1 **Revision1**

2 **Liquid properties in the Fe-FeS system under moderate pressure: tool box to model**
3 **small planetary cores**

4 Guillaume Morard[1], Johann Bouchet[2], Attilio Rivoldini[3], Daniele Antonangeli[1], Mathilde
5 Roberge[1], Eglantine Boulard[1], Adrien Denoeud[4], Mohamed Mezouar[5]

6 [1]*Institut de Minéralogie, de Physique des Matériaux, et de Cosmochimie (IMPMC), Sorbonne*

7 *Universités - UPMC, UMR CNRS 7590, Muséum National d'Histoire Naturelle, IRD UMR*

8 *206, F-75005 Paris, France.*

9 [2]*CEA, DAM, 91297 Arpajon, France*

10 [3]*Royal Observatory of Belgium; B-1180 Bruxelles Belgium*

11 [4]*Ecole Polytechnique, LULI, F-91128 Palaiseau, France*

12 [5]*European Synchrotron Radiation Facility, Grenoble F-38043 France*

13

14 **Abstract**

15 **Physical properties of liquid Fe-S alloys (from 10 to 50 at%S) under high**
16 **pressure were investigated by in situ X-ray diffraction (up to 5GPa and 1900 K) and by**
17 **ab initio calculations. The local structure of Fe-S liquid alloys clearly show how S**
18 **modifies the local arrangement of the Fe atoms. Density has been extracted from the**
19 **diffuse scattering by minimization of the oscillation in the short distance of the radial**
20 **distribution function g(r). Two different formalisms for the P-V-T-X equation of state**
21 **are presented in order to model density and sound velocity as a function of pressure,**
22 **temperature and sulfur content. Based on these results, Moon's core composition is**
23 **discussed. This coherent dataset will serve as a thermodynamically consistent ground for**
24 **modeling the core of small telluric planets and large icy satellites.**

25

26

27

1

Introduction

28

29   Elements lighter than iron are expected to be present in planetary cores, due to their

30   abundance in iron meteorites and their affinity with the metallic phase. Among the potential

31   light elements (Poirier 1994), sulphur is likely the most abundant in the cores of iron

32   meteorites parent bodies (Chabot 2004). From tungsten isotopes data (Kleine et al. 2009) and

33   experimental studies of percolation processes (Yoshino et al. 2003), core formation is

34   expected to occur within a few million years of the solar system formation, even in small

35   planetesimals (Greenwood et al. 2006). It is therefore important to constrain physical

36   properties of Fe-S liquid alloys in order to better understand core formation in the early stage

37   of the solar system.

38   Melting properties in the Fe-FeS system under high pressure have been intensively

39   investigated by *in situ* (Campbell et al. 2007; Morard et al. 2007b; Chen et al. 2008a; G.

40   Morard et al. 2008; Andrault et al. 2009) or *ex situ* methods (Chudinovskikh and Boehler

41   2007; Stewart et al. 2007; Chen et al. 2008b; Kamada et al. 2012). However, while the Fe-rich

42   side of the phase diagram begins to be relatively well described, we still lack precise

43   knowledge of important physical properties, especially in the liquid state, such as density or

44   viscosity (LeBlanc and Secco 1996; Sanloup et al. 2000; Vočadlo et al. 2000; Balog et al.

45   2003; Nishida et al. 2008).

46   As today, the inner structures and in particular the cores of planetary bodies in the Solar

47   system are not well known, mostly because of the absence of seismological data, with the

48   clear exception for the Earth and, to some extent, for the Moon. Inferences about planetary

49   cores can be obtained from geodesy, electrical and magnetic data, and size, density, and

50   composition have been estimated (e.g. Yoder et al. 2003; Margot et al. 2007; Rivoldini et al.

51   2009; Zhang and Pommier 2017). However, those inferences require detailed modeling of the

52   interior structure, and the precision of the estimates, in particular core composition, calls for

53   extensive knowledge about core material properties. In this study we investigated the density

54   of liquid Fe-S alloys up to 5 GPa and 1900 K and assessed how it affects the Lunar interior.

55   Simultaneous measurements of density and liquid structure have been performed to

56   emphasize the strong link between evolution of the local atomic arrangement and changes in

57   the liquid density. This experimental study has been complemented by ab initio calculations

58   of the liquid structure in similar P-T conditions. We present two models describing

59   thermoelastic properties of liquid Fe-S as a function of pressure, temperature, and S content

2

60 based on our data and results published in the literature. These models are finally applied to

61 estimate S content in Moon's core.

62

Experimental procedure

Paris-Edinburgh Press experiments

65 X-ray diffraction experiments were carried out at the High Pressure beamline ID27 at

66 ESRF in Grenoble, France (Mezouar et al. 2005) using a large volume VX5 type Paris-

67 Edinburgh press (PEP) (Besson et al. 1992; Klotz et al. 2005). This press allows large opening

68 angle in the equatorial plane. The very high brilliance X-ray beam delivered by two in-

69 vacuum undulators was collimated down to 50*50 microns (typical values). The X-ray

70 wavelength was fixed to $\lambda=0.24678$ Å (Gadolinium K-edge) using a Si(111) channel cut

71 monochromator. A multichannel collimator (Mezouar et al. 2002; Morard et al. 2011) was

72 used to minimize the X-ray background coming from sample environment materials. The data

73 were collected using a MAR345 imaging plate system (X-Ray research company GmbH,

74 Nodersted, Germany). The sample-detector distance was calibrated with a LaB_6 standard

75 powder and the diffraction images were treated and integrated using the Fit2D software

76 (Hammersley et al. 1996). Typical exposure time to obtain the hereby presented data is 300s.

77 The high-pressure chamber consists of two opposed tungsten carbide anvils which

78 have quasi-conical hollows. We used 7 mm boron epoxy gaskets with a classical cell

79 assembly (graphite cylinder furnace, MgO capsule used as pressure medium and electrical

80 insulator (Mezouar et al. 1999)). MgO polycrystalline capsule is softer than single crystal

81 alumina capsule, used for conventional X-ray radiography technique, so to minimize pressure

82 gradients in the cell (Nishida et al. 2016). Pressure was calibrated using equation of state

83 (EoS) of MgO (Utsumi et al. 1998) close to the sample, in order to reduce P-T uncertainties.

84 Temperature was fitted using a previously established calibration curve (Morard et al. 2007a).

85 By combined use of this calibration and MgO EoS, pressure was found to be stable up to 1570

86 K and to decrease at higher temperatures (up to 0.7 GPa for the highest temperature). With

87 increasing temperature we could track the structural transitions in Fe (Klotz et al., 2008) and

88 FeS (Urakawa et al., 2004), confirming the validity of the temperature calibration. As

89 addressed in details in a previous paper (Morard et al., 2007b), metrological uncertainties are

90 the following : 170 K in temperature and 0.6 GPa in pressure.

91   The samples were a mixture of pure Fe (99.99 %, Alfa Aesar) and FeS powders

92   (99.9%, Sigma Aldrich). Electron microprobe (EMP) analyses were performed on quenched

93   samples (Centre Camparis, UPMC, Paris) using a Cameca SX100 wavelength dispersive

94   spectrometer (WDS) to measure the three main elements in this study (Fe, S and O, as

95   potential pollutant). Operating conditions in both cases were 15 kV and 40 nA for a counting

96   time of 20 s on peak and 10 s on background. Standards for the three elements were Fe, FeS_2

97   and Fe_2O_3, respectively. Our samples show fine dendritic textures; therefore we used a

98   defocused beam of ~20 microns to average the compositions of quenched texture (Figure 1).

99   Density and liquid structure of liquid Fe-S alloys were extracted from the diffuse

100 scattering signal recorded under high pressure and high temperature. Diffuse signal with high

101 quality were recorded on a Q range up to almost 100 nm^{-1}, allowing measurements up to the

102 third oscillation of the structure factor S(Q) (Figure 2). Analysis of angle dispersive liquid

103 diffuse signal recorded using PEP is detailed in a previous paper (Morard et al., 2013).

104 Uncertainties on experimentally measured density values of ±3 atoms/nm^3 (equivalent to

105 ~250 kg/m^3) were estimated from Q range, self-absorption and minimal distance on the radial

106 distribution function g(r) (Table 1) (Morard et al, 2013).

107

Molecular Dynamics Calculations

109 Simulations were performed using the ABINIT package (Gonze et al. 2016). The

110 electrons are treated quantum mechanically using density functional theory (DFT) while the

111 ions movement is treated classically using the resulting forces. The calculations used the

112 projected augmented wave (PAW) (Blochl 1994; Torrent et al. 2008) method for the

113 computation of the electronic structure and the generalized gradient approximation (GGA)

114 following the parametrization of Perdew, Burke and Ernzerhof (PBE) for the exchange-

115 correlation energy and potential (Perdew et al. 1996). For iron we generated a pseudo-

116 potential with $3s$, $3p$, $3d$, and $4s$ states as valence electrons (see (Dewaele et al. 2008; Bouchet

117 et al. 2013) for a detailed description of the generation of the pseudopotential and a

118 comparison with recent experimental data). For sulfur the pseudo-potential includes $3s$ and $3p$

119 states as valence electrons. The simulations were performed using a cutoff energy, E_c, for the

120 plane wave basis chosen equal to 350 eV. The radius of the augmentation regions for the

121 PAW pseudo-potential were chosen small enough to avoid an overlapping of the spheres

122 surrounding each atom at the highest densities. An efficient scheme for the parallelization

4

123   present in ABINIT was used to perform the simulations involving a large number of atoms

124   and time steps (Bottin et al. 2008).

125   We used supercells of liquid Fe of 128 atoms and we replace 13, 17, 29, 38, 50 and 64

126   atoms of Fe by atoms of S to obtain composition of 10%atS, 23%atS, 30%atS, 39%atS, and

127   50%atS respectively. The simulations were first performed in the NPT (constant number of

128   atoms, pressure and temperature) ensemble to reach the desired pressure (5 GPa) and then in

129   the NVT (constant number of atoms, volume and temperature) ensemble in order to avoid any

130   fluctuations of cell parameters. The temperature was fixed to 2500 K and we systematically

131   used an electronic temperature equal to the ionic temperature in our simulations. This

132   relatively high temperature is necessary to ensure the complete melting of the supercells.

133   Once the box of simulated atoms is equilibrated (after at least 5 ps), partial radial

134   distributions functions, g(r), for Fe–Fe, Fe–S and S–S atoms were calculated from 2.5 ps time

135   averages taken different starting times to ensure the convergence. It is well known that at

136   room pressure the experimental equilibrium volume of iron is underestimated in DFT-GGA-

137   PBE calculations due to an incorrect modelling of magnetic effects (Dewaele et al. 2008) by

138   around 7% and therefore the density is overestimated by the same percentage. The bulk

139   modulus is also strongly overestimated (Dewaele et al. 2008), and therefore the density

140   discrepancies between DFT_GGA and experiments hold up to high pressure (around 150

141   GPa). Note that it is possible to correct the GGA results by using the dynamical mean-field

142   theory (Pourovskii et al. 2013) and to recover a good agreement with the experimental

143   equation of state, but this approximation cannot be used in molecular dynamics calculations

144   due to its enormous computational cost. For solid Fe-S in the B2 structure the density

145   overestimation is similar (Sherman 1995). We reproduce these discrepancies in our

146   calculations for liquid Fe-S with a constant overestimation of the experimental density by

147   about 1000 kg/m^3, due to the GGA-PBE, but also to a larger pressure in the calculations.

148   Noteworthy, the overall evolution of the density as a function of the sulfur composition is

149   comparable to that experimentally measured.

150

151   **Results and discussion**

152   *Liquid structure*

5

153   Analysis by Fourier transform of the diffuse X-ray scattering of liquid metals gives

154   access to the local structure g(r) of the liquid (Figure 3). In addition to the experimental

155   results, ab initio calculations have been performed on this system in a similar P-T range.

156   As already mentioned, inherent problems of calculations involving iron, without modeling

157   magnetic properties correctly, leads to a known overestimation of the density. However,

158   main features of experimental and theoretical liquid structures are relatively similar. It

159   should be noticed that oscillations present in the experimental data of the structure of pure

160   FeS liquid are not real but are related to spurious signal coming from limited Q range on

161   the corresponding structure factor.

162   Irrespectively of the density shift, simulations bring additional information impossible

163   to obtain with the present XRD experiments: partial g(r) have been be extracted from the

164   calculations (Figure 4), showing no S-S polymerization on the Fe-FeS side of the phase

165   diagram, in agreement with previous published calculations using smaller supercells (64

166   atoms compared to 128 in our MD simulations) (Alfè and Gillan 1998; Vočadlo et al.

167   2000). The S-S bond remains quite large, emphasizing S-S repulsion, and no formation of

168   S-S clusters for all studied compositions. This definitely rules out the idea that S-S

169   interactions were at the origin of the anomalous values of the viscosity (LeBlanc and

170   Secco 1996).

171   Partial g(r) do not show any drastic change in the bond lengths with increasing S

172   content (Figure 4). The Fe-S bond is shorter than the Fe-Fe bond, this is related to the

173   covalent status of this bond (Flory et al. 2005; Morard et al. 2008). The position of the

174   first peak in the g(r), directly related to the first coordinance sphere (CS), was observed in

175   the experiments to remain relatively unchanged up to ~30at%S and to drastically decrease

176   for larger sulfur concentrations (Figure 5). As the contribution of each X-X atomic pair to

177   the total g(r) probed by X-ray is related to the weight of the atoms, the first peak position

178   is essentially associated with the Fe-Fe network. S-S bond is relatively longer (3.4 Å) but

179   with lower intensity and larger dispersion, whereas Fe-S bonds are shorter (2.2 Å) than

180   Fe-Fe bonds (2.5 Å) and have a higher intensity. It is therefore the addition of Fe-S bonds

181   that influence the total g(r) observed in our experiments, and explained the shortening of

182   the observed first CS position (Figure 5). The hereby presented peak position are in

183   relative good agreement with previous results from (Kono et al. 2015).

184

185   *Comparison of our dataset with the literature*

186   The Fe-FeS binary system has been studied extensively over a large pressure range.

187   Density of liquid Fe-S alloys has been determined by ex-situ sink-float method (Balog et al.

188   2003; Nishida et al. 2008), by in situ X-ray radiography (J. Chen et al. 2014), and by X-ray

189   absorption (Sanloup et al. 2000; Nishida et al. 2011). These datasets do not provide a

190   consistent picture, and the derived densities show large discrepancies, even when

191   measurements have been performed with the same method. Sound velocities of liquid Fe-S

192   alloys have been probed in situ under high pressure by conventional ultrasonic method but, as

193   for the density measurements, the results by different research groups are in disagreement

194   (Nishida et al. 2013, 2016; Jing et al. 2014).   A thorough comparison of our new

195   measurements (Table 1) with literature results will sheds light on the properties of the Fe-S

196   binary system at high pressure and high temperature.

197   Regarding pure liquid FeS, previous studies have found contradictory results (Nishida et

198   al. 2011; B. Chen et al. 2014) in spite of using the same X-ray absorption technique. Chen et

199   al. argue that the reported density difference can be explained by the temperature difference.

200   Specifically, they claim that temperature difference of 150K can account for a density

201   difference of almost 400 kg/m^3. However such a large thermal expansion is incompatible with

202   ambient pressure measurements (for pure FeS, the liquid density only changes from ~3900

203   kg/m^3 to ~3820 kg/m^3 between 1473 K and 1623 K (Kaiura and Toguri 1979)). Furthermore,

204   a combined fit of either of the two high-pressure sets of density for pure liquid FeS with

205   ambient pressure results is impossible using conventional EoS values, and requires an

206   unrealistically small K_{T0} (Nishida et al. 2011). Conversely, the here-measured density for pure

207   liquid FeS at high pressure are in good agreement with ambient pressure measurements

208   (Nagamori 1969; Kaiura and Toguri 1979), while differ from the previous high-pressure

209   measurements (the difference between the present dataset at 4 GPa and 1900 K and previous

210   determination is 6% (Nishida et al. 2008), 10% (Nishida et al. 2011), and 20 % (J. Chen et al.

211   2014) (Figure 6).

212   Unlike liquid density measurements at high pressure, literature concerning measurements

213   on liquid Fe-S alloys at ambient pressure is rather limited and relatively old (Nagamori 1969;

214   Kaiura and Toguri 1979). It should also be noted that there are no density measurements over

215   a wide compositional range (0-40 at% S) at ambient pressure. Regarding pure liquid Fe,

216   measurements have been recently performed over a wide temperature range, allowing a very

7

217 good estimation of the density/temperature relation (Assael et al. 2006), which is used to

218 extract density of liquid Fe-S alloys at 1900 K as a function of S content (Figure 7).

219   The density of the liquid Fe-S alloys at ambient pressure (ρ_0) is a sensitive parameter in

220 our study. Drastically different models have been used in previous studies (Figure 7), with a

221 deviation of ~1000 kg/m^3 for close compositions in the 15-20 at% S range. We anchor our

222 study on ambient pressure measurements, fixing the density for the 40-50 at% S alloys on

223 those by Nagamori (1969) extrapolated at 1900 K using thermal expansion from Kaiura and

224 Togori (1979). A quadratic polynomial fit is then performed to interpolate between density of

225 S-rich alloys and that of pure liquid Fe, fixed to the value of Assael et al. (2006). This trend is

226 in relative good agreement with densities calculated by ab initio techniques (Kuskov and

227 Belashchenko 2016) for low S concentration (Figure 7). The so-derived second order

228 polynomial gives:

229 $$\rho = -3108 X_S^2 - 5176 X_S + 6950 \quad (1)$$

230   where X_S is the S concentration in at.%. Looking at this relation, it comes clearly out

231 that values of density from Sanloup et al., (2000) and the related model from Jing et al. (2014)

232 are too low, in particular for low S content, and in disagreement with our model (Figure 7).

233   Regarding sound velocity, most recent measurements (Nishida et al. 2016) and

234 calculations (Kuskov and Belashchenko 2016) are incompatible with ambient pressure

235 measurements (Nasch et al. 1997; Nasch and Manghnani 1998) (Figure 8 and 9), while

236 previous measurements on Fe-16at%S are (Jing et al. 2014) (Figure 9). Our model is therefore

237 adjusted to agree with Jing et al, (2014).

238   To conclude, a survey of the literature on Fe-S liquid alloys under high pressure show

239 relatively scattered results. Strong disagreement exists for density, sound velocity and thermal

240 expansion. Our approach is to anchor our model on ambient pressure measurements, with

241 only few assumptions, as for example the interpolation of liquid density between 0 and 40

242 at% S.

243

Parametrized equation of state

245   In order to fit our set of density data, we use a 3rd order Birch Murnaghan equation of state

246 relating pressure P and density ρ at the fixed temperature of 1900 K:

8

247
$$P = \frac{3}{2} K_{T0} \left[\left(\frac{\rho}{\rho_0} \right)^{7/3} - \left(\frac{\rho}{\rho_0} \right)^{5/3} \right] \left[1 + \frac{3}{4} \left(K_0^{'} - 4 \right) \left(\left(\frac{\rho}{\rho_0} \right)^{2/3} - 1 \right) \right] \quad (2)$$

248   where K_{T0} is the isothermal bulk modulus at ambient pressure and 1900 K, K' is the

249   pressure derivative of the bulk modulus and ρ_0 is the density at ambient pressure and 1900 K.

250   Each parameter is a function of molar S content in the liquid (X_S). The isothermal bulk

251   modulus at ambient pressure and its derivative can be expressed as follows (J. Chen et al.

252   2014):

253
$$K_{T0} = K_{T,Fe}^{1-X_S} * K_{T,S}^{X_S} \quad (3)$$

254   A linear mixing law for bulk moduli could be used, but for a shorter range of

255   composition (Morard et al. 2013). In the present study, we found more suitable to use such

256   type of mixing law. More details regarding different mixing law for bulk moduli can be found

257   in Chen et al, 2014.

258   For pure Fe we assume $K_{T,Fe}$=76 GPa. This value is deduced from sound velocity

259   measurements at 1bar (Nasch and Manghnani 1998), assuming a value for the specific heat at

260   constant volume C_V of 4R and the value of specific heat at constant pressure C_P as in (Nasch

261   and Steinemann 1995). Regarding sulfur, we take $K_{T,S}$=1.6 GPa (Tsuchiya 1994) as in Chen

262   et al. (2014), which gives an overall good agreement with compressibility data from Nishida

263   et al. (2011). However, it should be noticed that this value is measured at 673 K and not at

264   1900 K. Accordingly, this parameter should be rather considered a fitting parameter,

265   restraining the validity of our model only between Fe and FeS compounds.

266   As measurements in the 0-5 GPa range do not cover a large enough pressure range to

267   adequately constrain K' values, this is adjusted to fit the velocity measurements, following the

268   relation K'=K'$_{Fe}$+X_S*3, with K'$_{Fe}$=6.5.

269   As our measurements were performed at different temperatures, we also need to

270   estimate thermal expansion as a function of pressure, temperature, and S content. We assume

271   a linear dependence of density on temperature (experimentally proven for liquid iron(Assael

272   et al. 2006)). We calculate the thermal expansion at 1900 K, assuming linearity between Fe

273   and FeS:

9

274
$$\alpha_0 = -\frac{1}{\rho_0}\left(\frac{\partial\rho}{\partial T}\right)_0 \quad (4)$$

275
$$\left(\frac{\partial\rho}{\partial T}\right)_{Fe,0} = 0.926 \text{ from (Assael et al. 2006)}$$

276
$$\left(\frac{\partial\rho}{\partial T}\right)_{FeS,0} = 0.533 \text{ from (Kaiura and Toguri, 1979)}$$

277
$$\left(\frac{\partial\rho}{\partial T}\right)_0 = \left(\frac{\partial\rho}{\partial T}\right)_{Fe,0} - 2\left(\left(\frac{\partial\rho}{\partial T}\right)_{Fe,0} - \left(\frac{\partial\rho}{\partial T}\right)_{FeS,0}\right)X_S \quad (5)$$

278   Due to the lack of data on thermal expansion for intermediate compositions, we chose
279 a linear mixing for the thermal expansion mixing model. More detailed investigation is
280 required in the future to better constrain this linear model.

281   Then, thermal expansion at a given pressure is calculated under the assumption:

282
$$\alpha_0 K_{T,0} = \alpha K_T \quad (6)$$

283 With

284

285
$$K_T = \frac{K_{T0}}{2}\left[7\left(\frac{\rho}{\rho_0}\right)^{7/3} - 5\left(\frac{\rho}{\rho_0}\right)^{5/3}\right]\left[1 + \frac{3}{4}\left(K_0' - 4\right)\left(\left(\frac{\rho}{\rho_0}\right)^{2/3} - 1\right)\right] + \frac{3K_{T0}}{4}\left[\left(K_0' - 4\right)\left(\left(\frac{\rho}{\rho_0}\right)^3 - \left(\frac{\rho}{\rho_0}\right)^{7/3}\right)\right]$$

286   (7)

287   A parameter that could be directly derived from our Eos is the compressional sound
288 velocity in the liquid:

289
$$V_P = \sqrt{\frac{K_T\left(1 + \alpha\gamma T\right)}{\rho}} \quad (8)$$

290   The value of the Grüneisen parameter of the liquid Fe-S alloy is calculated from the
291 V_P of pure Fe and Fe-16%at. S (Nasch et al. 1997; Nasch and Manghnani 1998) (Figure 8,
292 inset) assuming that the Grüneisen parameter evolves linearly with the sulfur concentration.
293 The values obtained are in agreement with ab initio calculations in (Kuskov and
294 Belashchenko 2016) (Figure 8, inset). However, calculations from (Kuskov and Belashchenko

10

295   2016) argue for an increase of the sound velocity as a function of S content, whereas

296   experimental data show the opposite behavior (Figure 8). In addition, Grüneisen parameter is

297   assumed to be constant in the pressure range 0-10 GPa. This seems quite reasonable over a

298   relatively small pressure range (Kuskov and Belashchenko 2016). The Grüneisen parameter

299   varies here as $\gamma=1.52+2.5X_S$.

300

Thermodynamic model

302   In addition to the empirical parametrization introduced above, we also provide a

303   description of the thermoelastic properties of liquid Fe-S alloys based on thermodynamic

304   solution modeling. This approach is complementary to the previous one and is based on the

305   mixing of the end-members: pure liquid Fe and FeS. For liquid Fe we use the EoS of

306   Komabayashi (2014) and for liquid FeS, an EoS deduced from our density data and from

307   sound velocity data of Nishida et al. (2016). For both end-members we use a Vinet equation

308   for isothermal compression and an Anderson-Grüneisen parametrization for isobaric heating

309   (see (Komabayashi 2014). The parameters for liquid FeS EoS are given in Table 2. To assess

310   the solution model that best describes our density data and the sound velocity data of Nishida

311   et al (2016) over the entire Fe-FeS binary, we test three different mixing models that affect the

312   volume of the solution, assuming (a) ideality; (b) concentration dependent non-ideality; and

313   (c) concentration and pressure dependent non-ideality.

314   To model the excess contribution we use the Margules parameterization, introduced by

315   Buono and Walker (2011), to describe the non-ideal behavior of Fe-FeS liquidus on the iron-

316   rich side of the Fe-FeS phase diagram. In this parametrization, the excess contribution to the

317   Gibbs energy is linear in temperature. As a consequence, the thermal expansivity and isobaric

318   heat capacity of the solution depends only on the end-members.

319   The ideal and excess thermoelastic properties of the solution are obtained from its

320   Gibbs energy (e.g. Poirier et al. 2000), and the Grüneisen parameter required for calculating

321   the sound velocity (Eq 8) is computed from

322    $$\gamma = \left(\frac{C_p}{\alpha\,K_T V} - \alpha\,T\right)^{-1}, \quad (9)$$

323   where α, K_T, V, and C_p are the thermal expansivity, isothermal bulk-modulus, volume, and isobaric

324   heat capacity of the solution.

11

325 ***Ideal mixing***

326   The ideal mixing volume between the two end-members is described by the following

327 equation:

$$V = (1 - x)V_{Fe} + xV_{FeS} \, , \quad (10)$$

329 where V is the volume of the considered liquid alloy, x the mole fraction of FeS, and V_{Fe} the

330 volume of liquid Fe and V_{FeS} the volume of liquid FeS.

331   Such a simple model cannot reproduce our density dataset (Figure 10). The density

332 calculated from Eq.10 decreases too rapidly with increasing S concentration and does not

333 reproduce the positive curvature of density as function of S content seen in the data (Figure

334 10).

335 ***Pressure independent volume Margules parameters***

336   In this non-ideal mixing model, the volume is:

$$V = (1 - x)V_{Fe} + xV_{FeS} + (1 - x)x\big(W_{V,Fe}\,(1 - x) + W_{V,FeS}\,x\big), \quad (11)$$

338 where $W_{V,Fe}$ and $W_{V,FeS}$ are the volume Margules parameters. The values of those parameters

339 have been estimated by fitting Eq. 11 on the density data (case A) and on the sound velocity

340 data (case B) separately (Table 3).

341   The density data is well described in case A, but the predicted sound velocities do not

342 agree with the measurements. Conversely, a fit to the sound velocity data provides a good

343 representation for the sound velocity (case B), but fails to describe the experimental density

344 data. This simple Margules mixing model is well suited for modeling the Fe-rich side of the

345 Fe-S phase diagram and the density of Fe-S solutions however, as shown in case B, a different

346 non-ideal behavior is required to describe the sound velocity data. With Eq 11, the sound

347 velocity is only affected by the non-ideality through the volume but not through the bulk

348 modulus. A non-ideal contribution to the bulk modulus requires that the volume Margules

349 coefficients depend on pressure, as discussed in the next section.

350 ***Pressure dependent volume Margules parameters***

351   By trial and error, we have found that the density and sound velocity data can well be

352 described if we adopt the following parametrization for the volume Margules parameters:

12

353
$$W_{V,Fe} = W_{11} + W_{12} \ln\left(\frac{3}{2} + P\right) \quad (11)$$

354
$$W_{V,FeS} = W_{21} + W_{22}\, P. \quad (12)$$

355   The estimated values for the parameters W are given in Table 3. They have been
356 obtained by fitting the equations describing the volume and sound velocity on the density and
357 sound velocity data at the same time. As can be seen from Fig. 10, this parameterization for
358 the liquid solution gives an adequate description for the experimental data in the 0-8 GPa
359 pressure range. Note that this parametrization cannot be used to model thermoelastic
360 properties beyond that pressure range since an already moderate extrapolation in pressure
361 would lead to unphysical properties.

362

363 **Implications**

364   To infer the size and sulfur content of planetary cores from seismic or geodesy data
365 requires an accurate knowledge of density and velocity properties of solid and liquid iron
366 alloys as a function pressure, temperature and sulfur content. Until now, no consensus on
367 experimental measurements on Fe-S liquid alloys has been reached, with strong
368 contradictions between the different high-pressure studies, and also large disagreement with
369 ambient pressure data. In the present work, we presented new experimental density data of
370 liquid Fe-S alloys at high pressure and high temperature, together with ab initio liquid
371 structure calculations. Combining this new data set and literature data, we were able to
372 establish an empirical and a thermodynamic model for liquid Fe-S solutions that allow to
373 compute thermoelastic properties of the liquid alloy as a function of pressure, temperature,
374 and sulfur concentration.

375   To illustrate the effect of the new density data on the internal structure of small planets,
376 we compare the composition of the Moon's core predicted by our empirical and
377 thermodynamic Fe-S mixing model with a core model assuming ideal mixing between liquid
378 iron and liquid Fe-10wt%S (Figure 11). The thermoelastic properties of the core in the ideal
379 mixing model are calculated following (Dumberry and Rivoldini 2015) and are based on the
380 EoS of liquid Fe (Komabayashi 2014) and Fe-10wt%S (Balog et al. 2003). The aim of this
381 model is to emphasize that liquid Fe-S alloys EoS directly affect the Moon's core composition
382 deduced from its radius.

13

383   For our global Moon model, we use the density profile of the silicate part of the Moon

384   structure deduced by Weber et al. 2011 from seismic data, the core models listed in the

385   previous paragraph, and assume that the entire core is in the liquid state, convecting and

386   composed of iron and sulfur. In order to agree with the most recent moment of inertia estimate

387   (Williams et al. 2014), we had to reduce the density of the upper part of the mantle by about

388   0.1%. The pressure in the planet is calculated by solving the hydrostatic pressure equation and

389   Poisson equation. The temperature profile in the core is obtained by integrating the adiabatic

390   gradient equation in the core (e.g. (Dumberry and Rivoldini 2015)) assuming a core-mantle

391   boundary (CMB) temperature of 1750K. All thermoelastic properties of the core are

392   calculated from the mixing models as a function of pressure, temperature, and composition.

393   Our results show that for a given core radius, models based on the new elastic data require

394   approximately twice the amount of sulfur than models based on an equation of state deduced

395   from previous elastic data (Figure 11). Noteworthy, the sulfur concentrations required by the

396   empirical and the thermodynamic model are very similar, even though when the two models

397   are based on a different sets of acoustic velocity data. Models that agree at 1 sigma with the

398   moment of inertia have a core radius below about 360 km but, the specifcs of the core model

399   have only a very negligible effect on the moment inertia of the planet. However, the larger

400   amount of sulfur required by the new elastic data significantly affects the thermal evolution of

401   the core (i.e. the liquidus of the core decreases with increasing S content) and with it the

402   dynamo action, by delaying the onset of crystallization of iron-rich compounds in the core.

403   The present model assumes a specific CMB temperature (1750 K) which is expected in the

404   present day core of the Moon (Laneuville et al. 2014). Lowering the CMB temperature will

405   somewhat increase the sulfur content required for the core to match the mass constraint and

406   initiate the crystallization of iron-rich compounds close to the CMB, since the core isentrope

407   is likely steeper than the liquidus (Williams 2009; Breuer et al. 2015). Irrespectively of the

408   assumptions, the present model is a clear illustration of the impact of our two models on

409   Moon's core composition.

410   The present study, anchored on experimental measurements and theoretical calculations,

411   allows to present a coherent model for planetary cores, with applications ranging from the

412   direct simulations of small planetary cores dynamics to the inversion of seismic data (Garcia

413   et al. 2011; Weber et al. 2011; Antonangeli et al. 2015).

414

14

Acknowledgements

Figure Captions

Figure 1: Scanning Electron Microscope (SEM) images of polished cross sections of recovered samples. Here are presented two different compositions, with typical quench textures of S-poor and S-rich liquids. Microprobe measurements were performed on large area, of ~20 microns, in order to average the composition over these textures.

Figure 2: Structure factors S(Q) of liquid Fe-S alloys as a function of the composition for similar P-T conditions.

Figure 3: Comparison between pair distribution function g(r) obtained from ab initio calculations (5 GPa and 2500 K) and experimental results (similar P-T conditions and composition as in Figure 2).

Figure 4: Partial pair distribution function for different composition extracted from the ab initio calculations.

Figure 5: First peak position as a function of the S content for the different g(r), compared with theoretical work, and previous results from (Kono et al. 2015).

15

441

442 **Figure 6**: Density of liquid iron alloys from this study and the corresponding thermodynamic

443 model compared with available measurements. The color of the different symbol is related to

444 the composition, rounded to the closest nominal value.

445

446 **Figure 7:** Density of liquid Fe-S alloys at ambient pressure from different studies. Our

447 thermodynamic model uses an interpolation between the density of pure Fe from (Assael et al.

448 2006) and densities of S-rich liquids (Nagamori 1969) corrected for temperature difference

449 following (Kaiura and Toguri 1979).

450

451 **Figure 8**: Sound velocity fit for this model as a function of S content based on measurements

452 at ambient pressure from (Nasch et al. 1997; Nasch and Manghnani 1998), compared with

453 theoretical calculations from Kuskov and Belashchenko (2016). Inset: Gruneisen parameter

454 used in this model compared with ab initio calculations from Kuskov and Belashchenko

455 (2016).

456

457 **Figure 9**: Sound velocity extracted from our thermodynamic model compared to the available

458 literature (Nasch et al. 1997; Nasch and Manghnani 1998; Jing et al. 2014; Nishida et al.

459 2016). Different colors correspond to different compositions, rounded to the closest nominal

460 value. Representative error bars for the two high pressure studies have been added in the

461 figure legend.

462

463 **Figure 10**: Thermodynamic models of density and sound velocity of liquid Fe-S alloys at

464 1900 K. Four different models have been tested: ideal solution, pressure independent (Model

465 A and B) and pressure dependent Margules parameters. It is clear that the pressure

466 dependence of the Margules parameters is required to represent adequately the experimental

467 values.

468

16

469 **Figure 11**: Radius of Moon's core as a function of S content of an entirely liquid core, using

470 models presented in this study (parametrized EoS and thermodynamic model) compared with

471 an ideal solution based on previous density measurements (Balog et al. 2003). Calculations

472 were performed for a temperature at the Moon CMB of 1750 K.

473

474 **Tables**

Run number	Pressure (GPa)	Temperature (K)	xS (at%)	density (atoms/nm3)	Density (kg/m3)	Density at 1900 K (kg/m3)	CN1	CN2	r1 (nm)
31-32	4,2 ± 0,6	1900 ± 170	9.9	76,9 ± 3	6830 ± 270	6830 ± 270	8,05	9,26	2,564
34-35	4,1 ± 0,6	1980 ± 170	9.9	76,1 ± 3	6760 ± 270	6840 ± 270	7,94	9,12	2,567
61-62	2,2 ± 0,6	1780 ± 170	9.9	75,8 ± 3	6730 ± 270	6630 ± 270	7,97	9,18	2,578
65-66	2,1 ± 0,6	1860 ± 170	9.9	75 ± 3	6660 ± 270	6630 ± 270	7,85	9,05	2,581
35-36	3,2 ± 0,6	1860 ± 170	17.4	76,4 ± 3	6560 ± 260	6520 ± 260	7,88	9,14	2,569
49-50	2,9 ± 0,6	1780 ± 170	22.9	74 ± 3	6190 ± 250	6090 ± 250	7,64	8,88	2,571
53-54	2,9 ± 0,6	1860 ± 170	22.9	73,4 ± 3	6140 ± 250	6110 ± 250	7,54	8,75	2,572
89-90	1,7 ± 0,6	1780 ± 170	22.9	70,4 ± 3	5890 ± 250	5790 ± 250	7,32	8,45	2,59
91-92	1,5 ± 0,6	1860 ± 170	22.9	70 ± 3	5860 ± 250	5830 ± 250	7,26	8,4	2,589
42	5 ± 0,6	1750 ± 170	29.4	75,2 ± 3	6100 ± 240	5980 ± 240	7,71	8,95	2,552
63	2,7 ± 0,6	1690 ± 170	29.4	72,2 ± 3	5860 ± 240	5690 ± 240	7,43	8,61	2,566
17	3,5 ± 0,6	1600 ± 170	38	71,9 ± 3	5590 ± 230	5370 ± 230	6,86	8	2,543
25	5,2 ± 0,6	1870 ± 170	50	59,8 ± 3	4360 ± 220	4340 ± 220	3,96	4,5	2,415
48	2,6 ± 0,6	1770 ± 170	50	57,3 ± 3	4180 ± 220	4100 ± 220	3,77	4,28	2,423

475

476 **Table 1:** Pressure-temperature conditions, chemical composition of quenched samples,

477 densities measured and calculated at 1900 K.

478

Reference temperature T0 (K)	1650
Reference volume (after Nagamori corrected for T=1650 K) (cm3/mol)	11.8
Reference thermal expansion (after Kaiura) (K-1)	1.29E-04
KT0 (Gpa)	16.5 (0.5)
K'T0	6.21
γ	1
Q	0

479

480 **Table 2**: Parameters for liquid FeS Equation of state, following Vinet and Anderson-
481 Gruneisen parameterization (see (Komabayashi 2014) more details).

Model A	Model B

17

$W_{V,Fe}$	-6.74±0.63	4.93±0.92
$W_{V,FeS}$	-0.47±0.51	5.70±0.87
	P dependent model	
W11	-7.78±0.95	
W12	2.31±0.14	
W21	-2.32±0.88	
W22	0.057±0.024	

Table 3: Margules parameters for pressure independent and pressure dependent parameterization. These parameters are given cm^3/mol.

Bibliography

Alfè, ., and Gillan, M.J. (1998) First-principles simulations of liquid Fe-S under Earth ' s core conditions. Physical Review B, 58, 8248–8256.

Andrault, D., Bolfan-Casanova, N., Ohtaka, O., Fukui, H., Arima, H., Fialin, M., and Funakoshi, K. (2009) Melting diagrams of Fe-rich alloys determined from synchrotron in situ measurements in the 15-23 GPa pressure range. Physics of the Earth and Planetary Interiors, 174, 181–191.

Antonangeli, D., Morard, G., Schmerr, N.C., Komabayashi, T., Krisch, M., Fiquet, G., Fei, Y., and Mao, H.-K. (2015) Toward a mineral physics reference model for the Moon's core. Proceedings of the National Academy of Sciences of the United States of America, 112.

Assael, M.J., Kakosimos, K., Banish, R.M., Brillo, J., Egry, I., Brooks, R., Quested, P.N., Mills, K.C., Nagashima, A., Sato, Y., and others (2006) Reference Data for the Density and Viscosity of Liquid Aluminum and Liquid Iron. Journal of Physical and Chemical Reference Data, 35, 285–300.

Balog, P.S., Secco, R.A., Rubie, D.C., and Frost, D.J. (2003) Equation of state of liquid Fe-10 wt % S: Implications for the metallic cores of planetary bodies. Journal Of Geophysical Research-Solid Earth, 108.

Besson, J.M., Nelmes, R.J., Hamel, G., Loveday, J.S., Weill, G., and Hull, S. (1992) Neutron diffraction above 10 GPa. Physica B: Condensed Matter, 181, 907–910.

Blochl, P.E. (1994) Projector augmented-wave method. Physical Review B, 50.

Bottin, F., Leroux, S., Knyazev, A., and Zérah, G. (2008) Large-scale ab initio calculations based on three levels of parallelization. Computational Materials Science, 42, 329–336.

Bouchet, J., Mazevet, S., Morard, G., Guyot, F., and Musella, R. (2013) Ab initio equation of state of iron up to 1500 GPa. Physical Review B - Condensed Matter and Materials Physics, 87, 1–8.

Breuer, D., Rueckriemen, T., and Spohn, T. (2015) Iron snow, crystal floats, and inner-core growth: modes of core solidification and implications for dynamos in terrestrial planets

516 and moons. Progress in Earth and Planetary Science, 2, 1–26.

517 Buono, A.S., and Walker, D. (2011) The Fe-rich liquidus in the Fe-FeS system from 1bar to
518   10GPa. Geochimica et Cosmochimica Acta, 75, 2072–2087.

519 Campbell, A.J., Seagle, C.T., Heinz, D.L., Shen, G., and Prakapenka, V.B. (2007) Partial
520   melting in the iron-sulfur system at high pressure: A synchrotron X-ray diffraction study.
521   Physics of the Earth and Planetary Interiors, 162, 119–128.

522 Chabot, N.L. (2004) Sulfur contents of the parental metallic cores of magmatic iron
523   meteorites. Geochimica Cosmochimica Acta, 68, 3607–3618.

524 Chen, B., Gao, L., Leinenweber, K., Wang, Y., Sanehira, T., and Li, J. (2008a) In situ
525   investigation of high-pressure melting behavior in the Fe-S system using synchrotron X-
526   ray radiography. High Pressure Research, 28, 315–326.

527 Chen, B., Li, J., and Hauck, S.A. (2008b) Non-ideal liquidus curve in the Fe-S system and
528   Mercury's snowing core. Geophysical Research Letters, 35, 10–14.

529 Chen, B., Li, Z., Zhang, D., Liu, J., Hu, M.Y., Zhao, J., Bi, W., Alp, E.E., Xiao, Y., Chow, P.,
530   and others (2014) Hidden carbon in Earth's inner core revealed by shear softening in
531   dense Fe_7C_3. Proceedings of the National Academy of Sciences, 111, 17755–17758.

532 Chen, J., Yu, T., Huang, S., Girard, J., and Liu, X. (2014) Compressibility of liquid FeS
533   measured using X-ray radiograph imaging. Physics of the Earth and Planetary Interiors,
534   228, 294–299.

535 Chudinovskikh, L., and Boehler, R. (2007) Eutectic melting in the system Fe-S to 44??GPa.
536   Earth and Planetary Science Letters, 257, 97–103.

537 Dewaele, A., Torrent, M., Loubeyre, P., and Mezouar, M. (2008) Compression curves of
538   transition metals in the Mbar range: Experiments and projector augmented-wave
539   calculations. Physical Review B - Condensed Matter and Materials Physics, 78, 1–13.

540 Dumberry, M., and Rivoldini, A. (2015) Mercury ' s inner core size and core-crystallization
541   regime. ICARUS, 248, 254–268.

542 Flory, M.A., McLamarrah, S.K., and Ziurys, L.M. (2005) High-resolution spectroscopy of
543   CoS (X 4 ?? i): Examining 3d transition-metal sulfide bonds. Journal of Chemical
544   Physics, 123, 1–9.

545 Garcia, R.F., Gagnepain-beyneix, J., Chevrot, S., and Lognonné, P. (2011) Very preliminary
546   reference Moon model. Physics of the Earth and Planetary Interiors, 188, 96–113.

547 Gonze, X., Jollet, F., Abreu Araujo, F., Adams, D., Amadon, B., Applencourt, T., Audouze,
548   C., Beuken, J.M., Bieder, J., Bokhanchuk, A., and others (2016) Recent developments in
549   the ABINIT software package. Computer Physics Communications, 205, 106–131.

550 Greenwood, R.C., Franchi, I.A., Jambon, A., Barrat, J.A., and Burbine, T.H. (2006) Oxygen
551   Isotope Variation in Stony-Iron Meteorites. Science, 313, 1763.

552 Hammersley, A.P., Svensson, S.O., Hanfland, M., Fitch, A.N., and Hausermann, D. (1996)
553   Two-dimensionnal detector software: from real detector to idealised image or two-theta
554   scan. High Pressure Research, 14, 235–248.

555 Jing, Z., Wang, Y., Kono, Y., Yu, T., Sakamaki, T., Park, C., Rivers, M.L., Sutton, S.R., and
556   Shen, G. (2014) Sound velocity of Fe-S liquids at high pressure: Implications for the
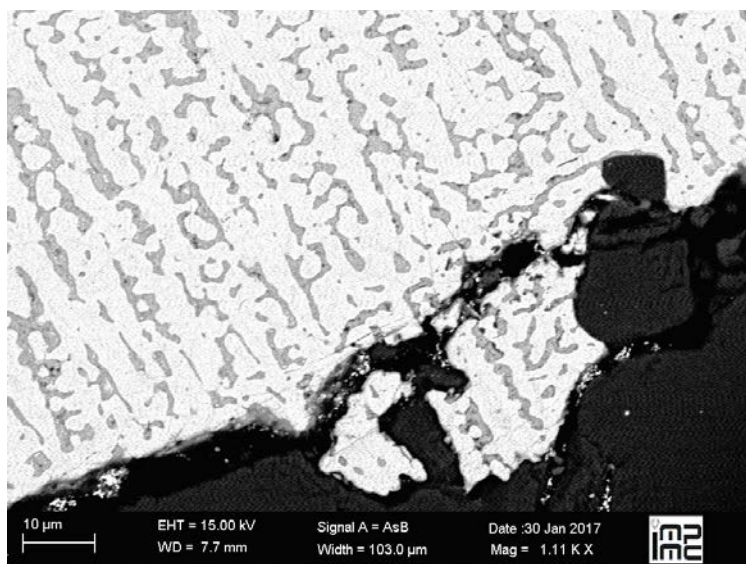557   Moon's molten outer core. Earth and Planetary Science Letters, 396, 78–87.

19

558 Kaiura, G.H., and Toguri, J.M. (1979) Densities of the molten FeS, FeS–Cu2S and Fe–S–O
559   systems—utilizing a bottom-balance Archimedean technique. . Canadian Metallurgical
560   Quarterly, 18, 155–164.

561 Kamada, S., Ohtani, E., Terasaki, H., Sakai, T., Miyahara, M., Ohishi, Y., and Hirao, N.
562   (2012) Melting relationships in the Fe-Fe3S system up to the outer core conditions. Earth
563   and Planetary Science Letters, 359–360, 26–33.

564 Kleine, T., Touboul, M., Bourdon, B., Nimmo, F., Mezger, K., Palme, H., Jacobsen, S.B.,
565   Yin, Q., and Halliday, A.N. (2009) Hf − W chronology of the accretion and early
566   evolution of asteroids and terrestrial planets. Geochimica et Cosmochimica Acta, 73,
567   5150–5188.

568 Klotz, S., Strässle, T., Rousse, G., Hamel, G., and Pomjakushin, V. (2005) Angle-dispersive
569   neutron diffraction under high pressure to 10 GPa. Applied Physics Letters, 86, 1–3.

570 Komabayashi, T. (2014) Thermodynamics of melting relations in the system Fe-FeO at high
571   pressure: Implications for oxygen in the Earth's core. Journal of Geophysical Research :
572   Solid Earth, 119, 4164–4177.

573 Kono, Y., Kenney-Benson, C., Shibazaki, Y., Park, C., Shen, G., and Wang, Y. (2015) High-
574   pressure viscosity of liquid Fe and FeS revisited by falling sphere viscometry using
575   ultrafast X-ray imaging. Physics of the Earth and Planetary Interiors, 241, 57–64.

576 Kuskov, O.L., and Belashchenko, D.K. (2016) Thermodynamic properties of Fe-S alloys from
577   molecular dynamics modeling: Implications for the lunar fluid core. Physics of the Earth
578   and Planetary Interiors, 258, 43–50.

579 Laneuville, M., Wieczorek, M.A., Breuer, D., Aubert, J., Morard, G., and Rückriemen, T.
580   (2014) A long-lived lunar dynamo powered by core crystallization. Earth and Planetary
581   Science Letters, 401.

582 LeBlanc, G.E., and Secco, R.A. (1996) Viscosity of an Fe-S liquid up to 1300 degrees C and
583   5 GPa. Geophysical Research Letters, 23, 213–216.

584 Margot, J.L., Peale, S.J., Jurgens, R.F., Slade, M.A., and Holin, I. V (2007) Large Longitude
585   Libration of Mercury Reveals a Molten Core. Science, 316, 710–714.

586 Mezouar, M., Le Bihan, T., Libotte, H., Le Godec, Y., and Häusermann, D. (1999) Paris-
587   Edinburgh large-volume cell coupled with a fast imaging plate system for structural
588   investigation at high pressure and high-temperature. Journal of Synchrotron Radiation, 6,
589   1115–1119.

590 Mezouar, M., Faure, P., Crichton, W., Rambert, N., Sitaud, B., Bauchau, S., and Blattmann,
591   G. (2002) Multichannel collimator for structural investigation of liquids and amorphous
592   materials at high pressures and temperatures. Review of Scientific Instruments, 73, 3570.

593 Mezouar, M., Crichton, W.A., Bauchau, S., Thurel, F., Witsch, H., Torrecillas, F., Blattman,
594   G., Marion, P., Dabin, Y., Chavanne, J., and others (2005) Development of a new state-
595   of-the-art beamline optimized for monochromatic single crystal and powder X-ray
596   diffraction under extreme conditions at the ESRF. Journal of Synchrotron Radiation, 12,
597   659–664.

598 Morard, G., Mezouar, M., Rey, N., Poloni, R., Merlen, A., Le Floch, S., Toulemonde, P.,
599   Pascarelli, S., San-Miguel, A., Sanloup, C., and others (2007a) Optimization of Paris-
600   Edinburgh press cell assemblies for in situ monochromatic X-ray diffraction and X-ray
601   absorption. High Pressure Research, 27.

602　Morard, G., Sanloup, C., Fiquet, G., Mezouar, M., Rey, N., Poloni, R., and Beck, P. (2007b)
603　　　　Structure of eutectic Fe-FeS melts to pressures up to 17 GPa: Implications for planetary
604　　　　cores. Earth and Planetary Science Letters, 263, 128–139.

605　Morard, G., Andrault, D., Guignot, N., Sanloup, C., Mezouar, M., Petitgirard, S., and Fiquet,
606　　　　G. (2008) In situ determination of Fe-Fe3S phase diagram and liquid structural properties
607　　　　up to 65 GPa. Earth and Planetary Science Letters, 272, 620–626.

608　Morard, G., Sanloup, C., Guillot, B., Fiquet, G., Mezouar, M., Perrillat, J.P., Garbarino, G.,
609　　　　Mibe, K., Komabayashi, T., and Funakoshi, K. (2008) In situ structural investigation of
610　　　　Fe-S-Si immiscible liquid system and evolution of Fe-S bond properties with pressure.
611　　　　Journal of Geophysical Research: Solid Earth, 113, 1–12.

612　Morard, G., Mezouar, M., Bauchau, S., Lvarez-Murga, M., Hodeau, J.L., and Garbarino, G.
613　　　　(2011) High efficiency multichannel collimator for structural studies of liquids and low-
614　　　　Z materials at high pressures and temperatures. Review of Scientific Instruments, 82, 2–
615　　　　7.

616　Morard, G., Siebert, J., Andrault, D., Guignot, N., Garbarino, G., Guyot, F., and Antonangeli,
617　　　　D. (2013) The Earth's core composition from high pressure density measurements of
618　　　　liquid iron alloys. Earth and Planetary Science Letters, 373.

619　Nagamori, M. (1969) Density of molten Ag–S, Cu–S, Fe–S, and Ni–S systems. Transactions
620　　　　of the Metallurgical Society AIME, 245, 1897–1902.

621　Nasch, P., Manghnani, M., and Secco, R. (1997) Anomalous behavior of sound velocity and
622　　　　attenuation in liquid Fe-Ni-S. Science, 277, 219.

623　Nasch, P.M., and Manghnani, M.H. (1998) Molar Volume , Thermal Expansion , and Bulk
624　　　　Modulus in Liquid Fe-Ni Alloys at 1 Bar : Evidence for Magnetic Anomalies ?
625　　　　Geophysical Monograph, 101, 307–317.

626　Nasch, P.M., and Steinemann, S.G. (1995) Density and Thermal Expansion of Molten
627　　　　Manganese , Iron , Nickel , Copper , Aluminum and Tin by Means of the Gamma-Ray
628　　　　Attenuation Technique GAMMA-RAY ATTENUATION TECHNIQUE. Physics and
629　　　　Chemistry of Liquids, 29, 43–58.

630　Nishida, K., Terasaki, H., Ohtani, E., and Suzuki, A. (2008) The effect of sulfur content on
631　　　　density of the liquid Fe-S at high pressure. Physics and Chemistry of Minerals, 35, 417–
632　　　　423.

633　Nishida, K., Ohtani, E., Urakawa, S., Suzuki, A., Sakamaki, T., Terasaki, H., and Katayama,
634　　　　Y. (2011) Density measurements of liquid FeS at high pressures using synchrotron X-ray
635　　　　absorption. American Mineralogist, 96, 864–868.

636　Nishida, K., Kono, Y., Terasaki, H., Takahashi, S., Ishii, M., Shimoyama, Y., Higo, Y.,
637　　　　Funakoshi, K.I., Irifune, T., and Ohtani, E. (2013) Sound velocity measurements in
638　　　　liquid Fe-S at high pressure: Implications for Earth's and lunar cores. Earth and
639　　　　Planetary Science Letters, 362, 182–186.

640　Nishida, K., Suzuki, A., Terasaki, H., Shibazaki, Y., Higo, Y., Kuwabara, S., Shimoyama, Y.,
641　　　　Sakurai, M., Ushioda, M., Takahashi, E., and others (2016) Towards a consensus on the
642　　　　pressure and composition dependence of sound velocity in the liquid Fe???S system.
643　　　　Physics of the Earth and Planetary Interiors, 257, 230–239.

644　Perdew, J.P., Burke, K., and Ernzerhof, M. (1996) Generalized gradient approximation made
645　　　　simple. Physical Review Letters, 77, 3865–3868.

Poirier, J.P. (1994) Light elements in the Earth's outer core: A critical review. Physics of the Earth and Planetary Interiors, 85, 319–337.

Pourovskii, L. V., Miyake, T., Simak, S.I., Ruban, A. V., Dubrovinsky, L., and Abrikosov, I.A. (2013) Electronic properties and magnetism of iron at the Earth's inner core conditions. Physical Review B - Condensed Matter and Materials Physics, 87.

Rivoldini, A., Van Hoolst, T., and Verhoeven, O. (2009) The interior structure of Mercury and its core sulfur content. Icarus, 201, 12–30.

Sanloup, C., Guyot, F., Gillet, P., Fiquet, G., Mezouar, M., and Martinez, I. (2000) Density measurements of liquid Fe-S alloys at high pressure. Geophysical Research Letters, 27, 811–814.

Sherman, D.M. (1995) pressure and the composition of the Earth's core. Earth and Planetary Science Letters, 132, 87–98.

Stewart, A.J., Schmidt, M.W., van Westrenen, W., and Liebske, C. (2007) Mars: A New Core-Crystallization Regime. Science, 316, 1323–1325.

Torrent, M., Jollet, F., Bottin, F., Zérah, G., and Gonze, X. (2008) Implementation of the projector augmented-wave method in the ABINIT code: Application to the study of iron under pressure. Computational Materials Science, 42, 337–351.

Tsuchiya, Y. (1994) The thermodynamics of structural changes in the liquid sulphur-tellurium system: compressibility and Ehrenfest's relations. Journal of Physics: Condensed Matter, 6, 2451.

Utsumi, W., Weidner, D.J., and Liebermann, R.C. (1998) Volume measurement of MgO at high pressures and high temperatures. Geophysical Monograph, 101, 327–333.

Vočadlo, L., Alfè, D., rice, G.D., and Gillan, M.J. (2000) First principles calculations on the diffusivity and viscosity of liquid Fe-S at experimentally accessible conditions. Physics of the Earth and Planetary Interiors, 120, 145–152.

Weber, R.C., Lin, P.-Y., Garnero, E.J., Williams, Q., and Lognonne, P. (2011) Seismic Detection of the Lunar Core. Science, 331, 309–312.

Williams, J.G., Konopliv, A.S., Boggs, D.H., Park, R.S., Yuan, D., Lemoine, F.G., Goossens, S., Mazarico, E., Nimmo, F., Weber, R.C., and others (2014) Lunar interior properties from the GRAIL mission. Journal of Geophysical Research : Planets, 119, 1546–1578.

Williams, Q. (2009) Bottom-up versus top-down solidification of the cores of small solar system bodies: Constraints on paradoxical cores. Earth and Planetary Science Letters, 284, 564–569.

Yoder, C.F., Konopliv, A.S., Yuan, D.N., Standish, E.M., and Folkner, W.M. (2003) Fluid Core Size of Mars from Detection of the Solar Tide. Science, 300, 299–303.

Yoshino, T., Walter, M.J., and Katsura, T. (2003) Core formation in planetesimals triggered by permeable flow. Nature, 422, 154–157.

Zhang, Z., and Pommier, A. (2017) Electrical Investigation of Metal-Olivine Systems and Application to the Deep Interior of Mercury. Journal of Geophysical Research: Planets, 122, 2702–2718.

Figure 1

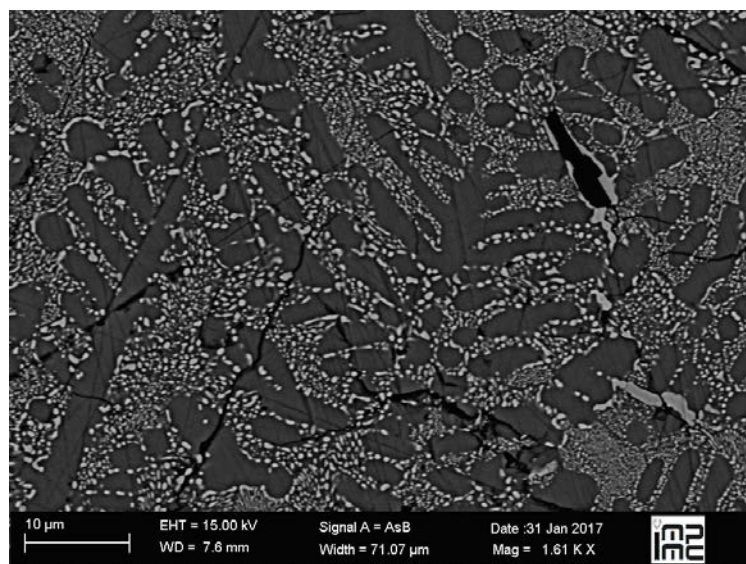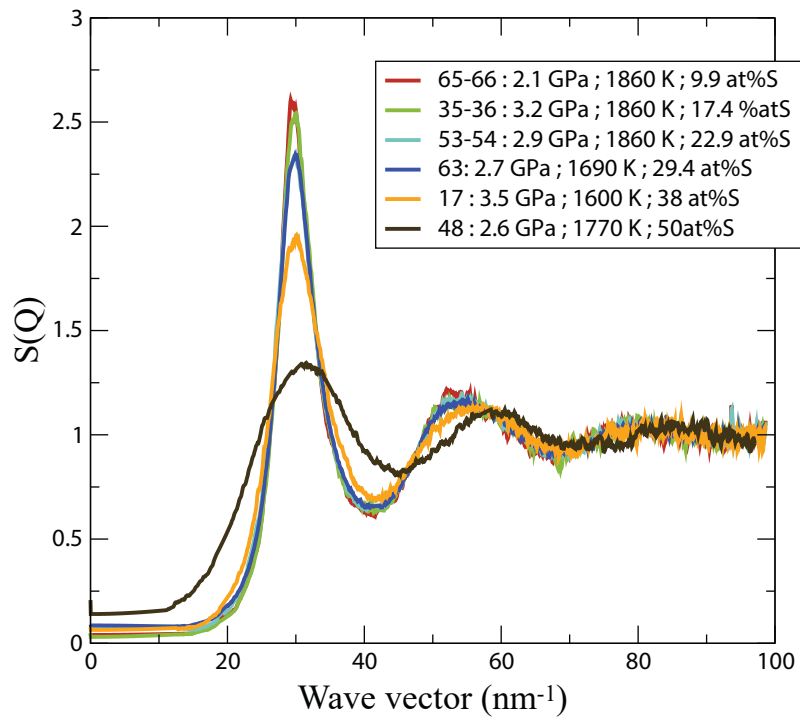Fe + 9.9 at%S   Fe + 38 at%S
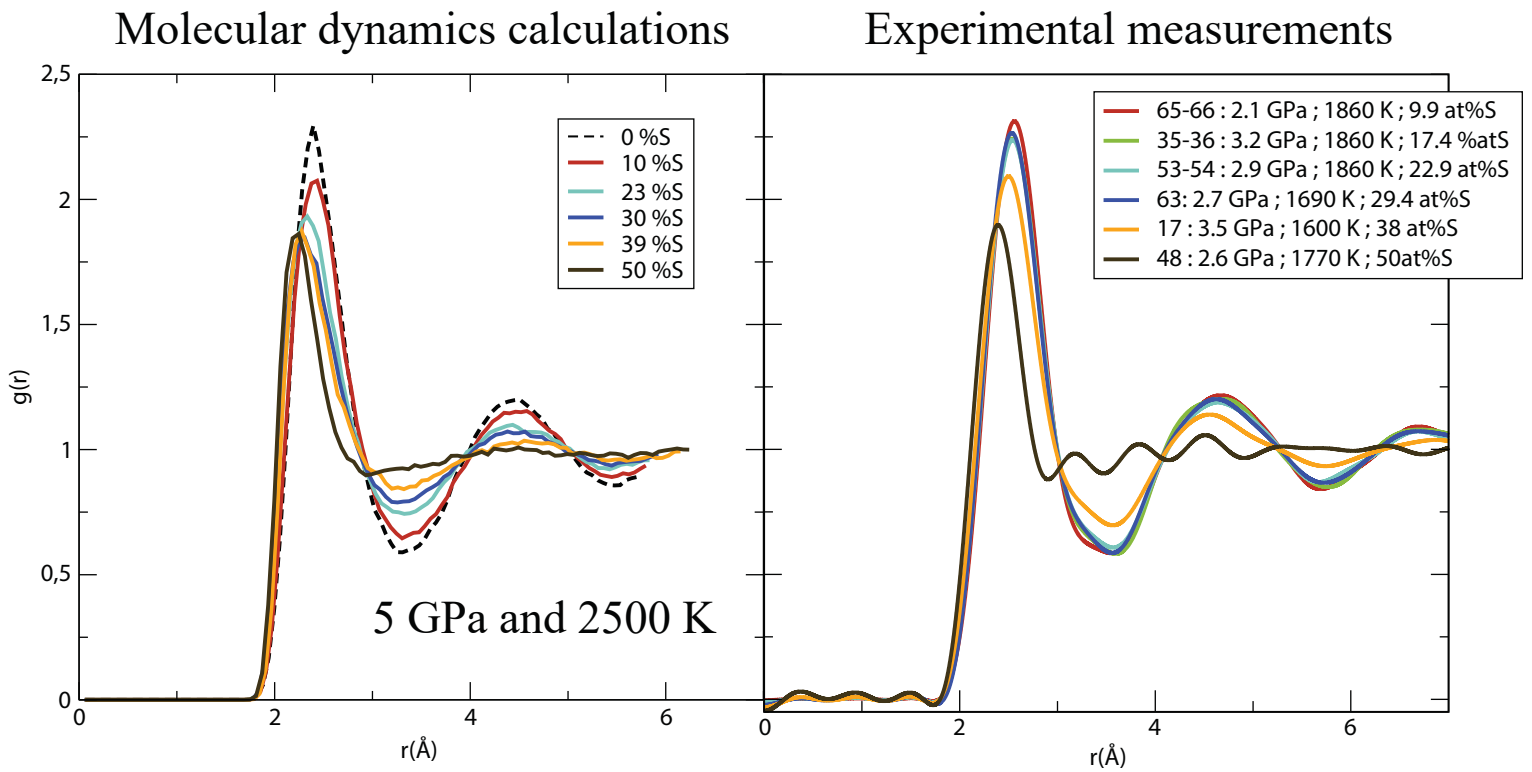
Figure 2

Figure 3

Figure 4

Fe-S bonds Fe-Fe bonds S-S bonds
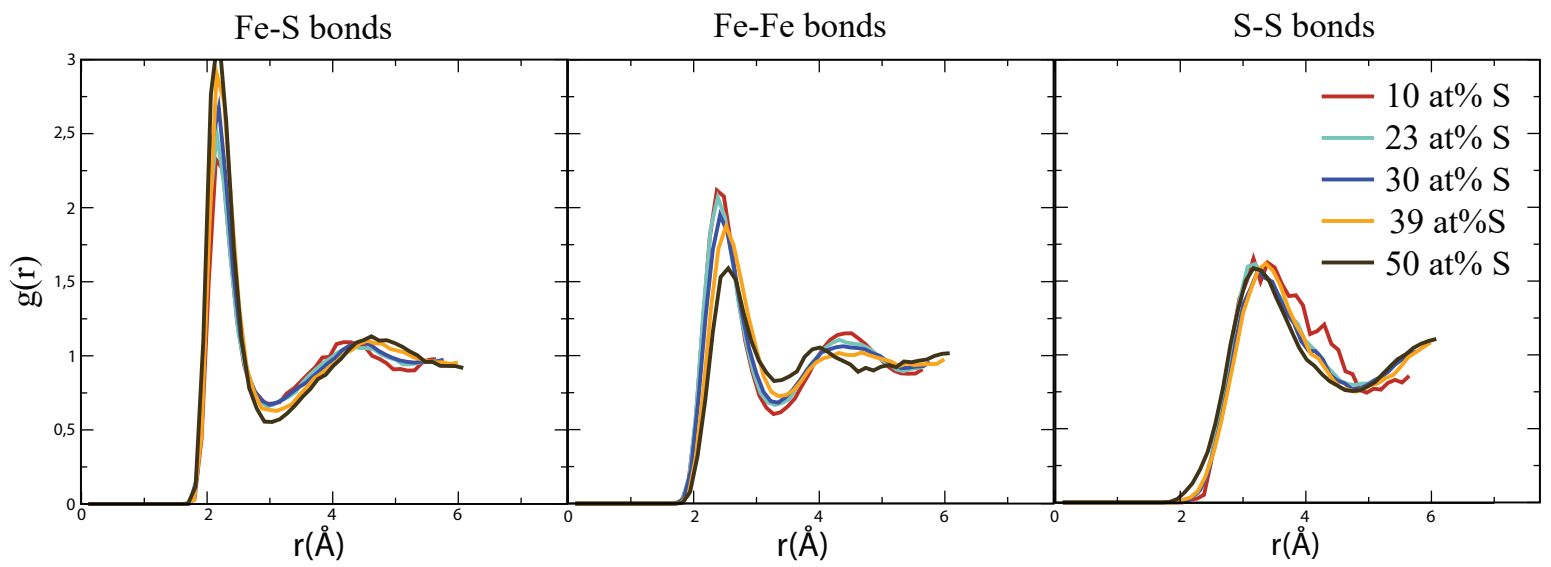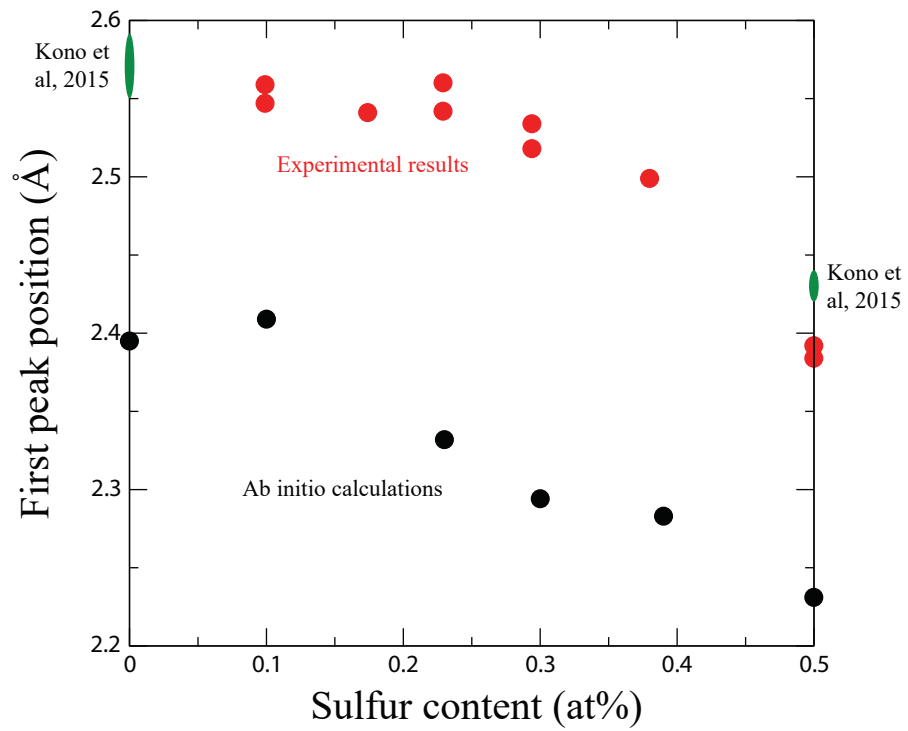
Legend:
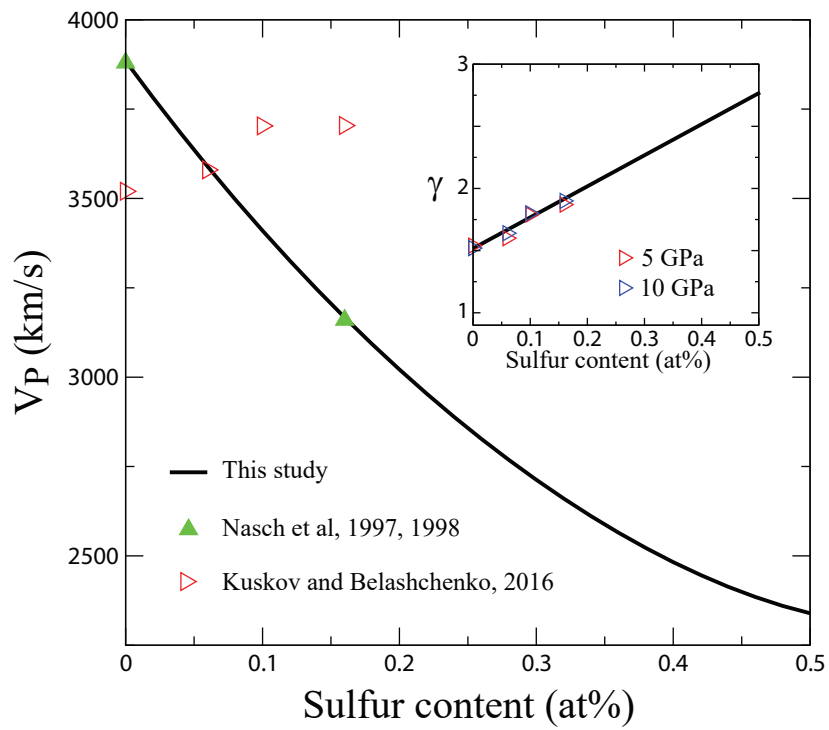- 10 at% S
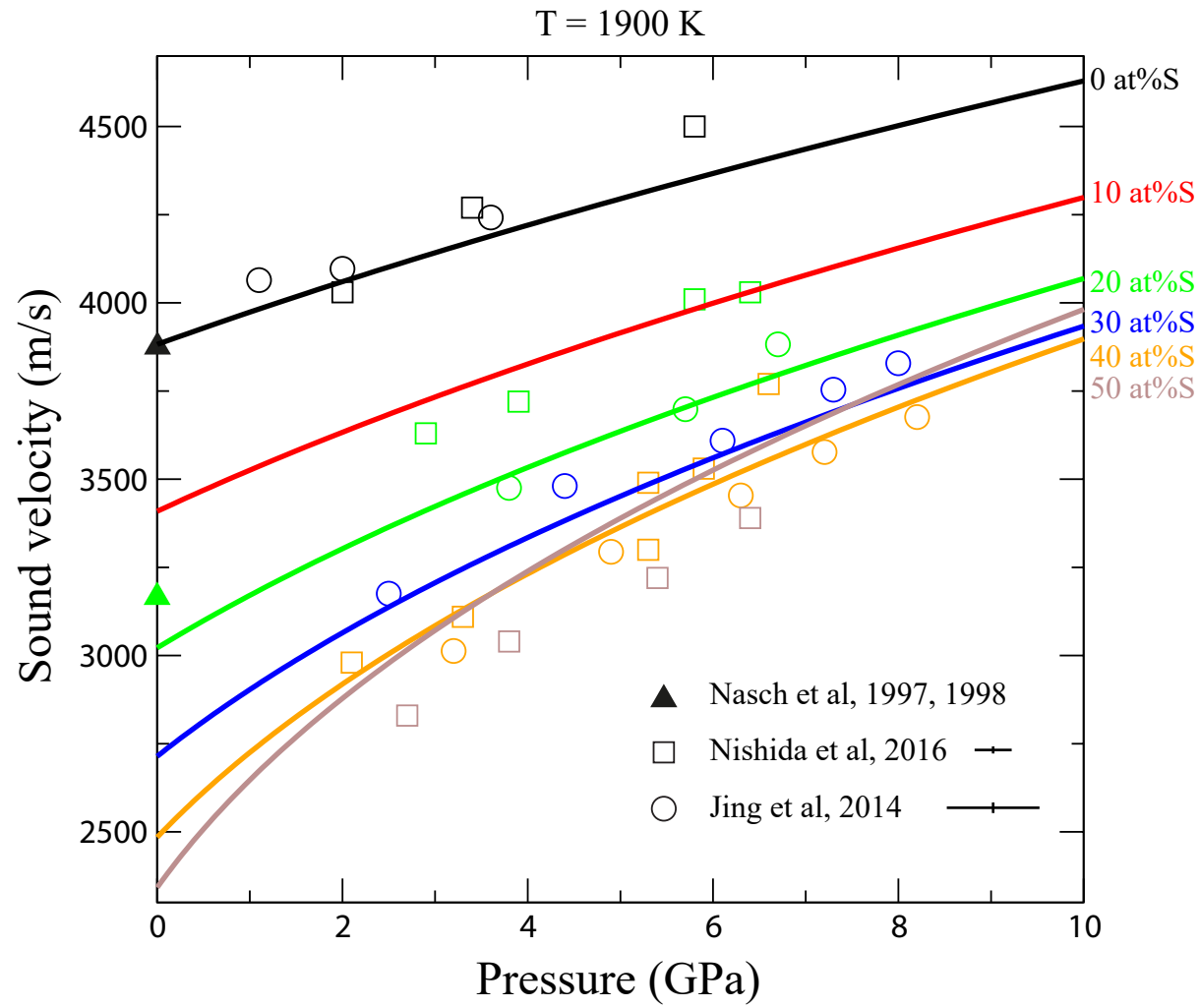- 23 at% S
- 30 at% S
- 39 at%S
- 50 at% S

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

T = 1900 K

Figure 10

Figure 11

CMB temperature : 1750 K