

1 **Effects of hydrogen on the phase relations in Fe–FeS at pressures**
2 **of Mars-sized bodies**

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Abstract

Hydrogen (H) and sulfur (S) are light element candidates to enter the core of planetary bodies. Although Fe–S and Fe–H systems have been studied individually, the Fe–S–H ternary system has only been investigated up to 16 GPa and 1723 K. We have investigated the Fe–S–H system at pressures and temperatures (P – T) relevant to the cores of Mars-sized planets (up to 45 GPa and well above the melting temperature of FeS) in the laser-heated diamond anvil cell combined with *in situ* synchrotron X-ray diffraction. We found that at high P – T , Fe₃S is unstable if H exists in the system. Instead, separate Fe–H and Fe–S phases appear at 23–35 GPa. At pressures above 35 GPa, we found a new phase appearing while Fe–S phases disappear and Fe–H phases remain. Our analysis indicates that the new phase likely contains both S and H in the crystal structure (tentatively FeSH). The observed pressure dependent changes in the phase relation may be important for understanding the structure and dynamics of the Martian core and the cores of Mars-sized exoplanets.

Plain Language Summary

The metallic cores of planets and satellites are believed to contain significant amounts of light elements such as hydrogen and sulfur. To understand how a planetary core forms and evolves through time, it is important to know how iron alloys behave at the pressure-temperature conditions of the cores. The iron-hydrogen and the iron-sulfur alloy systems are well known, even at conditions of the Earth's core. However, the iron alloy systems with both sulfur and hydrogen together have only been studied for depths of smaller bodies like Ganymede. Using new experimental techniques, we study the behavior of the iron-hydrogen-sulfur alloy system at higher pressures and temperatures. We found that at intermediate depths, sulfur and hydrogen form two separate iron alloys, while at greater depths, a new iron alloy with both sulfur and hydrogen may form in Mars-sized planets' cores. This change in mineralogy with depth therefore suggests that the structure and dynamics in the cores of Mars-sized planets could be much more complex if hydrogen can be added to the region as a light element.

Key points

- Hydrogen makes Fe₃S unstable at the pressures and temperatures relevant to Mars-sized planetary cores.

- 37 • At 23–35 GPa, separate FeS and FeH phases are stable, whereas above 35 GPa, a new
38 Fe alloy phase appears, which may contain both S and H.
- 39 • Crystallization from a Fe–S–H liquid would lead to a complex core structure.

40 **1 Introduction**

41 Significant amounts of light elements are necessary to explain the observed density
42 deficit of the Earth’s core from a pure Fe–Ni alloy [Dziewonski and Anderson, 1981]. Sili-
43 con, sulfur, oxygen, carbon, and hydrogen are strong candidates to lower the core’s density
44 because of their cosmochemical abundances and affinity with metallic iron at high pressures
45 and temperatures [Poirier, 1994] during core formation [Wade and Wood, 2005]. Although
46 a combination of light elements is more likely to explain the density deficit than just one ele-
47 ment, a consensus on the combination itself has yet to be reached [Badro *et al.*, 2014].

48 Sulfur (S) and hydrogen (H) were both abundantly available in the proto-planetary disk
49 from which planets and satellites in the solar system formed. Although S and H are both
50 volatile elements at 1 bar, they show siderophile (iron-loving) behaviors at pressures relevant
51 to core formation processes [Badding *et al.*, 1991; Pépin *et al.*, 2014; Li and Agee, 2001].
52 Fe–S and Fe–H systems, separately, have been extensively studied [e.g., Badding *et al.*, 1991;
53 Pépin *et al.*, 2014; Kamada *et al.*, 2010; Stewart *et al.*, 2007; Fei *et al.*, 1995]. Experiments
54 have shown that the solubility of H into metallic Fe increases significantly with increasing
55 pressure [Badding *et al.*, 1991; Pépin *et al.*, 2014] up to FeH₅ [Pépin *et al.*, 2017]. The Fe–
56 FeS system is eutectic up to 271 GPa, where Fe₃S is stable together with pure Fe [Stewart
57 *et al.*, 2007; Ozawa *et al.*, 2013]. S and H have been shown to both significantly lower the
58 melting temperature of pure Fe [Fei *et al.*, 1995; Morard *et al.*, 2007; Kamada *et al.*, 2010;
59 Sakamaki *et al.*, 2009; Hirose *et al.*, 2019]. Low melting temperatures (like those of Fe₃S
60 and FeH) could, for example, increase the longevity of a liquid core and therefore contribute
61 to the dynamics of the region. S and H should therefore have important implications for
62 planetary cores. A study up to 16 GPa reported the solubility of H into FeS, thus forming
63 a FeSH_{*x*} phase (where *x* ≈ 0.3) [Shibazaki *et al.*, 2011]. However, the behavior of the system
64 is unknown beyond these conditions.

65 Because H is very volatile and highly reactive, it is a challenging element to study
66 at high pressures and high temperatures. A few studies have investigated phase relations
67 for hydrogen-involved ternary systems. Narygina *et al.* [2011] and Ohta *et al.* [2019] have

68 shown that when reacting pure Fe together with paraffin (C_nH_{2n+2} , $n > 5$) up to 68 GPa, FeC
69 and FeH form separate solid phases under subsolidus conditions. *Hirose et al.* [2019] also
70 showed that up to 127 GPa at liquidus conditions, H preferentially partitions into the liquid,
71 thus limiting the solubility of C in the liquid. *Ohtani et al.* [2005] observed the formation
72 of separate FeO and FeH phases when reacting Fe with H_2O below 84 GPa, whereas above
73 84 GPa, FeOOH and FeH were observed [*Liu et al.*, 2017; *Yuan et al.*, 2018]. On the other
74 hand, H does not seem to alter the compressibility of hcp-FeSi or induce any phase separa-
75 tion like that observed for Fe–C and Fe–O systems [*Tagawa et al.*, 2016].

76 The co-solubility of H with another light element in iron alloy appears to be a complex
77 variable of pressure, temperature and composition. It is therefore difficult to interpolate the
78 geophysical implications of a ternary system from separate binary systems given the seem-
79 ingly complex relationships between light elements. Whether it is by experimental design or
80 not, studies using non pure H sources have to consider the potential effects of other elements,
81 such as C in the case of paraffin, or oxidized conditions in the case of H_2O . While more ideal
82 from a compositional point of view, the use of a pure H_2 source comes with its own set of
83 experimental challenges: the high mobility and diffusivity of H at high P – T make diamond
84 anvils much more brittle, therefore increasing the chance for experiment failure when a H
85 medium is combined with conventional continuous wave laser heating in the diamond-anvil
86 cell (DAC). Regardless, pure H_2 medium is the most ideal H source when studying the effect
87 of H on any system, and recent experimental progress with the advent of pulse laser-heating
88 systems [*Deemyad et al.*, 2005] combined with time-gated X-ray diffraction (XRD) [*Gon-*
89 *charov et al.*, 2010] now allow significant reduction of diamond embrittlement during experi-
90 ments with pure H, while still providing XRD patterns of sufficient quality.

91 We have conducted experiments on the phase relations in the Fe–S–H system at pres-
92 sures up to 45 GPa and temperatures above the melting of FeS, using laser-heated diamond-
93 anvil cell combined with synchrotron X-ray diffraction for phase characterization at *in situ*
94 high pressure and high temperature. We then discuss the potential implications of our experi-
95 mental observations for the crystallization of cores of Mars-sized planetary bodies.

2 Experimental methods

2.1 Starting Materials

The pure Fe₃S sample was synthesized in a 1000 tons multi-anvil press at ASU following the method presented in *Kamada et al.* [2014a]. A Fe + FeS mixture was encapsulated in MgO capsule and brought to a pressure of 21 GPa using 8/3 cell assemblies. Heating was conducted in a few steps: 5 minutes at 1533 K for melting and homogenization of the mixture, then 30 minutes at 1413 K to favor the crystallization of Fe₃S grains and finally 1 hour at 1273 K to enhance the growth of Fe₃S grains. The sample was then quenched to room temperature and progressively brought back to room pressure overnight. Energy-dispersive spectroscopy chemical mapping in scattering electron microscopy (SEM) and XRD data were acquired after recovery to examine the chemical composition and crystal structure of synthesized crystals, respectively (see Fig. S1 and Tab. S1) and confirmed the purity and homogeneity of the sample.

We also explored other compositions along the Fe–FeS joint: Fe + Fe₃S mixture and FeS. Pure FeS was obtained from Alfa Aesar chemicals. For the Fe + Fe₃S, we used a mechanical mixture of Fe and Fe₃S. Since only small amounts of multi-anvil samples were available, the mixture was not sufficiently homogeneous for maintaining the same compositions for diamond-anvil cell loadings. Therefore, we used the mixture data only to qualitatively supplement our main data from Fe₃S.

2.2 Diamond-anvil cell preparation

Pressures were achieved using diamond anvils ranging in size from 200 μm to 150 μm . We loaded a thin foil of the starting material into pre-indented and drilled rhenium gaskets. The rhenium gaskets were gold coated to reduce the diffusion of hydrogen into the gasket material, which can weaken the gasket and therefore result in anvil failure [*Pépin et al.*, 2014]. To ensure proper insulation from the diamonds during laser-heating, we propped the sample using small pieces of the same starting material. We used gold as a pressure marker [*Ye et al.*, 2017]. To prevent unwanted/unknown reactions between gold, hydrogen and the sample during high-temperature experiments, we chose not to mix gold with the sample but instead load it as a separate chip next to the sample. We then loaded pure hydrogen gas at a pressure of 1500 bar into the sample chamber using the hydrogen gas loading facility located at Arizona State University. After the gas loading, we compressed the cell to its target pres-

127 sure. In-house monitoring of pressure after hydrogen loading was enabled by the presence of
128 a small ruby chip placed in the sample chamber prior to hydrogen loading [Mao *et al.*, 1986].

129 **2.3 Synchrotron measurements**

130 We performed synchrotron X-ray diffraction (XRD) at *in situ* high-pressure and high-
131 temperature in the laser-heated diamond anvil cell. XRD patterns were acquired at the 13-
132 IDD beamline of the GSECARS sector of the Advanced Photon Source. A $3\times 4\ \mu\text{m}^2$ monochro-
133 matic X-ray beam with energy of 30 keV or 37 keV was co-axially aligned with double-sided
134 near-infrared laser-heating beam providing a $15\times 20\ \mu\text{m}^2$ heating spot. We used the pulsed-
135 laser heating technique to prevent significant anvil embrittlement enhanced by hydrogen at
136 high temperature [Deemyad *et al.*, 2005]. For this, the laser pulse was synchronized with
137 gated X-ray and temperature detectors to allow acquisition of XRD patterns at *in situ* high
138 P - T [Goncharov *et al.*, 2010]. To obtain diffraction patterns in sufficiently high quality, we
139 generated a series of 10^5 pulses to a repetition rate of 10 kHz and accumulated the obtained
140 diffraction patterns during heating. After temperature quench at high pressure we measured
141 XRD patterns in regular continuous-wave (CW) mode for higher quality.

142 The temperature was calculated by fitting a Planck equation to the thermal radiation
143 spectra collected on both sides of the DAC assuming a grey-body approximation [Prakapenka
144 *et al.*, 2008]. 2D diffraction images were collected using a Pilatus 1M CdTe detector. We
145 used a LaB_6 standard to calibrate and correct distortions and detector distance (~ 200 mm)
146 during integration from 2D images to 1D patterns in the Dioptas software [Prescher and
147 Prakapenka, 2015]. We used the PeakPo software package for peak identification and unit-
148 cell fitting [Shim, 2017].

149 **2.4 Electron Probe Micro-Analysis**

150 To resolve chemical compositions of the phases synthesized at high P - T , electron
151 probe micro-analysis (EPMA) was performed on starting materials synthesized in the multi-
152 anvil press, and on the recovered samples from the laser-heated diamond-anvil cell (LH-
153 DAC). X-ray intensity mapping and semi-quantitative point analysis were performed at Ari-
154 zona State University's Eyring Materials Center using a JEOL JXA-8530F. To avoid charge
155 build-up, samples were coated with a thin conductive C-layer to increase electron conductiv-
156 ity and improve sample imaging and analysis. Sample imaging was mainly done using back

157 scattered electrons (BSE). For energy dispersive spectroscopy (EDS) X-ray intensity map-
158 ping, the electron microprobe was operated at 20 kV with a current of 75 nA and a dwell time
159 of 50 ms, producing 128×96 pixel maps. For wavelength dispersive spectroscopy (WDS) X-
160 ray intensity mapping, the microprobe was operated at 20 kV with a current of 100 nA and a
161 dwelling time of 50 ms, resulting in 270×270 pixel maps.

162 Considering the beam penetration and the depth of electron interaction combined with
163 small grain sizes of the phases from LHDAC experiments, EPMA could sample signal from
164 underlying phases. This problem could have been reduced by making thin sections at the
165 laser-heated spots using a focused ion beam (FIB). However, the recovered samples appear to
166 be much weakened by intense chemical reaction with hydrogen, which should have been in
167 liquid state during heating. Therefore, we chose EPMA which requires minimal processing
168 of the mechanically weakened recovered samples.

169 **3 Results and discussion**

170 **3.1 Fe₃S + H**

171 We investigated the reaction between Fe₃S and pure hydrogen at pressures of 23–
172 45 GPa and temperatures up to 4000 K. In all the runs, no reaction of Fe₃S with hydrogen
173 was observed under cold compression to high pressures (i.e. before laser heating) (Fig. 1a),
174 and the measured unit-cell volume of the phase is similar to that of pure Fe₃S reported at the
175 same conditions [Fei *et al.*, 2000]. Therefore, we interpret that Fe₃S does not react with hy-
176 drogen at room temperature and high pressures. The behavior is in contrast with that of pure
177 Fe metal where it has been consistently reported that Fe metal reacts with hydrogen at high
178 pressures and 300 K and converts to double hexagonal close packed (dhcp) structure of FeH
179 [Badding *et al.*, 1991].

180 After a Fe₃S sample was heated in a H medium to 2830 K at 28 GPa, the phase com-
181 pletely disappeared from the diffraction patterns (Fig. 1b). The instability of Fe₃S at 28 GPa
182 is striking since Fe₃S is reported to be stable up to 271 GPa at 3300 K [Ozawa *et al.*, 2013]
183 This observation shows that the behavior of Fe₃S is fundamentally different when H is present
184 in the system. In place of Fe₃S at 28 GPa, we observed a mixture of dhcp-FeH and FeS(III).
185 Although the measured unit-cell volume of dhcp-FeH is similar to what is expected at 28 GPa
186 [Pépin *et al.*, 2014], FeS(III) has a noticeably greater unit-cell volume than reported at this
187 pressure [Kusaba *et al.*, 1997] (Fig. S2), suggesting incorporation of H into the FeS(III)

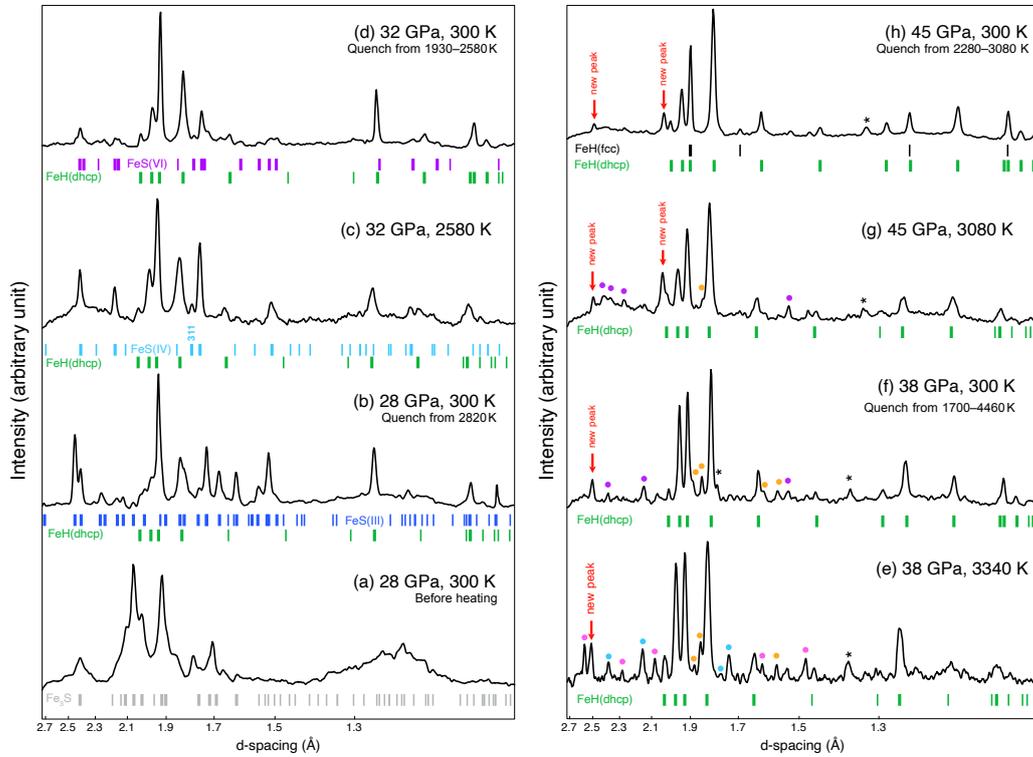


Figure 1. X-ray diffraction for runs starting with $\text{Fe}_3\text{S} + \text{H}_2$. The thin vertical ticks show all the expected d -spacing and intensity for a given phase and the thick vertical ticks highlight the observed ones. The colored dots highlight observed peaks from minor phases (orange: Fe_2S ; purple: FeS(VI) ; cyan: FeS(IV) ; pink: FeS_2). Unidentified lines are indicated by *. (a) Only Fe_3S is present before heating; (b) Fe_3S is not stable and transforms into a mixture of dhcp-FeH, FeS(VI) and FeH_2 after temperature quench; (c) Similar instability of Fe_3S was observed at a higher pressure during in situ heating; (d) FeS(IV) transforms to FeS(VI) and dhcp-FeH is present after temperature quench; (e) Fe_3S is not stable and transforms into a mixture of dhcp-FeH, FeS(IV) and FeS_2 during heating at 38 GPa. New peaks (red arrows) appear at >38 GPa; (f) After temperature quench, new peaks present with dhcp-FeH, while FeS(IV) transforms to FeS(VI) ; (g) At 45 GPa and 3080 K, Fe_3S is not stable and transforms into a mixture of dhcp-FeH, FeS(VI) and a new phase; (h) After temperature quench, dhcp-FeH, FeS(VI) and the new peaks are still present.

188 structure. The heating temperature, 2820 K, at 28 GPa is above the melting temperature of
 189 FeS [Boehler, 1992], FeH [Sakamaki *et al.*, 2009], and the eutectic temperature of Fe–Fe₃S
 190 [Kamada *et al.*, 2010] (Fig. 2a). Therefore, we interpret that liquid Fe₃S crystallized into the
 191 observed FeS and FeH phases. At 32 GPa, the same trend continues: disappearance of Fe₃S
 192 and appearance of dhcp-FeH and FeS (Fig. 1c-d) upon heating. Again here, the heating tem-
 193 peratures are higher than the expected melting temperatures of FeS and FeH. FeS(IV) and its
 194 higher temperature polymorph FeS(V) both feature NiAs-type structures, resulting in very
 195 similar diffraction patterns. The observation of FeS(IV) instead of FeS(V) above 1900 K (by
 196 the diagnostic 311 peak; Fig. 1c) is discrepant from reports for H-free FeS in the literature
 197 [Kavner *et al.*, 2001; Fei *et al.*, 1995; Urakawa *et al.*, 2004; Ohfuji *et al.*, 2007]. The mea-
 198 sured unit-cell volumes of FeS(IV) are somewhat higher than expected at 32 GPa [Urakawa
 199 *et al.*, 2004] (Fig. S2), which indicates that a small amount of H could stabilize FeS(IV)
 200 over FeS(V). Upon quench, FeS(IV) transforms to FeS(VI) (Fig. 1d), whereas in H-free sys-
 201 tems, FeS(IV) was instead observed to transform to FeS(III) upon temperature quench [Fei
 202 *et al.*, 1995; Urakawa *et al.*, 2004; Ohfuji *et al.*, 2007]. Ohfuji *et al.* [2007] did observe that
 203 FeS(IV) transforms to FeS(VI) with heating above 1300 K, but here the transition is observed
 204 upon temperature quench and could be an effect of H. Therefore, while a majority of H is al-
 205 loyed in Fe metal to form FeH when Fe₃S liquid crystallizes, some small amounts of H alloy
 206 with FeS phases and affect the phase behaviors.

207 At 38 GPa, unlike the results at lower pressures, we find a new peak appearing during
 208 heating at $d_{sp} = 2.87 \text{ \AA}$, which will be discussed later. A few weak lines also appear during
 209 or after heating. Although they can be assigned to either FeS₂ or *Pnma*-Fe₂S [Zurkowski,
 210 2020], because these peaks are mainly from weak spots in diffraction images, their assign-
 211 ments are not conclusive. Given the low intensity of these phases, they are likely related to
 212 thermal gradients during laser heating. Therefore, we interpret that they are not stable phases
 213 at the $P - T$ conditions with hydrogen.

214 At 45 GPa and 3080 K, Fe₃S completely transforms into dhcp-FeH, and FeS(VI) (Fig. 1g).
 215 The previously observed new peak is again present here, as well as an additional strong new
 216 peak ($d_{sp} = 2.24 \text{ \AA}$). Weak peaks, which can be assigned to FeS₂ progressively disap-
 217 pear with further heating in the 2280–2590 K range, regardless of temperature, and could
 218 be caused by thermal heterogeneity during laser heating. Similarly, intensities of the peaks
 219 which can be assigned to FeS(VI) and Fe₂S decrease with further heating, and Fe₂S has com-
 220 pletely disappeared with temperature quench. Dhcp-FeH and the new peaks, however, grow

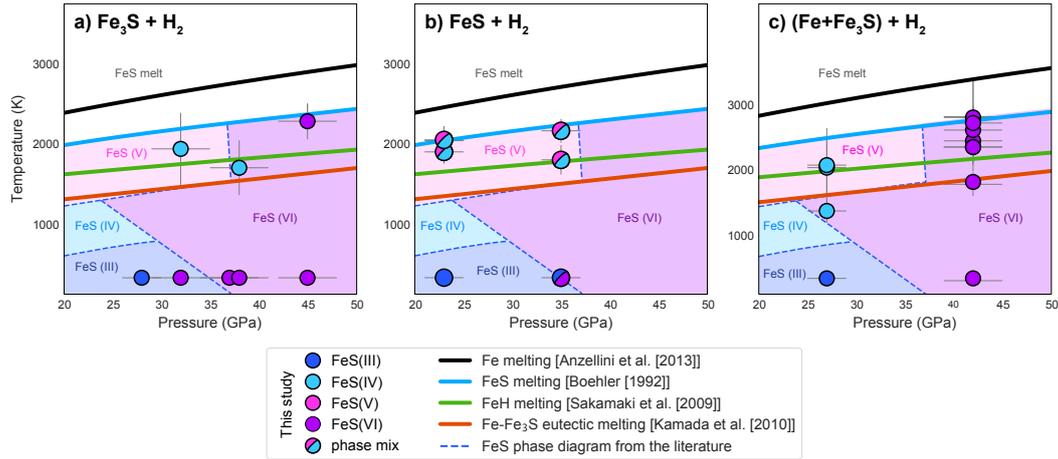


Figure 2. Pressure–temperature conditions for FeS phases in a hydrogen medium in: (a) $\text{Fe}_3\text{S} + \text{H}_2$, (b) $\text{FeS} + \text{H}_2$ and (c) $(\text{Fe} + \text{Fe}_3\text{S}) + \text{H}_2$ starting materials. In this figure, we show only the data points measured below FeS melting. The symbol colors refer to the observed polymorphs of FeS at the conditions (see legend). We also have some data points measured above melting temperatures of iron alloys and they can be found in Tab. S2. The reported polymorphs at 300 K are those observed after temperature quench. The solid lines represent the melting curves of different phases (black: pure Fe [Anzellini *et al.*, 2013], blue: FeS [Boehler, 1992], green: FeH [Sakamaki *et al.*, 2009], orange: eutectic for Fe–Fe₃S [Kamada *et al.*, 2010]). Stability fields for FeS polymorphs in H-free system are represented by different colors and boundaries are emphasized with blue dashed lines [Fei *et al.*, 1995; Kavner *et al.*, 2001; Urakawa *et al.*, 2004; Ono and Kikegawa, 2006; Ohfuji *et al.*, 2007].

stronger with subsequent heating and remain the major phases in the final quench (Fig. 1h). The stronger than expected intensity of the 004 dhcp-FeH peak ($d_{sp} = 2.05 \text{ \AA}$ at this pressure) in the pattern suggests that the observed peak intensity does not only result from the presence of dhcp-FeH. A legitimate candidate to explain the observation is fcc-FeH, which has been reported to form at high temperature at this pressure range [Thompson *et al.*, 2016; Kato *et al.*, 2020], and which 111 peak could account for the observed intensity.

3.2 FeS + H

To further understand the phase behavior of Fe–S–H system, we also studied pure FeS in a hydrogen medium using the same experimental procedure as for Fe₃S + H₂ at similar pressures. Before heating at 23 GPa, the pattern can be explained by a single FeS(III) phase. The measured unit-cell volume of the phase is slightly higher than that of pure FeS(III) at the same pressure (Fig. S2) [Kusaba *et al.*, 1997], suggesting some solubility of H in this FeS(III) phase even without heating. With heating, fcc-FeH appears in diffraction patterns as a major phase. Some minor peaks can also be assigned to dhcp-FeH (Fig. 3b). Dhcp-FeH was observed to be a more prominent phase in runs starting with Fe₃S. Although we do not have direct evidence for this, the prominence of fcc-FeH over dhcp-FeH in FeS + H₂ runs suggests that some S in the crystal structure may affect the stability of one structure with respect to another since the S content is the most notable difference between the Fe₃S + H₂ runs and the FeS + H₂ runs.

We also identify both FeS(IV) and FeS(V) at high temperature (Fig. 2b). FeS(V) was not observed in runs with the Fe₃S + H starting materials. Since FeS(V) is usually the stable polymorph at these $P - T$ conditions in H-free systems [Ono and Kikegawa, 2006], we attribute the existence of both FeS(IV) and FeS(V) to an incomplete reaction of FeS with H where FeS(IV) results from the reaction with H at high temperature and FeS(V) is the non reacted FeS phase. The absence of volume change from its expected volume at 23 GPa is also a good indicator that the phase did not react with hydrogen (Fig. S2). Upon temperature quench, both FeS phases transform to FeS(III) (Fig. 3b). The unit-cell volume for FeS(III) being higher than before heating [Kusaba *et al.*, 1997] suggests increased solubility of H in FeS(III) from laser heating.

At 35 GPa and 3674 K, FeS (III) in a pure hydrogen medium transforms to a FeS(IV)–FeS(V) mixture similarly to what is observed at 23 GPa. There are, however, a few impor-

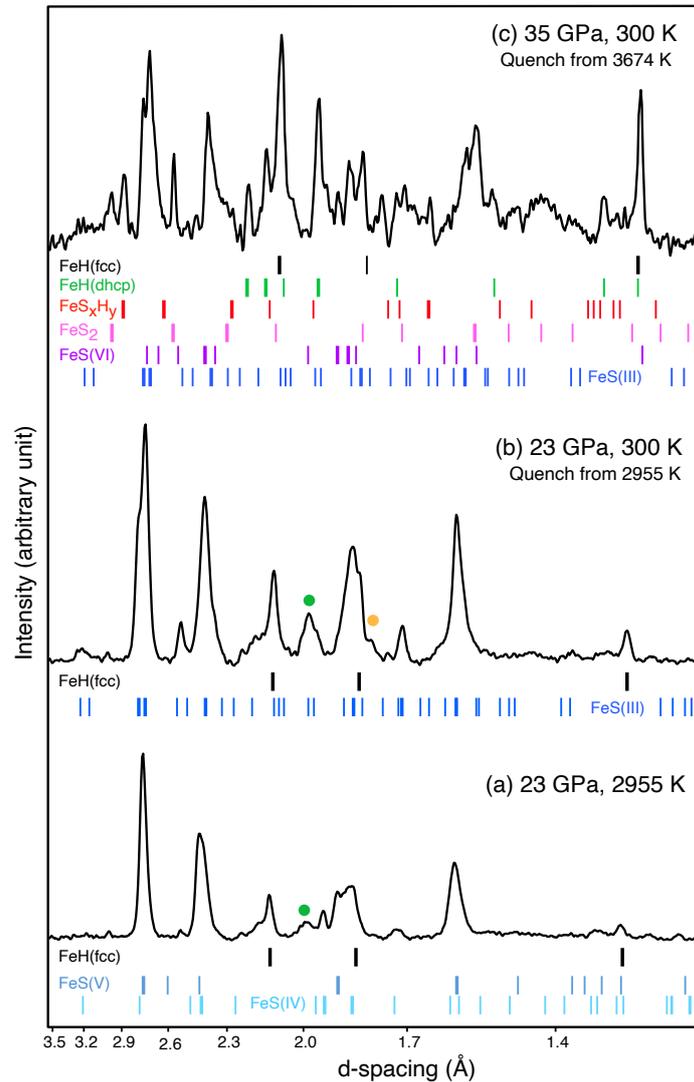


Figure 3. X-ray diffraction for runs starting with FeS + H₂. The thin vertical ticks show all the expected *d*-spacing and intensity for a given phase and the thick vertical ticks highlight the observed ones. The colored dots highlight observed peaks from minor phases (green: dhcp-FeH; orange: Fe₂S). (a) At 23 GPa and 2955 K, fcc-FeH and FeS(IV) form from the reaction of FeS and H₂, whereas FeS(V) most likely results from non reacted FeS with H₂. (b) Upon temperature quench FeS transforms entirely to FeS(III). Fcc-FeH remains a major phase and dhcp-FeH remains a minor phase. (c) Diffraction pattern measured after temperature quench from 3674 K at 35 GPa is more complex than at 23 GPa. The new phase (FeS_xH_y) is observed, as well as FeS (III and VI), FeS₂ and both fcc-FeH and dhcp-FeH are major phases here.

252 tant differences between the runs at 23 GPa and the one at 35 GPa. First, we found more
253 enhanced diffraction intensities from dhcp-FeH (Fig. 3c). The different behavior might be
254 related to extremely high temperature above melting achieved in this higher pressure run.
255 Second, we observed the same new peaks found in Fe₃S + H runs. The number of phases
256 observed in the diffraction pattern exceeds the number expected for thermal equilibrium in
257 Fe–S–H ternary. Because heating was conducted to a temperature much above melting, it is
258 possible that thermal gradients were more severe and therefore result in complex crystalliza-
259 tion during temperature quench.

260 In most of the experiments for the FeS + H₂ starting materials, we observed FeH and
261 FeS. The formation of FeH without S at lower pressures requires some amount of S either
262 dissolved in the H medium or reacting with H to form a S-H phase. However, S-H phases
263 would be challenging to detect in X-ray diffraction because of very low X-ray scattering cross
264 sections expected for the phases. Therefore, within our resolution, the absence of S-H phase
265 peaks cannot rule out the possibility of its existence in reaction product.

266 **3.3 Fe + Fe₃S + H**

267 Since no Fe–S alloy richer in Fe than Fe₃S exists, we used a mechanical mixture of
268 Fe and Fe₃S as a proxy to study how increasing amounts of metallic Fe in the bulk system
269 affects the results when reacted with H₂ (Tab. S2). At 27 GPa and 1100 K, we observed fcc-
270 FeH and FeS(IV). FeS(IV) persisted to higher heating temperatures (up to 2670 K). Again,
271 the presence of FeS(IV) instead of FeS(V) expected at these conditions (Fig. 2c), suggests
272 that FeS(IV) might host a significant enough amount of H in order to stabilize the structure at
273 the temperature. At 42 GPa and 2077 K, we observed peaks attributed to the new phase upon
274 heating, which confirms what was observed for pure Fe₃S and FeS starting runs. We also
275 observed FeH (mostly in dhcp). Although the existence of multiples of phases in this starting
276 mixture makes the interpretation more complicated, the main features we observed in Fe₃S +
277 H₂ runs and FeS + H₂ runs were reproduced in these experiments.

278 **3.4 A new phase in Fe–S–H**

279 Fig. 4 shows the pressure and temperature conditions for all the runs we conducted.
280 In the figure, we highlighted the conditions where the new diffraction lines were observed.

281 The new peaks were observed only above 35 GPa regardless of the starting composition. The
 282 stability of the phase does not seem to have a strong temperature dependence either.

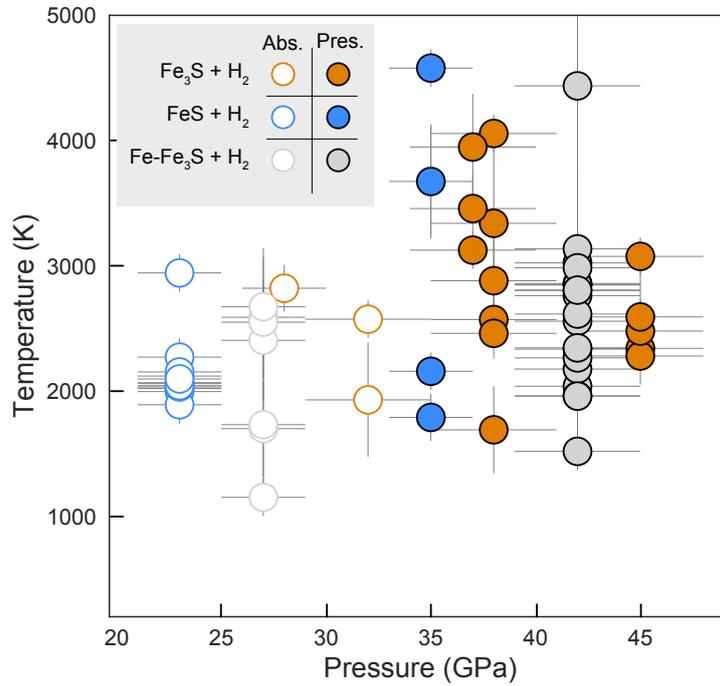


Figure 4. Pressure and temperature conditions for the observation of the new phase associated with the new diffraction peaks. The open and the close circles are for non-observation and observation of the new phase respectively.

283 Given the presence of Fe–S and Fe–H phases in our runs, a potential candidate to ex-
 284 plain the observed new peaks is a counterpart hydrogen sulfide phase. Neither *I4/mcm*-H₃S
 285 nor *I222*-H₃S, however, provides a match for the observed new peaks in terms of expected
 286 peak position or intensity [Strobel *et al.*, 2011; Duan *et al.*, 2014]. Although we cannot com-
 287 pletely exclude the formation of hydrogen sulfide in our runs, the relatively smaller X-ray
 288 scattering cross-section of H–S phases compared with iron-bearing phases, would make such
 289 a compound challenging to detect and therefore an unlikely source for the intense new lines
 290 observed in our diffraction patterns. Regarding the possibility for a Fe–S phase, Shibasaki
 291 *et al.* [2011] reported the formation of FeSH_x(IV) and FeSH_x(V) at 16.5 GPa and above
 292 800 K. However, volume expanded versions of FeS(IV) and FeS(V) would only change the
 293 peak position.

294 The presence of FeH in our runs suggests that the new peaks could also be iron hy-
295 dride. At the investigated P - T range, the stable iron-hydrogen alloys are dhcp-FeH and fcc-
296 FeH [Badding *et al.*, 1991; Narygina *et al.*, 2011]. We found that the observed new lines can
297 be well indexed with a tetragonal unit cell. The positions of all four new peaks can be fit to
298 a FeH₂-like tetragonal structure [Pépin *et al.*, 2014], albeit with an increased unit-cell vol-
299 ume by +60% uniformly along all three directions (Fig. 5 and Tab. S3). Increased hydrogen
300 solubility in iron hydrides also leads to volume expansion and it was observed for interstitial
301 hydrogen in fcc-FeH [Narygina *et al.*, 2011] and for molecular hydrogen in FeH₂ and FeH₅
302 [Pépin *et al.*, 2014, 2017] through the formation of additional layers of hydrogen. However,
303 FeH₅, which was reported to form above 135 GPa [Pépin *et al.*, 2017], does not explain the
304 new peaks (Fig. 5). Due to the layered nature of the FeH₂ structure (alternating layers of Fe
305 and H), it is unlikely that more H would explain the observed homogeneous volume expan-
306 sion to all three directions, but rather would be directional. It is worth noting that FeH₂ was
307 reported to appear only above 67 GPa [Pépin *et al.*, 2014]. Therefore, formation of a similar
308 structure at significantly lower pressures requires some other stabilizing sources. Since S can
309 also increase the unit-cell volume, this phase may contain both S and H.

310 We constructed a diffraction intensity map for the new phase using the most intense
311 line. The map shows that the phase is populated mostly near the rim of the laser heated spot.
312 (Fig. 5b). The chemical maps of the same heated spot also reveals a rim like structure around
313 the hot spot (Fig. 5b). The areas can be divided into: i) non reacted material around the
314 heated area of Fe₃S composition as confirmed by point analysis (the green area in the S
315 map), ii) S-poor/free areas at the laser heated center most likely the remnants of unquench-
316 able FeH converted into Fe metal and iii) S-rich areas at the rim of the heated spot (the red
317 rim in the S map). As shown in the figure, the new phase is located in the S-rich area and
318 therefore should contain higher S content than the starting material, Fe₃S. The S-rich rim
319 area should also have FeS(VI) as well as the new phase according to our X-ray diffraction
320 analysis. Unfortunately, our EPMA results cannot resolve the difference in Fe:S ratio be-
321 tween FeS(VI) and the new phase. The reason for this is that the typical grain size of the
322 phases in LHDAC experiments is a few hundreds of nanometers. The thickness of the recover-
323 ed sample is approximately 10 μ m and the excitation depths by the electron beam should be
324 large enough for the thickness. Therefore, phases beneath the surface could contaminate the
325 chemical composition measured in the EMPA of the LHDAC recovered sample. For accurate
326 measurements, thinning of the heated area using focused ion beam (FIB) and chemical anal-

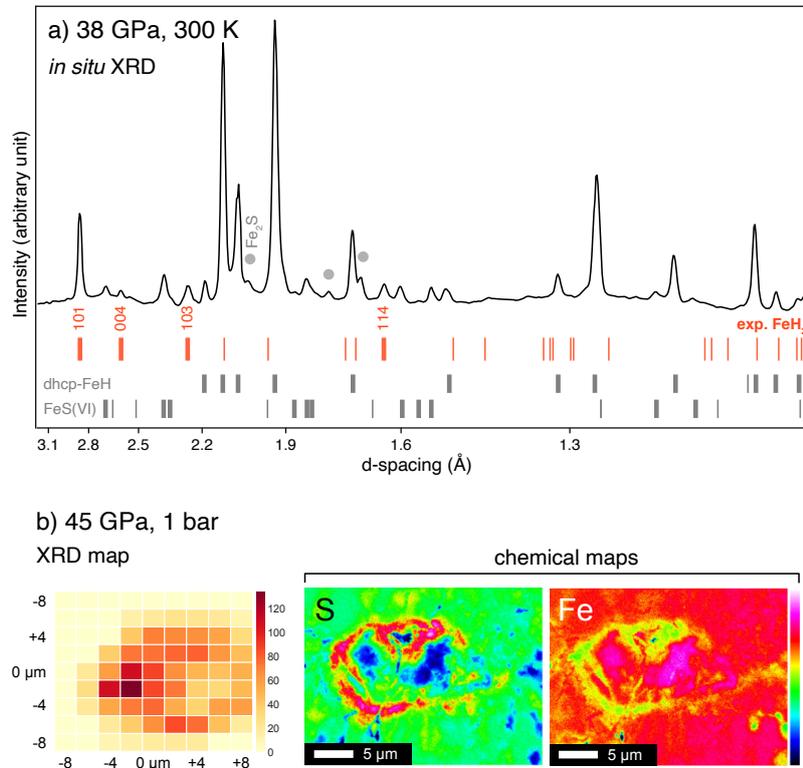


Figure 5. a) An X-ray diffraction pattern for the new phase at 38 GPa and 300 K upon temperature quench after reaction of $\text{Fe}_3\text{S} + \text{H}_2$ at temperatures in the 1700–4460 K range. The thin vertical ticks show all the expected d -spacing and intensity for a given phase and the thick vertical ticks highlight the observed ones. The expanded FeH_2 (red ticks) structure provides the best fit for the new observed peaks with four peaks uniquely matching without overlaps with other phases (bold ticks). Additionally, peaks at 2.1, 1.7, and 1.1 Å, while overlapping peaks from other phases, can also match and to some degree enhance the intensity of observed peaks. The gray dots indicate weak peaks which can be assigned to a small amount of Fe_2S . b) A map of the diffraction intensity of the FeS_xH_y 101 peak in the laser heated area from run r320 at 45 GPa (starting with $\text{Fe}_3\text{S} + \text{H}_2$) (left). The map was constructed from diffraction patterns collected after temperature quench in a $16 \times 16 \mu\text{m}$ grid with $2 \mu\text{m}$ steps. The map shows that the phase is populated in the outer part of the heated area. Composition maps for S and Fe (right) of the recovered heated area show that the center of the heated spot is mostly Fe-rich while the edge is more S-rich.

327 ysis in Transmission Electron Microscopy would be required. However, samples synthesized
 328 in a H medium are mechanically weak and were not suitable for such sample processing.

329 While the exact ratio between Fe and S is unknown for the new phase, as discussed,
 330 EPMA results combined with XRD analysis can constrain the ratio to be close to 1:1. We
 331 performed unit-cell volume measurement during decompression to 1 bar for the new phase
 332 synthesized in two runs (r220 and r231c; Fig. 6). While the measured volume of the new
 333 phase is very close to that of FeS(VI), it is systematically greater throughout the pressure
 334 range. Increasing solubility of H in iron hydrides at high pressure has shown to contribute
 335 to increase in unit-cell volumes [Badding *et al.*, 1991; Narygina *et al.*, 2011; Pépin *et al.*,
 336 2014]. Fitting to a Vinet equation [Vinet *et al.*, 1987] for fixed pressure derivative of bulk
 337 modulus ($K' = 4$) yielded $V_0 = 110.4(5)$ and $K_0 = 159(7)$ for the new phase. The equation
 338 of state curve of the new phase is nearly parallel to that of FeS(VI) and therefore the volume
 339 difference between FeS(VI) and the new phase remains nearly constant within the pressure
 340 range.

341 Fig. 6 shows the volume per one Fe of the phases in the Fe–H and Fe–S system. Such a
 342 representation gives qualitative insights on how substituting S and H would increase the vol-
 343 ume of Fe alloys. However, this representation requires knowledge of the number of formula
 344 units in the unit-cell (Z). The Z number is unknown for the new FeS_xH_y phase. Since we
 345 indexed the diffraction lines of the new phase to a tetragonal FeH_2 -like structure, we choose
 346 to use the same Z number (4). We calculated the volume differences between hcp-Fe and
 347 different iron sulfides and iron hydrides, as well as between iron hydrides and iron sulfides
 348 themselves (Tab. S4). We obtained an average value for $\Delta V_{\text{H}} = 2.02 \text{ \AA}^3$ corresponding to
 349 the average volume increase caused by one atom of H. Therefore, the near constant volume
 350 difference between FeS(VI) and the new phase can be explained by $y \approx 1$ for FeS_xH_y where
 351 $x = 1$ from the EMPA data. While the assignment for the new phase here remains tentative
 352 because of the uncertainties in the crystal structure, from the arguments above built from our
 353 observations, it is reasonable to assume that the new phase is close to FeSH ($x = 1$ and $y = 1$
 354 for FeS_xH_y). Therefore, in the remainder of the text we refer to the new phase as FeSH.

355 In pure Fe, H escapes from the crystal structure during decompression [Okuchi, 1997].
 356 As H expands the unit-cell volume, H loss can result in a sudden volume decrease. For the
 357 new FeSH phase, we did not observe any significant volume decrease during decompression
 358 and the measured P – V data show a smooth trend extended to near 1 bar (Fig. 6). At 1 bar,

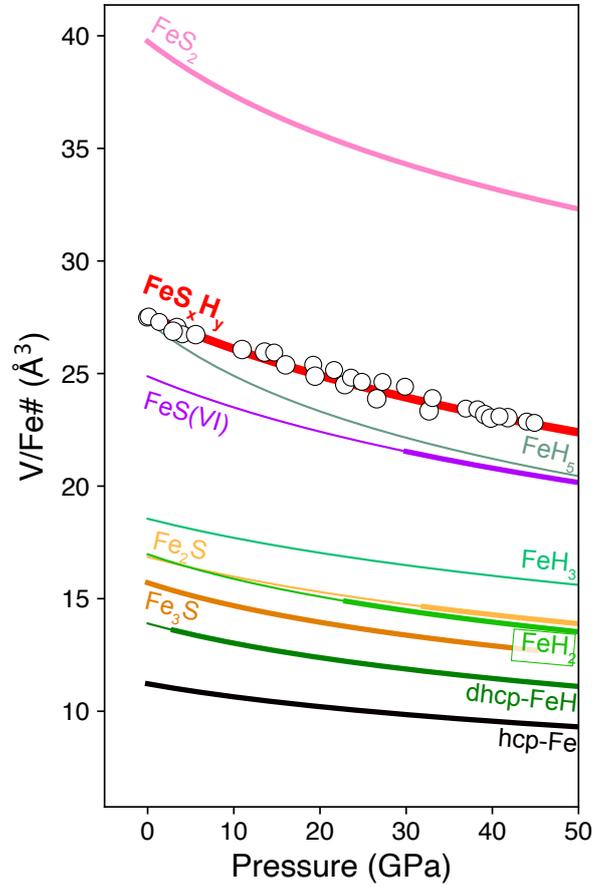


Figure 6. Pressure-volume relation of the new phase (FeS_xH_y , open circles) and the fitted equation of state (the thick red curve). We also show other phases in the Fe–S–H system from the literature for comparison (thick lines correspond to the pressure range at which the phase is observed to be stable; thin lines correspond to pressure range outside the phase stability where the fitted volume is extrapolated). Fe: *Dewaele et al.* [2006]; dhcp-FeH, FeH_2 and FeH_3 : *Pépin et al.* [2014]; FeH_5 : *Pépin et al.* [2017]; Fe_3S : *Kamada et al.* [2014b]; Fe_2S : *Zurkowski* [2020]; FeS(VI) : *Ono and Kikegawa* [2006]; FeS_2 : *Merkel et al.* [2002]. The unit-cell volumes are divided by the number of Fe atoms in the unit-cell. Note that we assume the new phase has the same number of Fe atom as regular FeH_2 , which is 4.

359 the diffraction patterns of the sample quenched from 42 GPa show some new diffraction
 360 peaks as well as those existing at high pressures and assigned to the new phase (Fig. S3). The
 361 new lines appearing in the quench diffraction pattern could not be indexed with any known
 362 phases in Fe–S. It is feasible that FeSH may convert to a different crystal structure (either
 363 partially or completely) at 1 bar. Therefore, it is difficult to index the diffraction lines and the
 364 volume of the new phase remains uncertain at 1 bar.

365 4 Discussion

366 4.1 Phase relations in Fe–S–H up to 45 GPa

367 In all our experimental runs, we observed the striking disappearance of Fe₃S upon
 368 heating in a H-rich environment, regardless of pressure, temperature, and starting compo-
 369 sition between Fe and FeS. The formation of FeH (dhcp and or fcc) is also common to all
 370 the runs. The differences observed between runs are whether FeS or FeSH was the main S-
 371 bearing phase at high pressure and high temperature. Although we do not have tight con-
 372 straints on the melting behaviors of the studied system, we observed some clear pressure-
 373 dependent changes in the Fe₃S + H₂ experiments. Based on the information, we built provi-
 374 sional ternary Fe–S–H phase diagrams in Fig. 7.

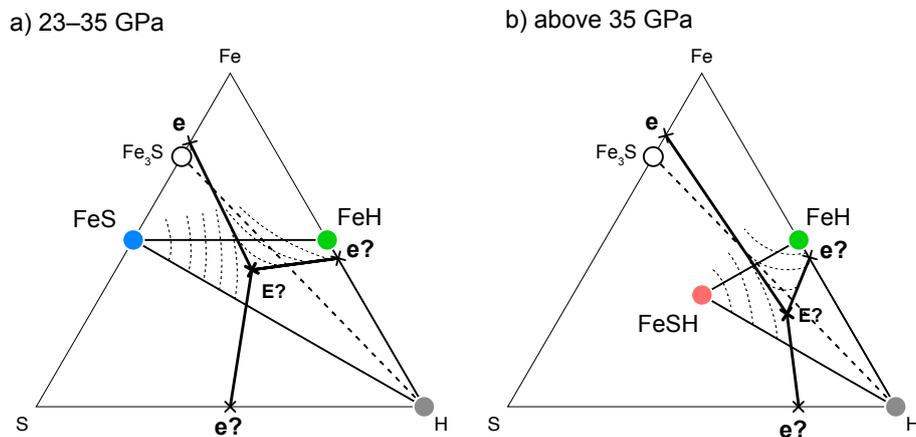


Figure 7. Provisional ternary Fe–S–H phase diagrams at 23–35 GPa (a) and above 35 GPa (b). *e*'s show the eutectic points in the Fe–S, Fe–H, and H–S binaries and *E* is the eutectic of the ternary. The colored circles show major phases observed at the pressures. The thick dashed lines connect the starting phases. The thin dashed lines represent possible isotherms. Note that the details of these diagrams remain uncertain and therefore the diagrams should be regarded as tentative.

375 At 23–35 GPa, we observed FeH and FeS phases in temperature quench (Fig. 7a).
 376 However, according to Gibbs' phase rule, if thermodynamical equilibrium is reached (pos-
 377 sibly locally in LHDAC), three phases are expected for a degree of freedom of 2. Although
 378 the third phase remains uncertain, it should not contain Fe, otherwise it would appear in
 379 XRD patterns. Therefore, we tentatively assign the third phase to H. It is feasible that a H-
 380 S phase instead is stable in our experimental runs. The Fe–S binary phase diagram is well
 381 constrained at pressures in the 23–40 GPa range [Stewart *et al.*, 2007] and features a eutec-
 382 tic behavior with eutectic composition close to Fe₃S at pressures below 35 GPa. The Fe–H
 383 binary phase diagram, on the other hand, is less well constrained but likely features a solid-
 384 solution for FeH_x where $x \leq 1$. Shibazaki *et al.* [2014] proposed a Fe–H binary phase diagram
 385 featuring a eutectic for $x > 1$ in FeH_x at 15 GPa. However, the subsequent discovery of FeH₂,
 386 FeH₃ [Pépin *et al.*, 2014] and FeH₅ [Pépin *et al.*, 2017] at higher pressures raises questions
 387 on the position of the eutectic along the Fe–H joint. Although many aspects of the phase di-
 388 agram shown in Fig. 7a remains tentative, the crystallization of the FeS and FeH phases in
 389 our study at the pressure range is at least consistent with a global ternary eutectic point in the
 390 phase diagram.

391 Above 35 GPa after extended cycles of heating runs, only FeH and FeSH remained
 392 from the reaction of Fe₃S with H₂, whereas FeS almost completely disappears (Fig. 7b).
 393 Similarly to the case at 23–35 GPa, we assume that either H or H-S phase exists as the third
 394 phase. The key observation at this pressure range is that FeS is unlikely stable anymore and
 395 a phase including both S and H may appear in the phase diagram. Assuming that eutectic
 396 behavior along all three joints persists with increasing pressure, the position of the ternary
 397 eutectic may move towards the H end-member. However, the precise positions of the eutectic
 398 points remain to be constrained through additional experiments.

399 **4.2 Implications for crystallization of Mars-sized planetary cores**

400 The pressure range we studied for Fe–S–H overlaps with the range expected for the
 401 Martian core, 20–40 GPa [Helffrich, 2017]. For the Martian core, sulfur has been considered
 402 as the main light element based on its abundance in Martian meteorites and theoretical mod-
 403 els of nebular condensation [Dreibus and Wänke, 1985; Wänke and Dreibus, 1988; Lodders
 404 and Fegley, 1997]. Although there are different views [Wang and Becker, 2017], existing
 405 models prefer 14–17% of S in the Martian core [Gaetani and Grove, 1997; Urakawa *et al.*,
 406 2004; Khan *et al.*, 2017], which is close to Fe₃S. The amount of hydrogen stored in the Mar-

407 tian core is currently unknown. For the Martian mantle, recent estimates (100–300 wt ppm in
408 H₂O) are at least similar to that of the Earth’s mantle [Leshin, 2000; McCubbin *et al.*, 2010;
409 Hallis *et al.*, 2012; Usui *et al.*, 2012]. Therefore, H remains as a viable candidate for a light
410 element in the Martian core, as it can partition preferentially to the core from its affinity to
411 metal at high pressures [Okuchi, 1997]. Although further improvements are expected, re-
412 cent InSight data analysis found a much larger size for the Martian core, which may require
413 a lower density than previously believed [Stähler *et al.*, 2021]. While more S can lower the
414 density, the low density could also be explained by the presence of other light elements to-
415 gether with S. Because it can severely lower the melting temperature of iron metal [Sakamaki
416 *et al.*, 2009], hydrogen could explain largely molten state of the present-day core proposed by
417 a geophysical study [Yoder *et al.*, 2003]. Our experimental study also provides essential data
418 to model the cores of Mars-sized planets found outside of the solar system [Jontof-Hutter
419 *et al.*, 2015]. While detection and mass measurement are very challenging because of their
420 small size, with their potential habitability and improved technology in coming missions,
421 more data will likely be available for Mars-sized exoplanets.

422 According to our experimental observations, at 23–35 GPa (therefore, at much of the
423 Martian core or at the core of sub-Mars), either FeS or FeH would crystallize first depending
424 on the S/H ratio of the system. For example, if the bulk composition of the system is on the
425 S-rich side (left of the eutectic line in Fig. 7a), FeS would likely be the first solid to crystal-
426 lize and the liquid would become progressively enriched in H as crystallization of FeS pro-
427 ceeds. Layering of the core would then depend on the density contrast between the different
428 phases, as well as mixing properties and local dynamics at play. The density difference be-
429 tween liquid FeH and liquid FeS is not known. However, solid FeH is denser than solid FeS
430 because H tends to be incorporated in the interstitial site of the densely packed structure of
431 Fe. If such relationship is applicable between solid FeS and liquid FeH, solid FeS could even
432 “float” at the outer part of the core. Above 35 GPa (therefore, at the innermost Martian core
433 or at the cores of super-Mars and sub-Earths), the appearance of a new FeSH phase could
434 change the crystallization of the core. In this case, either FeSH or FeH would crystallize first.
435 H would likely decrease the melting temperature of the new phase below that of FeS, but
436 whether it would decrease the melting temperature below that of FeH is unknown. A few
437 important measurements are therefore to be made to further understand Fe–S–H ternary in
438 Mars-sized rocky planets’ cores. Measurements of melting of FeSH are needed to further
439 constrain the crystallization behavior of the system above 35 GPa. Our data mostly reside on

440 the H rich side of the Fe–S–H ternary (Fig. 7). Although some of the phases we identified
441 here could still appear in low H systems, it would be important to conduct measurements on
442 systems with smaller amounts of H, which would be more relevant for planets with a smaller
443 amount of H.

444 Although not directly relevant to the Earth, our results shed additional light on the
445 complexity of light element partitioning between solid and liquid Fe, especially when H is
446 involved. The observed density difference between the solid and liquid Earth’s core suggests
447 that the liquid outer core is enriched in light elements with respect to the solid inner core
448 [Birch, 1952; Poirier, 1994]. Melting experiments on Fe–S alloys have shown that all light
449 elements do not necessarily preferentially partition into liquid Fe. Mori *et al.* [2017] showed
450 that the partition coefficient of S between solid and liquid iron increases with increasing
451 pressure and the trend persists up to 254 GPa, which in turn suggests that with increasing
452 pressure S tends to be more soluble into solid Fe than into liquid Fe. The preferential par-
453 titioning of S towards solid Fe with increasing pressure was later confirmed by Yokoo *et al.*
454 [2019] who performed melting experiments on the Fe–O–S system up to 208 GPa. Our study
455 of the Fe–S–H system at 23–35 GPa confirms what has been observed in the literature for
456 Fe–C–H [Narygina *et al.*, 2011; Ohta *et al.*, 2019; Hirose *et al.*, 2019] and Fe–O–H up to
457 80 GPa [Ohtani *et al.*, 2005; Liu *et al.*, 2017; Yuan *et al.*, 2018]: H may not necessary alloy
458 with other light elements but could preferentially partition into a phase that does not contain
459 the other light element. However, like in the Fe–O–H system above 80 GPa with the forma-
460 tion of FeOOH, pressure appears to promote the formation of a ternary alloy (FeSH, the new
461 phase we observed) in Fe–S–H as well, albeit at lower pressure. The relevance of FeSH for
462 Earth-size planets remains to be tested at the required pressures, temperature and composi-
463 tional conditions. If this behavior was to persist up to Earth’s core pressure, and given that S
464 prefers solid Fe, upon crystallization of a Fe–S–H rich core, an inner core could be enriched
465 in S, whereas the liquid outer core could be enriched in H. First principle studies have shown
466 that H can explain the density and compressional velocity of the Earth’s outer core and there-
467 fore could be the primary light element in the outer core up to 1 wt.% [Umemoto and Hirose,
468 2015]. However, Caracas [2015] showed that solid Fe–H cannot explain the shear velocities
469 observed in the inner outer core. Therefore, another light element like S, or a combination of
470 light elements with an affinity for solid iron could be the primary light element(s) in the inner
471 core.

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485 **Data Availability Statement**

486 Datasets for this research are included in this paper (and its supplementary information
487 files): *Piet et al.* [2021].

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