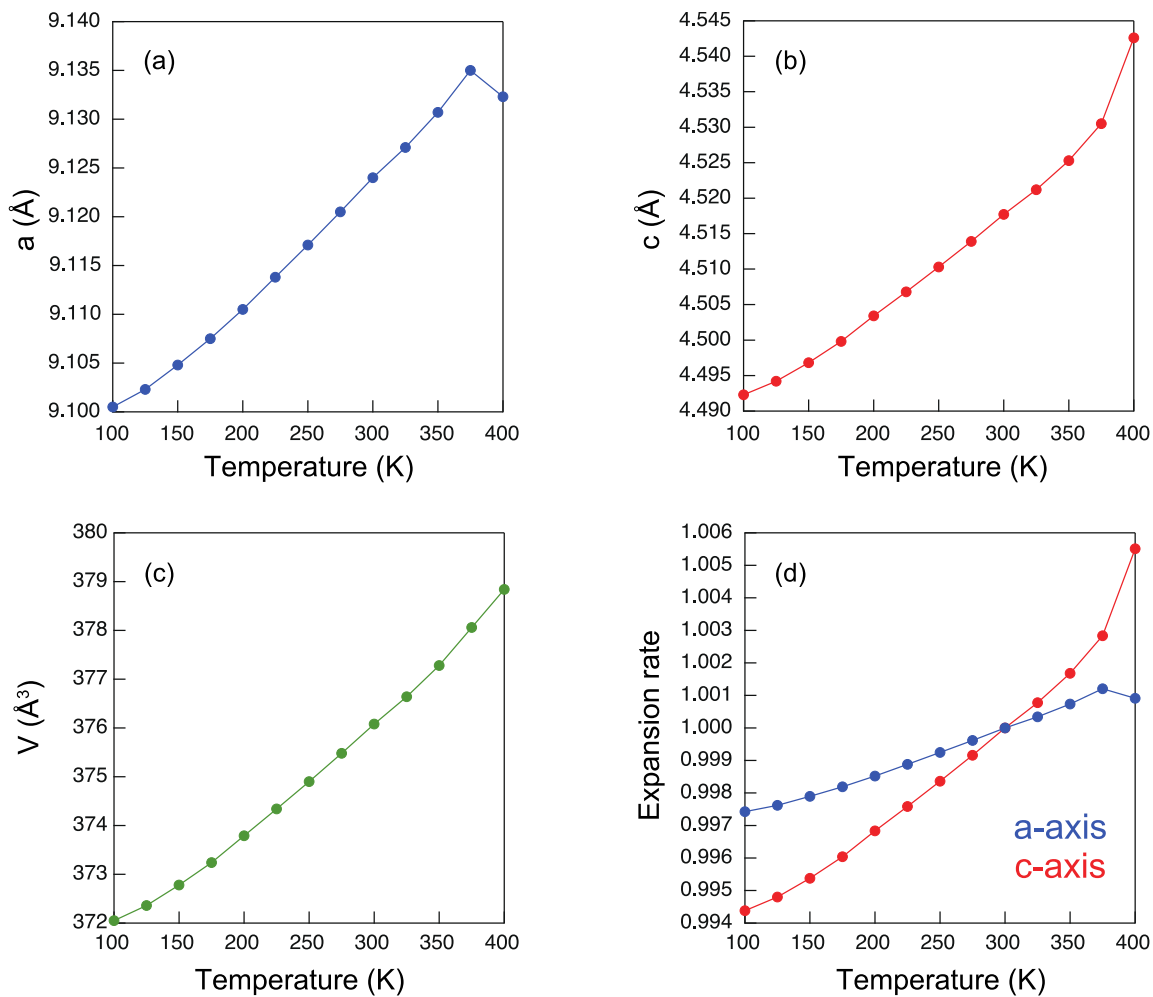
471 **FIGURE 6.** Crystal structure of Fe<sub>46.5</sub>Ni<sub>28.5</sub>S<sub>25</sub> at 300 K with anisotropic displacement

472 ellipsoids at 80% probability level. Red and yellow symbols indicate the thermal

473 vibrations of Fe/Ni and S, respectively.

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478 **FIGURE 7.** Temperature dependencies of unit-cell parameters(a) *a* (blue), (b) *c* (red),

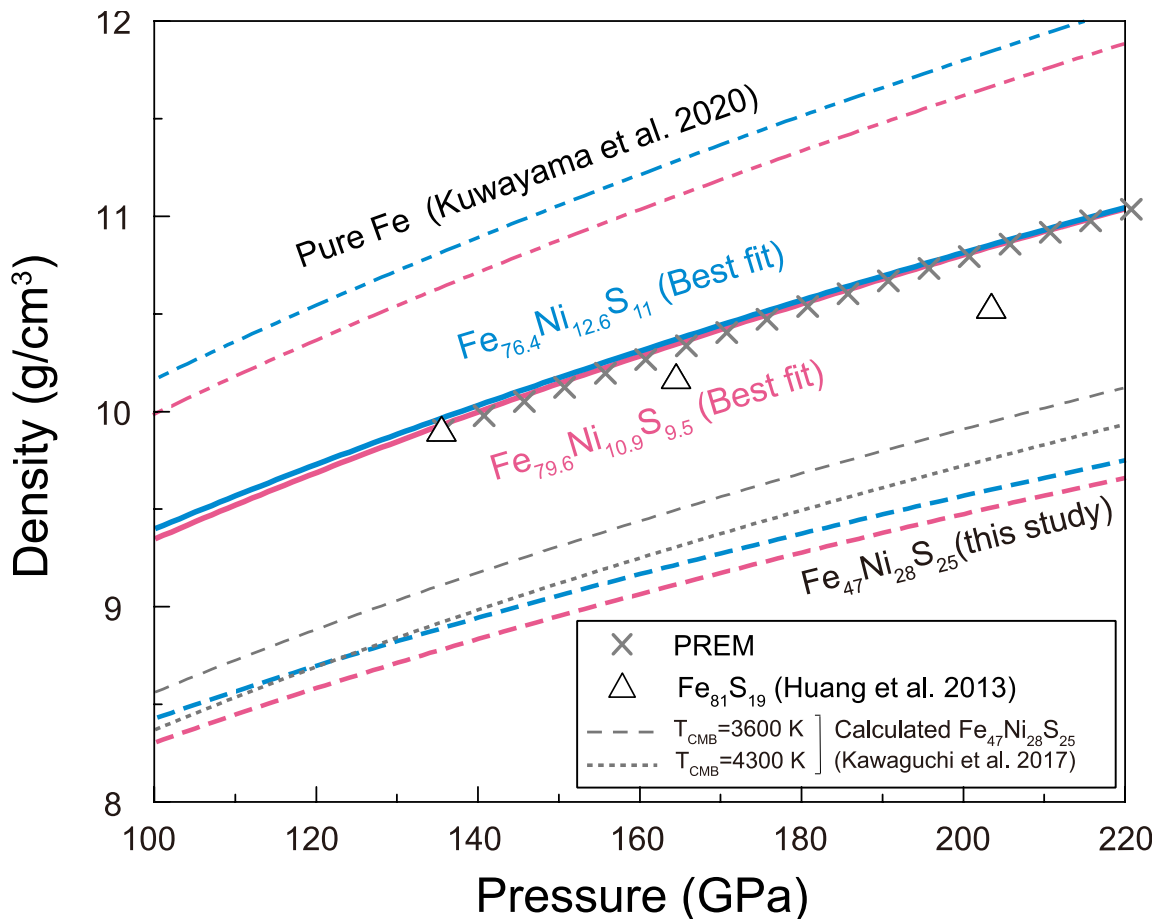
479 and (c) unit-cell volume *V* (purple); (d) a comparison of the expansion rates of the a and

480 c axes based on the values at 300 K.

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485 **FIGURE 8.** Densities of liquid Fe–Ni–S alloys and Fe along adiabats with  $T_{CMB} = 3600$

486 and 4300 K (blue and pink curves, respectively). Density profiles of  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$

487 calculated from the present results and pure Fe (Kuwayama et al. 2020) are shown with

488 broken and dashed lines, respectively. Solid blue and red curves indicate the best fits to

489 PREM (crosses) with liquid  $\text{Fe}_{76.4}\text{Ni}_{12.6}\text{S}_{11}$  ( $T_{CMB} = 3600 \text{ K}$ ) and  $\text{Fe}_{79.6}\text{Ni}_{10.9}\text{S}_{9.5}$  ( $T_{CMB} =$   
490  $4300 \text{ K}$ ), respectively. The calculated density profiles of  $\text{Fe}_{46.5}\text{Ni}_{28.5}\text{S}_{25}$  from the sound  
491 velocity data of Kawaguchi et al. (2017) are shown by gray dashed ( $T_{CMB} = 3600 \text{ K}$ ) and  
492 dotted ( $T_{CMB} = 4300 \text{ K}$ ) lines.

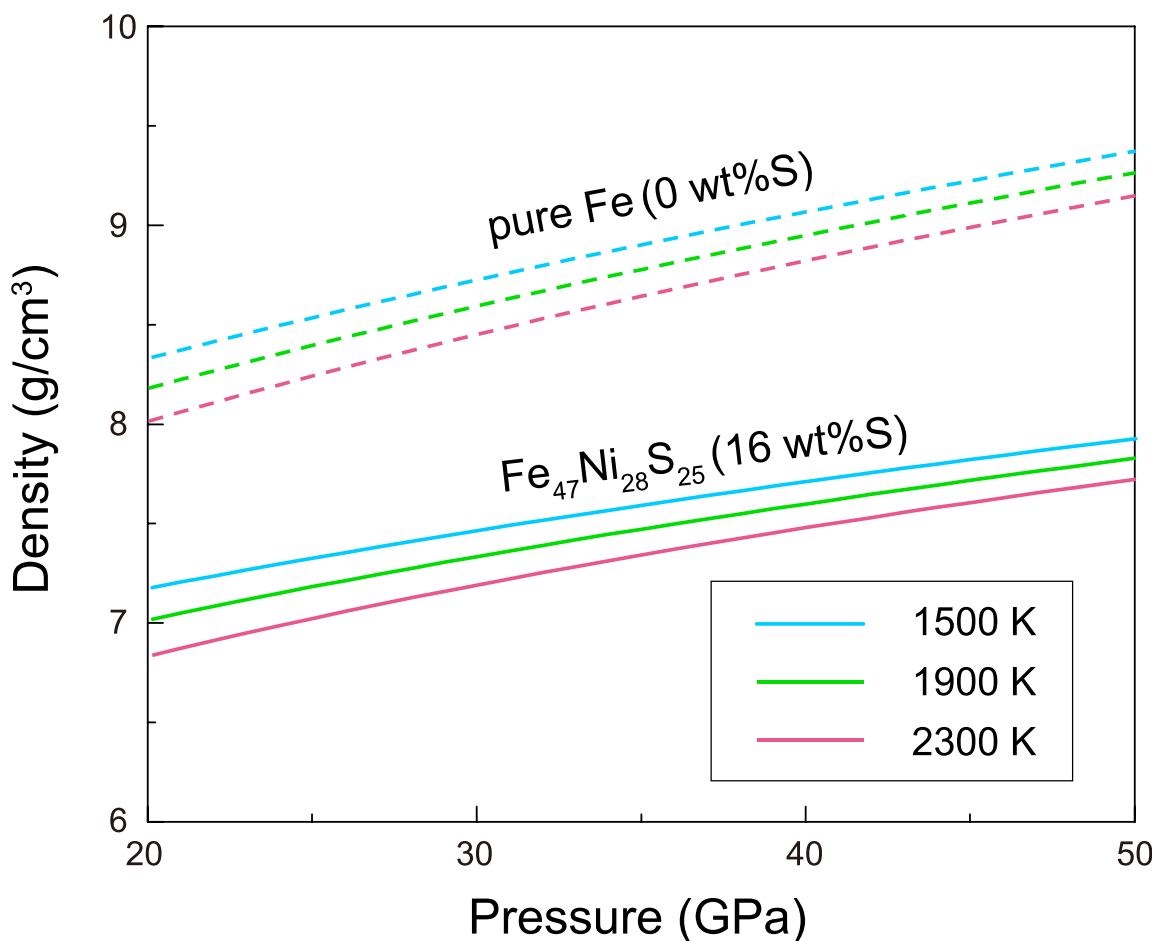
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498 **FIGURE 9.** Isothermal density profiles of liquid Fe<sub>46.5</sub>Ni<sub>28.5</sub>S<sub>25</sub> (16wt% S) and pure Fe

499 (0 wt% S) in the pressure range corresponding to the Martian core at 1500 (blue), 1900

500 (green), and 2300 K (pink).

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**TABLE 1.** *P-T* conditions, unit-cell volumes of KCl B2, and the obtained calculation properties of Fe<sub>47</sub>Ni<sub>28</sub>S<sub>25</sub>

| Run No.              | <i>P</i> (GPa) | <i>T</i> (K) | KCl volume (Å <sup>3</sup> ) | $\rho$ (g/cm <sup>3</sup> ) | $r_{min}$ (Å) | $\rho_0$ (atoms/Å <sup>3</sup> ) ×10 <sup>-2</sup> | BG factor | $\chi^2$ |
|----------------------|----------------|--------------|------------------------------|-----------------------------|---------------|--|-----------|----------|
| X-ray energy: 30 keV |                |              |                              |                             |               |  |           |          |
| 1                    | 33.8(12)       | 3200         | 35.79(4)                     | 7.035                       | 1.59          | 8.333  | 0.941     | 0.127    |
| 2                    | 44.0(14)       | 3900         | 33.77(2)                     | 7.342                       | 1.54          | 8.697  | 0.954     | 0.176    |
| 3                    | 55.9(12)       | 3200         | 30.95(5)                     | 7.510                       | 1.60          | 8.897  | 0.924     | 0.924    |
| 4                    | 59.1(12)       | 3500         | 30.60(3)                     | 7.639                       | 1.52          | 9.048  | 0.905     | 0.103    |
| 5                    | 69.5(12)       | 3200         | 29.00(1)                     | 7.872                       | 1.58          | 9.324  | 0.911     | 0.167    |
| 6                    | 70.4(14)       | 3700         | 29.12(9)                     | 7.771                       | 1.62          | 9.230  | 0.902     | 0.344    |
| 7                    | 74.2(14)       | 3700         | 28.67(12)                    | 8.027                       | 1.66          | 9.508  | 0.900     | 1.048    |
| X-ray energy: 50 keV |                |              |                              |                             |               |  |           |          |
| 8                    | 24.6(10)       | 2700         | 38.64(14)                    | 6.434                       | 1.66          | 7.621  | 0.926     | 0.358    |
| 9                    | 37.0(13)       | 3500         | 35.24(13)                    | 6.852                       | 1.74          | 8.116  | 0.964     | 0.188    |

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**TABLE 2.** Fitting results using the Vinet equation of state

| $T_0$ (K) | $K_{TP_r}$ (GPa) | $K_{TP_r}'$ | $\rho_{Pr}$ (g/cm <sup>3</sup> ) | $P_r$ (GPa) |
|-----------|------------------|-------------|----------------------------------|-------------|
| 3400      | 110.5(250)       | 7.2(25)     | 6.434                            | 24.6        |

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