

1 Electronic transitions of iron in almandine- 2 composition glass to 91 GPa

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21 **Abstract**

22 Valence and spin states of Fe were investigated in a glass of almandine ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$)
23 composition to 91 GPa by X-ray emission spectroscopy and energy- and time-domain
24 synchrotron Mössbauer spectroscopy in the diamond anvil cell. Changes in optical properties,
25 total spin moment and Mössbauer parameters all occur predominantly between 1 bar and ~30
26 GPa. Over this pressure range, the glass changes from translucent brown to opaque and black.
27 The total spin moment of the glass derived from X-ray emission spectroscopy decreases by
28 ~20%. The two Mössbauer spectroscopy approaches reveal consistent changes in sites
29 corresponding to 80-90% Fe^{2+} and 10-20% Fe^{3+} . The high-spin Fe^{2+} doublet exhibits a
30 continuous decrease in isomer shift and increase in line width and asymmetry. A high-spin Fe^{3+}

31 doublet with quadrupole splitting of ~ 1.2 mm/s is replaced by a doublet with quadrupole splitting
32 of ~ 1.9 mm/s, a value higher than all previous measurements of high-spin Fe^{3+} and consistent
33 with low-spin Fe^{3+} . These observations suggest that Fe^{3+} in the glass undergoes a gradual
34 transition from high to low spin state between 1 bar and ~ 30 GPa. Almandine glass is not
35 expected to undergo any abrupt transitions in electronic state at deep mantle pressures.

36 Keywords: silicate glass; spin transitions; Mössbauer spectroscopy; nuclear forward
37 scattering; X-ray emission spectroscopy

38 **1. Introduction**

39 The high-pressure behavior of Fe-rich silicate liquids is key to the differentiation of the
40 mantle from a primordial magma ocean (Labrosse et al. 2007; Stixrude et al. 2009; Lee et al.
41 2010) and to understanding observations of possible dense melt-rich regions near the core-mantle
42 boundary (Williams and Garnero 1996). The dynamics of melt in the deep mantle is largely
43 controlled by the behavior of Fe, Earth's densest major elemental component. A density
44 crossover in the deep mantle, with negatively-buoyant Fe-rich silicate melt relative to solid
45 mantle silicates, has been suggested based on the compressibility of melt (Stixrude et al. 2009;
46 Thomas et al. 2012; Muñoz Ramo and Stixrude 2014) and partitioning of Fe into the liquid phase
47 (Nomura et al. 2011; Andraut et al. 2012). However, detailed characterization of mantle melt is
48 challenging due both to experimental difficulty of stable melting at mantle pressures and limited
49 capability to probe liquid structures at extreme conditions. As low-temperature analogues to
50 melts, silicate glasses have been explored in recent high-pressure experiments (e.g. Nomura et al.
51 2011) and computational studies (e.g. Stixrude and Karki 2005). In both silicate liquids and

52 glasses a range of coordination environments may evolve continuously with composition and
53 pressure (Stixrude and Karki 2005), but a surprising sharp transition was recently reported at ~70
54 GPa in Fe-bearing melt and glass and attributed to a spin transition (Nomura et al. 2011).

55 Spin transitions in crystalline mantle phases and their implications for seismic properties
56 and chemical partitioning have been the focus of much recent study, particularly of ferropericlase
57 (Badro et al. 2003) and silicate perovskite (Badro et al. 2004). In ferropericlase, a spin transition
58 occurs in 6-fold-coordinated Fe^{2+} at pressures between 50 and 90 GPa, depending on Fe content
59 (Speziale et al. 2005; Fei et al. 2007). In silicate perovskite (now known as bridgmanite), the
60 presence of multiple sites and valence states makes characterizing the spin state more complex,
61 but both experiments and density functional theory results indicate that a spin transition occurs in
62 6-fold-coordinated Fe^{3+} at 15-50 GPa (Catalli et al. 2010; Hsu et al. 2011; Lin et al. 2012). At
63 high temperatures relevant to Earth's mantle, the effects of Boltzmann statistics and kinetics have
64 been predicted (Sturhahn et al. 2005; Tsuchiya et al. 2006; Lin and Tsuchiya 2008) and observed
65 (Lin et al. 2007; Kantor et al. 2009) to broaden each of these spin transitions to occur over a
66 pressure interval extending for ~30-50 GPa.

67 Liquids and glasses are characterized by continuous structural evolution under
68 compression that may also contribute to the pressure-broadening of spin transitions. At mantle
69 temperatures, the spin transition in liquid Fe_2SiO_4 has been predicted to take place over a >200
70 GPa pressure range (Muñoz Ramo and Stixrude 2014). While this transition might affect the
71 depth of a solid-liquid density crossover in the mantle, it would not be observable as a
72 discontinuity. In contrast, Nomura et al. (2011) reported a sharp change in Fe partitioning in
73 partially-melted $(\text{Mg}_{0.89}\text{Fe}_{0.11})_2\text{SiO}_4$ between 73 and 76 GPa. At similar pressures, between 59

74 and 77 GPa, they also observed that X-ray emission spectra of $(\text{Mg}_{0.95}\text{Fe}_{0.05})\text{SiO}_3$ glass indicated
75 a complete spin transition. Other studies are not consistent with abrupt spin transitions in liquids
76 and melts. No sharp change in partitioning was observed in chondritic melt at pressures up to 120
77 GPa (Andraut et al. 2012). Studies of several different Fe-bearing silicate glass compositions—
78 10-50% FeSiO_3 , $\text{Fe}^{3+}/\Sigma\text{Fe}$ from 0-78%, with and without Al—showed either no change in spin
79 state (Mao et al. 2014; Prescher et al. 2014) or a gradual, partial change (Gu et al. 2012;
80 Murakami et al. 2014) at high pressures. Gradual increases in cation coordination rather than spin
81 transitions were inferred to be primarily responsible for pressure-induced changes in these glasses
82 (Mao et al. 2014; Prescher et al. 2014).

83 Studies of Fe spin state at extreme pressures rely on two complementary synchrotron
84 techniques: X-ray emission spectroscopy and Mössbauer spectroscopy. X-ray emission
85 spectroscopy (XES) measures energies of electron exchange between $3p$ and $3d$ orbitals, which
86 depend on bonding, coordination, valence and spin states (Peng et al. 1994; Rueff et al. 1999;
87 Mattila et al. 2007). This technique was the first used to identify pressure-induced spin transitions
88 in major lower mantle phases (Badro et al. 2003, 2004). However, XES only provides a
89 constraint on the total spin moment of the bulk material, not of individual states or sites.
90 Mössbauer spectroscopy provides a complementary constraint on coordination, site occupancy,
91 valence, and spin states of Fe via the energies of recoil-free nuclear resonance in solid materials.
92 The technique can be applied to glasses but not silicate liquids; for insights on melt structures, a
93 wide variety of silicate glass compositions have been examined at ambient pressure by
94 Mössbauer spectroscopy (MS) with a conventional radioactive source (e.g. Mao et al. 1973;
95 Virgo and Mysen 1985; Jayasuriya et al. 2004; Dunlap and McGraw 2007; Rossano et al. 2007;

96 Cottrell and Kelley 2011). ^{57}Fe nuclei of each site, species and spin state resonate at energies with
97 isomer shift (IS), quadrupole splitting (QS) and hyperfine splitting that reflect the local electric
98 and magnetic fields. The relative intensities of each site indicate the abundance of Fe^{2+} and Fe^{3+}
99 in each spin state and coordination environment. For Mössbauer spectroscopy of materials at high
100 pressures, synchrotron radiation can provide a more brilliant, highly-focused source. Energy-
101 domain synchrotron Mössbauer spectroscopy (E-SMS) is identical to MS with the exception of a
102 more brilliant source obtained by monochromatizing a synchrotron beam to $\sim\text{neV}$ linewidth
103 (Smirnov et al. 1997; Mitsui et al. 2009; Potapkin et al. 2012). Mössbauer parameters IS and QS
104 can also be derived from nuclear forward scattering (also known as time-domain synchrotron
105 Mössbauer spectroscopy, T-SMS), in which nuclear resonance is observed in $\sim\text{few hundred}$
106 nanosecond time windows between pulses of synchrotron radiation (Jackson et al. 2005;
107 Sturhahn et al. 2005). The combination of XES, E-SMS and T-SMS techniques offers the best
108 approach for separation of competing effects and thus understanding complex Fe-bearing
109 materials such as silicates at lower mantle conditions.

110 Fe,Al-bearing silicate glass compositions examined in previous studies are rich in ferric
111 iron; glass of almandine garnet composition provides a useful contrast as it is rich in both
112 aluminum and ferrous iron. Almandine is also of particular interest among silicate minerals for its
113 unusual electronic structure, with high quadrupole splitting at ambient conditions and at high
114 pressures (Dyar et al. 2006; Mao et al. 2013). At ~ 80 GPa and 2500 K, almandine end-member
115 $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ has been observed to transform to a single-phase orthorhombic perovskite
116 consistent with stoichiometry $(\text{Fe}_{0.75}\text{Al}_{0.25})(\text{Al}_{0.25}\text{Si}_{0.75})\text{O}_3$ (Dorfman et al. 2012). Structural

117 refinement of X-ray diffraction data for this phase shows that nearly all Fe resides in the larger A-
118 site and there are no discontinuities in its equation of state up to 150 GPa.

119 In this work, we apply multiple techniques to characterize the pressure-dependence of
120 valence and spin states in almandine glass at pressures up to 91 GPa. Total spin moment is
121 determined by XES. Valence, spin, and coordination states are constrained by E-SMS and T-
122 SMS.

123 2. Material and methods

124 ^{57}Fe -enriched almandine glass was prepared from a stoichiometric mixture of $^{57}\text{Fe}_2\text{O}_3$
125 (Cambridge Isotope Laboratories, Inc., ^{57}Fe 94.3%), Al_2O_3 (Alfa Aesar 99.9%) and SiO_2
126 (Johnson Matthey, 99.995%) after the method described by Geiger et al. (1987). Approximately
127 300 mg of reagents were placed in a covered graphite crucible and heated from 1000°C to
128 1200°C at a rate of 4°C/min. The sample was held at 1200°C for 6 minutes before being
129 quenched in air. To ensure a homogeneous product the resultant material was subsequently arc
130 melted under an argon atmosphere. The composition and homogeneity of the glass were
131 confirmed by microprobe analysis (Supplementary Table 1). The normalized formula,
132 $\text{Fe}_{2.69}\text{Al}_{2.14}\text{Si}_{2.93}\text{O}_{12}$, is slightly depleted in Fe and enriched in Al relative to pure almandine.

133 The valence state of Fe in the starting material was determined by Mössbauer
134 spectroscopy. MS was performed over ~1 day with a ^{57}Co radioactive source at the Advanced
135 Photon Source (APS) sector 3 offline Mössbauer laboratory. The spectrum was fit to a two-site
136 model (Figure 1, Table 1) using MossA software (Prescher et al. 2012). The dominant site, 82(3)
137 percent of the iron, has QS of 2.08(3) mm/s and IS relative to an iron standard of 0.982(14)

138 mm/s. These parameters are typical of Fe²⁺ in silicates (Dyar et al. 2006) and glasses (Dyar 1985;
139 Virgo and Mysen 1985; Burkhard 2000; Jayasuriya et al. 2004; Mysen 2006; Rossano et al. 2007;
140 Gu et al. 2012; Mao et al. 2014; Murakami et al. 2014; Prescher et al. 2014). The QS of Fe²⁺ in
141 almandine glass is considerably lower than the 3.53 mm/s observed in crystalline almandine
142 (Woodland and Ross 1994; Dyar et al. 2006). A significant minority site was observed with
143 QS=1.23(11) mm/s and IS=0.39(5) mm/s, consistent with Fe³⁺ in silicate glasses but with higher
144 QS than Fe³⁺ in silicate garnets. This analysis yields Fe³⁺/ΣFe of 18(3)%.

145 High-pressure experiments were performed using symmetric diamond anvil cells (DAC).
146 Glass samples were loaded with a ~8 μm ruby ball in NaCl, cryogenically-cooled Ar or
147 pressurized Ne (Rivers et al. 2008) (Figure 2). A 50 to 80-μm diameter hole was drilled through a
148 Re or Be gasket to serve as a sample chamber. Diamond anvils with 150, 200 and 300-μm culet
149 size were used in separate experiments to reach maximum pressures of 91, 86, and 66 GPa,
150 respectively. Pressure was calibrated by ruby fluorescence (Mao et al. 1986) or Raman
151 spectroscopy of the tip of the diamond anvil (Akahama and Kawamura 2006).

152 XES was performed at pressures up to 66 GPa at beamline GALAXIES of Synchrotron
153 SOLEIL (Rueff et al. 2015). At GALAXIES, the beam size was 30x80 microns, incident energy
154 was 10 keV and typical count rates were 70-150 counts/s. The emission signal was maximized by
155 directing incident radiation through the diamond and collecting spectra at an angle of
156 approximately 10° minimizing the path through the beryllium gasket.

157 T-SMS experiments were conducted at pressures up to 85 GPa using beamline 16-ID-D of
158 the APS. Kirkpatrick-Baez mirrors were used to focus the X-ray beam to 30x40 μm. The storage

159 ring was operated in standard-mode with 24 bunches separated by 153 ns. Data were collected
160 between 14 and 130 ns after excitation. Measurements were taken both with and without a 0.5-
161 μm thick ^{57}Fe -enriched stainless steel foil as a reference. Sample count rates at high pressure
162 were 30-150 counts/s and spectra were typically collected for 30-60 minutes. At ambient
163 pressure, both T-SMS and MS give consistent results (Figure 1, Tables 1-2).

164 E-SMS experiments were conducted at pressures up to 91 GPa at beamline ID18 of the
165 European Synchrotron Radiation Facility (ESRF) (Rüffer and Chumakov 1996; Potapkin et al.
166 2012). The synchrotron beam was focused to $9 \times 14 \mu\text{m}$ and monochromatized to a bandwidth of
167 $\sim 5.5 \text{ neV}$ at the ^{57}Fe resonant energy by a $^{57}\text{FeBO}_3$ single crystal. The crystal monochromator
168 was oscillated in a sinusoidal mode over $\pm 5 \text{ mm/s}$ to provide a range of energies for absorption
169 measurements via the Doppler effect. Source velocity was calibrated with an $\alpha\text{-Fe}$ foil. The
170 linewidth and center shift of the source were verified before and after each measurement with
171 $\text{K}_2\text{Mg}^{57}\text{Fe}(\text{CN})_6$ standard.

172 **3. Results**

173 Glass samples were compressed without heating to maximum pressures up to 91 GPa. At
174 ambient conditions, the glass is honey-brown and translucent, but darkens with pressure,
175 becoming black and opaque by 34 GPa (Figure 2). Pressure-induced color change of
176 $(\text{Mg}_{0.8}\text{Fe}_{0.2})\text{SiO}_3$ enstatite-composition glass was determined by optical absorption spectroscopy
177 to occur from $\sim 15\text{-}50 \text{ GPa}$ (Murakami et al. 2014). An analogous color-change in crystalline
178 samples is known to be associated with the garnet-perovskite transition (O'Neill and Jeanloz
179 1994; Kesson et al. 1995; Dorfman et al. 2012) but is not observed in cold-compressed almandine

180 to pressures above 1 Mbar (Dorfman et al. 2012). This change in optical properties decreases
181 radiative thermal conductivity of Fe-bearing silicates in the mantle and may be associated with
182 changes in electronic configuration (Murakami et al. 2014).

183 **3. 1. X-ray emission spectroscopy**

184 The observed Fe $K\beta$ X-ray emission spectrum at ambient conditions is composed of a
185 main $K\beta_{1,3}$ peak and a well-resolved lower-energy satellite $K\beta'$ peak and is consistent with iron
186 entirely in the high spin state (Figure 3). Up to 66 GPa in almandine glass, the $K\beta'$ peak intensity
187 continuously decreases and breadth increases (Figure 3). These changes may be due to either a
188 gradual spin-pairing transition or pressure-induced broadening effects (Gu et al. 2012; Mao et al.
189 2014; Murakami et al. 2014).

190 Distinguishing between a gradual spin transition and spectral broadening depends on
191 quantitative comparison with reference spectra. Several methods have been proposed for
192 quantifying spin crossovers (Kantor et al. 2006; Vankó et al. 2006; Mao et al. 2014) and each
193 may result in a different interpretation of the data. Simple peak-fitting techniques do not
194 adequately model the $K\beta$ spectrum due to the complexity of the energy multiplets from which the
195 broader features are composed (Vankó et al. 2006). Instead, the spin state is derived from an
196 integrated difference between spectra and reference high- and low-spin standard spectra.
197 Relevant standards are keys to this method. Spectral differences can be due to differences in
198 instrument resolution, crystallographic environment, and stress conditions as well as spin state, so
199 these confounding factors must be minimized between standards and experiments (De Groot
200 2001; Vankó et al. 2006; Mao et al. 2014). A modification of the integrated difference technique

201 was recently proposed to minimize the effects of pressure-induced broadening (Mao et al. 2014).
202 Difference spectra are summed such that negative differences at $K\beta'$ are offset by positive
203 differences in the shoulder between $K\beta'$ and $K\beta_{1,3}$. This integrated relative difference (IRD)
204 method was suggested to better model pressure-induced spin transitions both in (Mg,Fe)O
205 ferropericlase and in Fe-bearing silicate glass (Mao et al. 2014).

206 The IRD analysis was applied to the almandine glass XES using as references (Mg,Fe)O
207 from Lin et al. (2010) and the ambient-pressure glass spectrum. No significant difference is
208 observed between the glass at 1 bar and (Mg,Fe)O at 1 bar. IRD at high pressure relative to either
209 high-spin standard is identical within symbol size. Between 1 bar and the first high-pressure
210 measurement at 9 GPa, a decrease in total spin moment begins. Total spin moment decreases
211 gradually to ~80% of the high-spin standard by 27 GPa (Figure 3). At higher pressures up to 66
212 GPa there is no significant further change in spin. The gradual change in the spectrum above 27
213 GPa reflects only broadening due to pressure and/or differential stress.

214 In previous work on silicate glass at high pressure, analysis by the integrated absolute
215 difference (IAD) method of Vankó et al. (2006) showed a gradual spin transition (Gu et al. 2012)
216 while the IRD method showed only broadening (Mao et al. 2014). Analysis of our spectra with
217 the IAD method also produces an apparent gradual loss of spin moment over the entire pressure
218 range (Supplementary Figure 1). We thus confirm that the IRD analysis removes pressure-
219 induced broadening and reduces the apparent change in spin relative to the IAD analysis, but we
220 still observe partial loss of spin moment. The spin change can be linked to a valence state and site
221 using Mössbauer spectroscopy.

3. 2. Synchrotron Mössbauer spectroscopy

Synchrotron Mössbauer spectroscopy was performed on almandine glass at high pressures in both energy- and time-domain modes. E-SMS (Figure 4) and T-SMS spectra (Supplementary Figure 2) evolve continuously with pressure. The major feature in E-SMS spectra is the asymmetrical doublet identified as Fe^{2+} . With compression the Fe^{2+} doublet broadens and becomes increasingly asymmetrical. Pressure-induced changes in the Fe^{2+} doublet are consistent with previous E-SMS measurements of Fe^{2+} -rich glasses with compositions $(\text{Mg}_{0.8}\text{Fe}_{0.2})\text{SiO}_3$ and $(\text{Mg}_{0.823}\text{Fe}_{0.135})(\text{Al}_{0.057}\text{Si}_{0.982})\text{O}_3$ (Murakami et al. 2014; Prescher et al. 2014). The small shoulder observed between the Fe^{2+} lines (Figure 4) is identified as one leg of the Fe^{3+} doublet. At higher pressures, a shoulder appears at higher velocity on the Fe^{2+} doublet.

T-SMS spectra (Supplementary Figure 2) at low pressure have a sharp beat at ~ 60 ns and a broad decay after ~ 100 ns. At higher pressures, the beat shifts with pressure to faster times and becomes less distinct. Above 26 GPa, another small beat appears at ~ 80 ns. Despite differences in $\text{Fe}^{3+}/\Sigma\text{Fe}$ and total iron content, qualitatively similar spectra were observed at high pressure in $(\text{Mg}_{0.80}\text{Fe}_{0.20})\text{SiO}_3$ ($\sim 10\%$ Fe^{3+}) and $(\text{Mg}_{0.75}\text{Fe}_{0.20}\text{Al}_{0.10}\text{Si}_{0.95})\text{O}_3$ ($\sim 35\%$ Fe^{3+}) glasses by Gu et al. (2012) and $(\text{Mg}_{0.79}\text{Fe}_{0.10}\text{Al}_{0.10}\text{Si}_{0.96})\text{O}_3$ (78% Fe^{3+}) glass by Mao et al. (2014). However, starting from 17 GPa and increasing with pressure in the almandine glass studied here, resonant intensity is observed at ~ 110 ns. Neither previous study reports this structure, either due to difference in electronic states or effective sample thickness.

Modeling Mössbauer spectra of glasses is challenging due to the range of coordination environments and site geometries in a disordered structure. A simple two-site model with a distribution over IS or QS cannot fit the asymmetry observed in E-SMS and the complex

244 structure in T-SMS. An asymmetrical Fe^{2+} doublet is observed in silicate glasses due to a range
245 of coordination environments (Mao et al. 1973; Alberto et al. 1996). For glasses at both ambient
246 conditions (Alberto et al. 1996; Lagarec and Rancourt 1997) and high pressures (Prescher et al.
247 2014), a correlated distribution over both IS and QS fits the asymmetrical Fe^{2+} doublet
248 (Supplementary Figure 3). E-SMS data in this study were analyzed using the correlated
249 distribution model of Lagarec and Rancourt (1997) implemented for fitting E-SMS spectra in
250 MossA software (Prescher et al. 2012). The correlated distribution for Fe^{2+} can also be modeled
251 with a pair of doublets of approximately equal intensity, one representing low-IS, low-QS and the
252 other high-IS, high-QS (Supplementary Figure 3) (Virgo and Mysen 1985; Jayasuriya et al.
253 2004). T-SMS data in this study were analyzed using a paired Fe^{2+} doublet model with fixed
254 weighting in the CONUSS software package (Sturhahn 2000). T-SMS fits with a pair of doublets
255 for Fe^{2+} are consistent with observed E-SMS spectra (Supplementary Figure 2). Fe^{3+} doublets are
256 not fully resolved but assumed to be symmetric as previously observed at ambient pressure
257 (Virgo and Mysen 1985) and high pressure (Prescher et al. 2014).

258 Our results demonstrate consistent pressure-dependence of Mössbauer parameters in three
259 separate compression experiments with two SMS techniques (Figure 5, Tables 1-2). Observed
260 Mössbauer parameters for the Fe^{2+} doublet(s) at all conditions studied are consistent with
261 previous observations of high-spin Fe^{2+} in glasses (Dyar 1985; Virgo and Mysen 1985; Burkhard
262 2000), with average QS of 2.0-2.3 mm/s and IS of 0.8-1.1 mm/s. The QS of high-spin Fe^{2+}
263 increases slightly from 1 bar to 30 GPa and then slightly decreases up to the maximum pressure
264 of 91 GPa. The IS of high-spin Fe^{2+} decreases with pressure. The most significant change in the
265 Fe^{2+} component is an increase in the correlated broadening parameter related to the covariance of

266 QS and IS, ρ , particularly between 1 bar and ~40 GPa. In T-SMS fits, the increase in correlated
267 broadening is modeled as a divergence of both QS and IS of two high-spin Fe^{2+} doublets. The
268 weight of the high-spin Fe^{2+} component does not change significantly. If the change in spin state
269 indicated by XES corresponds to a high-to-low spin transition in Fe^{2+} , we would expect a
270 decrease in QS of the Fe^{2+} site, as for the high-to-low spin transition in Fe^{2+} in bridgmanite (Hsu
271 et al. 2010), but this is not observed. Our data also do not support pressure-induced growth of an
272 intermediate spin Fe^{2+} component with parameters as reported by Murakami et al. (2014). The
273 broadening of the Fe^{2+} doublet could be interpreted as a gradual transition of half of the Fe^{2+}
274 component to intermediate spin below ~40 GPa. This is consistent with the total spin moment
275 measured by XES, but unlikely as there is no obvious reason why the spin transition would stop,
276 incomplete, at ~40 GPa.

277 Observations of the Fe^{3+} component(s) are consistent with a high-to-low spin transition.
278 At pressures >30 GPa, the values of QS for the Fe^{3+} site are 1.7-2.0 mm/s. These values are
279 outside the range of previous observations for high-spin Fe^{3+} at ambient conditions (Figures 5-6)
280 (Dyar 1985; Virgo and Mysen 1985; Burkhard 2000) and similar to previous observations of low-
281 spin Fe^{3+} -bearing compounds (Greenwood and Gibb 1971; Pasternak et al. 2002). Moreover, both
282 the weight of the Fe^{3+} component, ~20% of the total Fe, and the pressure at which the
283 Fe^{3+} shoulder completes its shift, ~30 GPa, match the decrease in spin moment observed in XES
284 data (Figure 3). A high-to-low spin transition in Fe^{3+} should be observed as a decrease in the
285 intensity of the high-spin doublet and corresponding growth of the low-spin doublet with lower
286 IS and higher QS (Pasternak et al. 2002). We have thus chosen a model with two Fe^{3+} doublets,
287 although these two doublets are not fully resolved in our MS data. We are also unable to resolve

288 the minimum pressure at which the low-spin Fe^{3+} appears, but at 15 GPa ~30% of the Fe^{3+} is in
289 the low-spin state. The high- and low-spin doublets coexist over a wider pressure range in the
290 glass sample loaded in NaCl vs. Ne medium. This suggests that differential stress may result in a
291 broader spin transition, as reported in (Mg,Fe)O (Lin et al. 2009).

292 Previous Mössbauer studies of silicate glasses found generally similar QS and IS values
293 and changes with pressure as in our study (Figure 6). QS and IS for all sites in the almandine
294 glass are similar to those constrained by previous E-SMS studies on Fe-bearing silicate glasses at
295 high pressures (Murakami et al. 2014; Prescher et al. 2014). Studies using both E-SMS and T-
296 SMS techniques on a wide range of compositions have found an increase in QS of Fe^{2+} at
297 pressures up to 20-40 GPa (Gu et al. 2012; Mao et al. 2014; Murakami et al. 2014; Prescher et al.
298 2014). A similar QS of high-pressure Fe^{3+} was observed in Fe^{3+} -rich glass studied by Prescher et
299 al. (2014) and Gu et al. (2012), but not by Mao et al. (2014). IS of Fe^{2+} was observed to decrease
300 with pressure in both previous E-SMS studies (Murakami et al. 2014; Prescher et al. 2014).
301 However, previous studies have offered different interpretations of these observations: no spin
302 transition (Mao et al. 2014; Prescher et al. 2014), a gradual high-to-low spin transition in
303 Fe^{3+} (Gu et al. 2012) or a high-to-intermediate spin transition in Fe^{2+} (Murakami et al. 2014). In
304 addition to differences in composition between these studies, differences in interpretation of
305 Mössbauer parameters are due to details of E-SMS and T-SMS fitting and availability and
306 interpretation of XES data.

307 **4. Discussion**

308 The multiple techniques used in this study enable us to provide a strong constraint on the
309 pressure-dependence of spin states of Fe in almandine glass. Optical properties, XES, and
310 Mössbauer parameters of Fe³⁺ all exhibit changes between 1 bar and ~30 GPa. These results
311 support a gradual, complete transition of Fe³⁺ in almandine glass from high to low spin and no
312 detectable change in spin state of Fe²⁺.

313 This transition in Fe³⁺ could not be reliably identified in previous studies that did not use
314 multiple experimental techniques. Fitting T-SMS spectra alone suffers from non-unique
315 constraints on Mössbauer parameters. Gu et al. (2012) model spectra using a pair of Fe²⁺ doublets
316 similar to those in this study, but their strong change in intensity with pressure is inconsistent
317 with other studies of silicate glasses and may be an artifact of non-unique fitting. Mao et al.
318 (2014) restrict their model to two sites of constant intensity, one each for high spin Fe²⁺ and Fe³⁺,
319 but their modeled energy-domain spectra exhibit varying degrees of asymmetry which is not
320 explained. The previous E-SMS study of Fe³⁺-rich silicate glass (Prescher et al. 2014) finds a
321 similar increase in QS as in our observations of almandine glass (Figure 6). The doublet
322 identified at pressures above 20 GPa as intermediate spin Fe²⁺ by Murakami et al. (2014) is
323 consistent with Fe³⁺ at high pressures in this study and Prescher et al. (2014) (Figure 6).
324 However, previous studies using the E-SMS technique were not combined with XES
325 measurements and thus were unable to relate changes in Mössbauer parameters to changes in
326 total spin moment.

327 While our results and previous studies cover a wide range of compositions, all time- or
328 energy-domain Mössbauer studies of glass to date consistently find that there is no sharp
329 transition in spin or structure with pressure up to 126 GPa (Gu et al. 2012; Mao et al. 2014;

330 Murakami et al. 2014; Prescher et al. 2014). Almandine glass is much richer in Fe than the
331 compositions studied in other work; this may promote a spin transition at relatively lower
332 pressures (Prescher et al. 2014). The sharp spin transition observed in XES data by Nomura et al.
333 (2011) in $(\text{Mg}_{0.95}\text{Fe}_{0.05})\text{SiO}_3$ glass at 76 GPa is inconsistent with this and other studies. Similar
334 experimental methods were used by Nomura et al. (2011) and more recent studies, and thus these
335 results remain unexplained and unreplicated.

336 A spin transition in Fe^{3+} in silicate glasses is analogous to transitions in crystalline Fe-
337 bearing silicates. In bridgmanite, Fe^{3+} in the 6-fold-coordinated B-site is predicted theoretically to
338 undergo a spin transition at 40-70 GPa, but both Fe^{3+} and Fe^{2+} in the 8-fold-coordinated A-site
339 remain high-spin throughout the lower mantle pressure range (Hsu et al. 2010, 2011). Spin
340 transitions in Fe^{3+} have been observed at various pressures in the range of 13-70 GPa by several
341 experimental studies of bridgmanite (e.g. Catalli et al. 2010, 2011; Mao et al. 2011; Lin et al.
342 2012) and other Fe^{3+} -bearing perovskites (Xu et al. 2001; Pasternak et al. 2002; Rozenberg et al.
343 2005). In addition, a discontinuity in volumetric compression was attributed to a spin transition in
344 6-fold-coordinated Fe^{3+} in andradite garnet at 60-70 GPa (Friedrich et al. 2014). No spin
345 transition has been observed in 8-fold-coordinated Fe^{2+} in pyrope-almandine garnets, but studies
346 of the equation of state and electronic configuration of these garnets have only reached ~30 GPa
347 (e.g. Mao et al. 2013).

348 In silicate glass, Fe^{3+} and Fe^{2+} both occupy a range of coordination environments. In
349 MgSiO_3 glasses, the average coordination number is 6 in the Mg-site and 4 in the Si-site, and
350 these averages increase with pressure (Funamori et al. 2004). The average coordination of Si in
351 SiO_2 glass has been suggested by experiments and simulations to increase stepwise or

352 continuously with compression (e.g. Meade et al. 1992). While compression alone generally
353 increases QS while decreasing IS (e.g. Pasternak et al. 2002; Kantor et al. 2006), increasing
354 coordination of Fe increases both QS and IS (Dyar et al. 2006). Observed increases in QS of Fe²⁺
355 with pressure in silicate glasses have been interpreted to show densification by increasing
356 coordination number to 8-12 (Mao et al. 2014). However, in the almandine glass we observe not
357 only a slight increase in QS but an increase in broadening of the Fe²⁺ site. This doublet represents
358 a superposition of multiple sites with different coordination which cannot be resolved in the
359 glass. Pressure-induced changes in Mössbauer parameters of Fe²⁺ do not depend on pressure
360 medium and are thus unlikely to be due to non-hydrostatic stress. The increase in correlated
361 broadening of the Fe²⁺ doublet with compression (Figure 7) suggests a broadening of the range of
362 coordination environments. The population of Fe²⁺ with highest QS and IS, in higher
363 coordination, would thus increase with pressure without completely replacing Fe²⁺ with lowest
364 QS and IS, in 4- to 6-fold coordination.

365 **5. Implications**

366 A sharp spin transition in iron in silicate glasses would suggest a discontinuity in the
367 properties of melt in the lower mantle or deep in a magma ocean; conversely, no sharp spin
368 transition in the glass supports a smooth variation of the properties of silicate melts with depth.
369 This study represents the first high-pressure examination of almandine glass and the first
370 combination of energy- and time-domain synchrotron Mössbauer spectra and X-ray emission
371 spectra techniques at high pressure for any silicate glass. All methods consistently support a
372 broad spin transition in Fe³⁺ between 1 bar and ~30 GPa without an abrupt discontinuity. Our

373 observations differ from the previous observation of a sharp transition in Fe-bearing glass and
374 accompanying changes in solid-melt iron partitioning. We would expect that in a melt of
375 almandine composition, effects of temperature may further broaden the spin transition to a
376 greater range than the ~30-GPa interval observed in the glass. Our study supports the expectation
377 that spin transitions in iron-bearing silicate melts in Earth's mantle should be broad with respect
378 to transitions in their crystalline counterparts. No discontinuities are expected to occur under
379 compression in the density or transport properties of Fe-rich mantle melts.

380 In addition, the bonding of Fe²⁺ shifts to a broader range of coordination numbers over 1
381 bar to ~60 GPa. These changes are accompanied by a change in color from transparent to black,
382 suggesting a pressure-induced reduction in radiative thermal conductivity in Fe-rich silicate
383 liquids. This increasing diversity of bonding styles may have important implications for transport
384 properties of the glass or melt network in the Earth's deep mantle or early magma ocean.

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406 **References**

- 407 Akahama, Y., and Kawamura, H. (2006) Pressure calibration of diamond anvil Raman gauge to
408 310 GPa. *Journal of Applied Physics*, 100, 043516–4.
- 409 Alberto, H.V., Pinto da Cunha, J.L., Mysen, B.O., Gil, J.M., and Ayres de Campos, N. (1996)
410 Analysis of Mössbauer spectra of silicate glasses using a two-dimensional Gaussian
411 distribution of hyperfine parameters. *Journal of Non-Crystalline Solids*, 194, 48–57.
- 412 Andrault, D., Petitgirard, S., Nigro, G.L., Devidal, J.-L., Veronesi, G., Garbarino, G., and
413 Mezouar, M. (2012) Solid-liquid iron partitioning in Earth's deep mantle. *Nature*, 487,
414 354–357.
- 415 Badro, J., Fiquet, G., Guyot, F., Rueff, J.-P., Struzhkin, V.V., Vankó, G., and Monaco, G. (2003)
416 Iron Partitioning in Earth's Mantle: Toward a Deep Lower Mantle Discontinuity. *Science*,
417 300, 789–791.

- 418 Badro, J., Rueff, J.-P., Vanko, G., Monaco, G., Fiquet, G., and Guyot, F. (2004) Electronic
419 Transitions in Perovskite: Possible Nonconvecting Layers in the Lower Mantle. *Science*,
420 305, 383–386.
- 421 Burkhard, D.J.M. (2000) Iron-bearing silicate glasses at ambient conditions. *Journal of Non-
422 Crystalline Solids*, 275, 175–188.
- 423 Catalli, K., Shim, S.-H., Prakapenka, V.B., Zhao, J., Sturhahn, W., Chow, P., Xiao, Y., Liu, H.,
424 Cynn, H., and Evans, W.J. (2010) Spin state of ferric iron in MgSiO₃ perovskite and its
425 effect on elastic properties. *Earth and Planetary Science Letters*, 289, 68–75.
- 426 Catalli, K., Shim, S.-H., Dera, P., Prakapenka, V.B., Zhao, J., Sturhahn, W., Chow, P., Xiao, Y.,
427 Cynn, H., and Evans, W.J. (2011) Effects of the Fe³⁺ spin transition on the properties of
428 aluminous perovskite—New insights for lower-mantle seismic heterogeneities. *Earth and
429 Planetary Science Letters*, 310, 293–302.
- 430 Cottrell, E., and Kelley, K.A. (2011) The oxidation state of Fe in MORB glasses and the oxygen
431 fugacity of the upper mantle. *Earth and Planetary Science Letters*, 305, 270–282.
- 432 De Groot, F. (2001) High-resolution X-ray emission and X-ray absorption spectroscopy.
433 *Chemical Reviews*, 101, 1779–1808.
- 434 Dorfman, S.M., Shieh, S.R., Meng, Y., Prakapenka, V.B., and Duffy, T.S. (2012) Synthesis and
435 equation of state of perovskites in the (Mg, Fe)₃Al₂Si₃O₁₂ system to 177 GPa. *Earth and
436 Planetary Science Letters*, 357–358, 194–202.
- 437 Dunlap, R.A., and McGraw, J.D. (2007) A Mössbauer effect study of Fe environments in impact
438 glasses. *Journal of Non-Crystalline Solids*, 353, 2201–2205.
- 439 Dyar, M.D. (1985) A review of Moessbauer data on inorganic glasses; the effects of composition
440 on iron valency and coordination. *American Mineralogist*, 70, 304–316.
- 441 Dyar, M.D., Agresti, D.G., Schaefer, M.W., Grant, C.A., and Sklute, E.C. (2006) Mössbauer
442 spectroscopy of Earth and planetary materials. *Annual Review of Earth and Planetary
443 Sciences*, 34, 83–125.
- 444 Fei, Y., Zhang, L., Corgne, A., Watson, H., Ricolleau, A., Meng, Y., and Prakapenka, V. (2007)
445 Spin transition and equations of state of (Mg, Fe)O solid solutions. *Geophysical Research
446 Letters*, 34, L17307.
- 447 Friedrich, A., Winkler, B., Morgenroth, W., Ruiz-Fuertes, J., Koch-Müller, M., Rhede, D., and
448 Milman, V. (2014) Pressure-induced spin collapse of octahedrally coordinated Fe³⁺ in
449 Ca₃Fe₂[SiO₄]₃ from experiment and theory. *Physical Review B*, 90, 094105.

- 450 Funamori, N., Yamamoto, S., Yagi, T., and Kikegawa, T. (2004) Exploratory studies of silicate
451 melt structure at high pressures and temperatures by in situ X-ray diffraction. *Journal of*
452 *Geophysical Research: Solid Earth*, 109, B03203.
- 453 Geiger, C., Newton, R., and Kleppa, O. (1987) Enthalpy of mixing of synthetic almandine-
454 grossular and almandine-pyrope garnets from high-temperature solution calorimetry.
455 *Geochimica et Cosmochimica Acta*, 51, 1755–1763.
- 456 Greenwood, N.N., and Gibb, T.C. (1971) Low-spin Iron(II) and Iron(III) Complexes. In
457 *Mössbauer Spectroscopy* pp. 169–193. Springer Netherlands.
- 458 Gu, C., Catalli, K., Grocholski, B., Gao, L., Alp, E., Chow, P., Xiao, Y., Cynn, H., Evans, W.J.,
459 and Shim, S.-H. (2012) Electronic structure of iron in magnesium silicate glasses at high
460 pressure. *Geophysical Research Letters*, 39.
- 461 Hsu, H., Umemoto, K., Blaha, P., and Wentzcovitch, R.M. (2010) Spin states and hyperfine
462 interactions of iron in (Mg,Fe)SiO₃ perovskite under pressure. *Earth and Planetary*
463 *Science Letters*, 294, 19–26.
- 464 Hsu, H., Blaha, P., Cococcioni, M., and Wentzcovitch, R.M. (2011) Spin-State Crossover and
465 Hyperfine Interactions of Ferric Iron in MgSiO₃ Perovskite. *Physical Review Letters*, 106,
466 118501.
- 467 Jackson, J.M., Sturhahn, W., Shen, G., Zhao, J., Hu, M.Y., Errandonea, D., Bass, J.D., and Fei,
468 Y. (2005) A synchrotron Mössbauer spectroscopy study of (Mg,Fe)SiO₃ perovskite up to
469 120 GPa. *American Mineralogist*, 90, 199–205.
- 470 Jayasuriya, K.D., O'Neill, H.S.C., Berry, A.J., and Campbell, S.J. (2004) A Mössbauer study of
471 the oxidation state of Fe in silicate melts. *American Mineralogist*, 89, 1597–1609.
- 472 Kantor, I., Dubrovinsky, L., McCammon, C., Steinle-Neumann, G., Kantor, A., Skorodumova,
473 N., Pascarelli, S., and Aquilanti, G. (2009) Short-range order and Fe clustering in
474 Mg_{1-x}Fe_xO under high pressure. *Physical Review B*, 80, 014204.
- 475 Kantor, I.Y., Dubrovinsky, L.S., and McCammon, C.A. (2006) Spin crossover in (Mg,Fe)O: A
476 Mössbauer effect study with an alternative interpretation of x-ray emission spectroscopy
477 data. *Physical Review B*, 73, 100101.
- 478 Kesson, S.E., Fitzgerald, J.D., Shelley, J.M.G., and Withers, R.L. (1995) Phase relations,
479 structure and crystal chemistry of some aluminous silicate perovskites. *Earth and*
480 *Planetary Science Letters*, 134, 187–201.
- 481 Labrosse, S., Hernlund, J.W., and Coltice, N. (2007) A crystallizing dense magma ocean at the
482 base of the Earth's mantle. *Nature*, 450, 866–869.

- 483 Lagarec, K., and Rancourt, D.G. (1997) Extended Voigt-based analytic lineshape method for
484 determining N-dimensional correlated hyperfine parameter distributions in Mössbauer
485 spectroscopy. *Nuclear Instruments and Methods in Physics Research Section B: Beam*
486 *Interactions with Materials and Atoms*, 129, 266–280.
- 487 Lee, C.-t. A., Luffi, P., Hoink, T., Li, J., Dasgupta, R., and Hernlund, J. (2010) Upside-down
488 differentiation and generation of a “primordial” lower mantle. *Nature*, 463, 930–933.
- 489 Lin, J.-F., and Tsuchiya, T. (2008) Spin transition of iron in the Earth’s lower mantle. *Physics of*
490 *the Earth and Planetary Interiors*, 170, 248–259.
- 491 Lin, J.-F., Vankó, G., Jacobsen, S.D., Iota, V., Struzhkin, V.V., Prakapenka, V.B., Kuznetsov, A.,
492 and Yoo, C.-S. (2007) Spin Transition Zone in Earth’s Lower Mantle. *Science*, 317, 1740
493 –1743.
- 494 Lin, J.-F., Wenk, H.-R., Voltolini, M., Speziale, S., Shu, J., and Duffy, T.S. (2009) Deformation
495 of lower-mantle ferropericlase (Mg,Fe)O across the electronic spin transition. *Physics and*
496 *Chemistry of Minerals*, 36, 585–592.
- 497 Lin, J.-F., Mao, Z., Jarrige, I., Xiao, Y., Chow, P., Okuchi, T., Hiraoka, N., and Jacobsen, S.D.
498 (2010) Resonant X-ray emission study of the lower-mantle ferropericlase at high
499 pressures. *American Mineralogist*, 95, 1125–1131.
- 500 Lin, J.-F., Alp, E.E., Mao, Z., Inoue, T., McCammon, C., Xiao, Y., Chow, P., and Zhao, J. (2012)
501 Electronic spin states of ferric and ferrous iron in the lower-mantle silicate perovskite.
502 *American Mineralogist*, 97, 592–597.
- 503 Mao, H.K., Virgo, D., and Bell, P.M. (1973) Analytical Study of the Orange Lunar Soil Returned
504 by the Apollo 17 Astronauts. In *Year Book Carnegie Institution of Washington* pp. 631–
505 638. Carnegie Institution of Washington, Washington, D.C.
- 506 Mao, H.-k., Xu, J., and Bell, P.M. (1986) Calibration of the Ruby Pressure Gauge to 800 kbar
507 Under Quasi-Hydrostatic Conditions. *Journal of Geophysical Research*, 91, 4673–4676.
- 508 Mao, Z., Lin, J.F., Scott, H.P., Watson, H.C., Prakapenka, V.B., Xiao, Y., Chow, P., and
509 McCammon, C. (2011) Iron-rich perovskite in the Earth’s lower mantle. *Earth and*
510 *Planetary Science Letters*, 309, 179–184.
- 511 Mao, Z., Lin, J.-F., Huang, S., Chen, J., Xiao, Y., and Chow, P. (2013) Synchrotron Mössbauer
512 study of Fe-bearing pyrope at high pressures and temperatures. *American Mineralogist*,
513 98, 1146–1152.
- 514 Mao, Z., Lin, J.-F., Yang, J., Wu, J., Watson, H.C., Xiao, Y., Chow, P., and Zhao, J. (2014) Spin
515 and valence states of iron in Al-bearing silicate glass at high pressures studied by
516 synchrotron Mössbauer and X-ray emission spectroscopy. *American Mineralogist*, 99,
517 415–423.

- 518 Mattila, A., Rueff, J.-P., Badro, J., Vankó, G., and Shukla, A. (2007) Metal-ligand interplay in
519 strongly correlated oxides: A parametrized phase diagram for pressure-induced spin
520 transitions. *Physical Review Letters*, 98, 196404.
- 521 Meade, C., Hemley, R.J., and Mao, H.K. (1992) High-pressure x-ray diffraction of SiO₂ glass.
522 *Physical Review Letters*, 69, 1387–1390.
- 523 Mitsui, T., Hirao, N., Ohishi, Y., Masuda, R., Nakamura, Y., Enoki, H., Sakaki, K., and Seto, M.
524 (2009) Development of an energy-domain ⁵⁷Fe-Mössbauer spectrometer using
525 synchrotron radiation and its application to ultrahigh-pressure studies with a diamond
526 anvil cell. *Journal of Synchrotron Radiation*, 16, 723–729.
- 527 Muñoz Ramo, D., and Stixrude, L. (2014) Spin crossover in Fe₂SiO₄ liquid at high pressure.
528 *Geophysical Research Letters*, 41.
- 529 Murakami, M., Goncharov, A.F., Hirao, N., Masuda, R., Mitsui, T., Thomas, S.-M., and Bina,
530 C.R. (2014) High-pressure radiative conductivity of dense silicate glasses with potential
531 implications for dark magmas. *Nature Communications*, 5.
- 532 Mysen, B.O. (2006) The structural behavior of ferric and ferrous iron in aluminosilicate glass
533 near meta-aluminosilicate joins. *Geochimica et Cosmochimica Acta*, 70, 2337–2353.
- 534 Nomura, R., Ozawa, H., Tateno, S., Hirose, K., Hernlund, J., Muto, S., Ishii, H., and Hiraoka, N.
535 (2011) Spin crossover and iron-rich silicate melt in the Earth's deep mantle. *Nature*, 473,
536 199–202.
- 537 O'Neill, B., and Jeanloz, R. (1994) MgSiO₃-FeSiO₃-Al₂O₃ in the Earth's lower mantle:
538 Perovskite and garnet at 1200 km depth. *Journal of Geophysical Research*, 99, 19,901–
539 19,915.
- 540 Pasternak, M.P., Xu, W.M., Rozenberg, G.K., and Taylor, R.D. (2002) Electronic, Magnetic and
541 Structural Properties of the RFeO₃ Antiferromagnetic-Perovskites at Very High Pressures.
542 In *Symposium D – Perovskite Materials Vol. 718*.
- 543 Peng, G., Wang, X., Randall, C.R., Moore, J.A., and Cramer, S.P. (1994) Spin selective x-ray
544 absorption spectroscopy: Demonstration using high resolution Fe K β fluorescence.
545 *Applied Physics Letters*, 65, 2527–2529.
- 546 Potapkin, V., Chumakov, A.I., Smirnov, G.V., Celse, J.-P., Ruffer, R., McCammon, C., and
547 Dubrovinsky, L. (2012) The ⁵⁷Fe Synchrotron Mössbauer Source at the ESRF. *Journal of*
548 *Synchrotron Radiation*, 19, 559–569.
- 549 Prescher, C., McCammon, C., and Dubrovinsky, L. (2012) MossA: a program for analyzing
550 energy-domain Mössbauer spectra from conventional and synchrotron sources. *Journal of*
551 *Applied Crystallography*, 45, 329–331.

- 552 Prescher, C., Weigel, C., McCammon, C., Narygina, O., Potapkin, V., Kuppenko, I., Sinmyo, R.,
553 Chumakov, A.I., and Dubrovinsky, L. (2014) Iron spin state in silicate glass at high
554 pressure: Implications for melts in the Earth's lower mantle. *Earth and Planetary Science*
555 *Letters*, 385, 130–136.
- 556 Rivers, M., Prakapenka, V., Kubo, A., Pullins, C., Holl, C.M., and Jacobsen, S.D. (2008) The
557 COMPRES/GSECARS gas-loading system for diamond anvil cells at the Advanced
558 Photon Source. *High Pressure Research*, 28, 273–292.
- 559 Rossano, S., Behrens, H., and Wilke, M. (2007) Advanced analyses of ^{57}Fe Mössbauer data of
560 alumino-silicate glasses. *Physics and Chemistry of Minerals*, 35, 77–93.
- 561 Rozenberg, G.K., Pasternak, M.P., Xu, W.M., Dubrovinsky, L.S., Carlson, S., and Taylor, R.D.
562 (2005) Consequences of pressure-instigated spin crossover in RFeO_3 perovskites; a
563 volume collapse with no symmetry modification. *EPL (Europhysics Letters)*, 71, 228.
- 564 Rueff, J.-P., Kao, C.-C., Struzhkin, V.V., Badro, J., Shu, J., Hemley, R.J., and Mao, H.K. (1999)
565 Pressure-Induced High-Spin to Low-Spin Transition in FeS Evidenced by X-Ray
566 Emission Spectroscopy. *Physical Review Letters*, 82, 3284.
- 567 Rueff, J.-P., Ablett, J.M., Céolin, D., Prieur, D., Moreno, T., Balédent, V., Lassalle-Kaiser, B.,
568 Rault, J.E., Simon, M., and Shukla, A. (2015) The GALAXIES beamline at the SOLEIL
569 synchrotron: inelastic X-ray scattering and photoelectron spectroscopy in the hard X-ray
570 range. *Journal of Synchrotron Radiation*, 22.
- 571 Ruffer, R., and Chumakov, A.I. (1996) Nuclear Resonance Beamline at ESRF. *Hyperfine*
572 *Interactions*, 97-98, 589–604.
- 573 Smirnov, G.V., van Bürck, U., Chumakov, A.I., Baron, A.Q.R., and Ruffer, R. (1997)
574 Synchrotron Mössbauer source. *Physical Review B*, 55, 5811–5815.
- 575 Speziale, S., Milner, A., Lee, V.E., Clark, S.M., Pasternak, M.P., and Jeanloz, R. (2005) Iron spin
576 transition in Earth's mantle. *Proceedings of the National Academy of Sciences of the*
577 *United States of America*, 102, 17918–17922.
- 578 Stixrude, L., and Karki, B. (2005) Structure and Freezing of MgSiO_3 Liquid in Earth's Lower
579 Mantle. *Science*, 310, 297–299.
- 580 Stixrude, L., de Koker, N., Sun, N., Mookherjee, M., and Karki, B.B. (2009) Thermodynamics of
581 silicate liquids in the deep Earth. *Earth and Planetary Science Letters*, 278, 226–232.
- 582 Sturhahn, W. (2000) CONUSS and PHOENIX: Evaluation of nuclear resonant scattering data.
583 *Hyperfine Interactions*, 125, 149–172.
- 584 Sturhahn, W., Jackson, J.M., and Lin, J.-F. (2005) The spin state of iron in minerals of Earth's
585 lower mantle. *Geophysical Research Letters*, 32, L12307.

- 586 Thomas, C.W., Liu, Q., Agee, C.B., Asimow, P.D., and Lange, R.A. (2012) Multi-technique
587 equation of state for Fe₂SiO₄ melt and the density of Fe-bearing silicate melts from 0 to
588 161 GPa. *Journal of Geophysical Research: Solid Earth*, 117, B10206.
- 589 Tsuchiya, T., Wentzcovitch, R.M., da Silva, C.R., and de Gironcoli, S. (2006) Spin transition in
590 magnesiowüstite in Earth's lower mantle. *Physical Review Letters*, 96, 198501.
- 591 Vankó, G., Neisius, T., Molnár, G., Renz, F., Karpáti, S., Shukla, A., and de Groot, F.M.F.
592 (2006) Probing the 3d spin momentum with X-ray emission spectroscopy: The case of
593 molecular-spin transitions. *The Journal of Physical Chemistry B*, 110, 11647–11653.
- 594 Virgo, D., and Mysen, B.O. (1985) The structural state of iron in oxidized vs. reduced glasses at
595 1 atm: A ⁵⁷Fe Mössbauer study. *Physics and Chemistry of Minerals*, 12, 65–76.
- 596 Williams, Q., and Garnero, E.J. (1996) Seismic Evidence for Partial Melt at the Base of Earth's
597 Mantle. *Science*, 273, 1528–1530.
- 598 Woodland, A.B., and Ross, C.R. (1994) A crystallographic and Mössbauer spectroscopy study of
599 Fe₃²⁺Al₂Si₃O₁₂-Fe₃²⁺Fe₂³⁺Si₃O₁₂, (almandine-"skiaigite") and Ca₃Fe₂³⁺Si₃O₁₂-
600 Fe₃²⁺Fe₂³⁺Si₃O₁₂ (andradite-"skiaigite") garnet solid solutions. *Physics and Chemistry of*
601 *Minerals*, 21, 117–132.
- 602 Xu, W.M., Naaman, O., Rozenberg, G.K., Pasternak, M.P., and Taylor, R.D. (2001) Pressure-
603 induced breakdown of a correlated system: The progressive collapse of the Mott-
604 Hubbard state in RFeO₃. *Physical Review B*, 64, 094411.

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607 **List of figure captions**

608 Table 1: Mössbauer parameters observed by energy-domain Mössbauer spectroscopy for glass
609 compressed in Ne or NaCl medium. QS=quadrupole splitting, IS=isomer shift, ρ =correlation
610 parameter, FWHM=line full width at half maximum.

611 **Table 2:** Mössbauer parameters observed by time-domain Mössbauer spectroscopy for glass
612 compressed in Ne medium. QS=quadrupole splitting, Δ IS=difference in isomer shift between
613 Fe^{2+} and Fe^{3+} doublets, FWHM=full width at half maximum. Δ IS is given due to limited absolute
614 reference constraint on IS. Starred parameters were fixed in fits. Fitting uncertainties for QS and
615 IS are ~ 0.01 mm/s.

616 Figure 1: a) Conventional (energy-domain) and b) synchrotron Mössbauer (time-domain) spectra
617 of almandine glass at 1 bar and 2-site fit (solid line). Residual for energy-domain fit is shown by
618 gray dots in the upper part of the figure. Fe^{2+} and Fe^{3+} doublets are shown in dark and light gray,
619 respectively.

620 Figure 2: Photomicrograph of opaque, black glass sample at 34 GPa in Ne medium with ruby
621 ball.

622 Figure 3: XES spectra for almandine glass normalized to area and shifted to position of the main
623 peak (Mao et al. 2014). Difference spectra below are relative to the low-spin (Mg,Fe)O reference
624 (Lin et al. 2010). Inset: total spin moment calculated from XES spectra (black) and from weight
625 of low-spin Fe^{3+} component in E-SMS spectra (red). TSM for XES was determined from the

626 integrated relative difference (IRD) between spectra and high- and low-spin (Mg,Fe)O references
627 (Lin et al. 2010).

628 Figure 4: Energy-domain synchrotron Mössbauer spectra for almandine glass in a neon pressure
629 medium. Data are displayed as open circles. Curves are high-spin Fe^{2+} doublet fit (blue), high-
630 spin Fe^{3+} doublet fit (pink), low-spin Fe^{3+} doublet fit (red), baseline (gray) and total fit (black).

631 Figure 5: Observed Mössbauer parameters from almandine glass. Fe^{2+} component is represented
632 by two doublets in time-domain measurements (open symbols) and a single doublet with
633 correlated quadrupole splitting and isomer shift in energy-domain measurements (filled symbols).
634 Separate high- and low-spin Fe^{3+} components are modeled in energy-domain measurements. a)
635 Quadrupole splitting of each doublet. Triangles joined by lines represent the two Fe^{2+} sites used
636 to model the range of Fe^{2+} environments in time-domain fits. b) Weight of each doublet. Two
637 Fe^{2+} doublets of equal weight are used for time-domain fits.

638 Figure 6: Quadrupole splitting vs. isomer shift for silicate and inorganic glasses derived from
639 energy-domain Mössbauer spectroscopy. Literature values for glasses at ambient conditions are
640 shown in small open black squares (Dyar 1985; Virgo and Mysen 1985; Burkhard 2000). Colors
641 indicate Fe species identified at high pressure: dark blue=high-spin Fe^{2+} , light blue = intermediate
642 spin Fe^{2+} , pink=high-spin Fe^{3+} , red= low-spin Fe^{3+} . Glasses at high pressures are shown with
643 filled symbols (triangles=Prescher et al. (2014), diamonds=Murakami et al. (2014), circles= this
644 study). Arrows indicate change observed with increasing pressure.

645 Figure 7: Correlation parameter of distribution of QS and IS in fits of Fe^{2+} doublet. Solid
646 symbols: compression in Ne medium. Open symbols: compression in NaCl medium.

647

648 Table 1

High spin Fe ²⁺								
Pressure (GPa)	Weight (%)	QS (mm/s)	IS (mm/s)	ρ				
Ambient								
0.0001	82(3)	2.08(3)	0.982(14)	0.273				
Ne medium								
0.2	81(12)	1.99(2)	1.089(10)	0.525				
5	87(4)	2.07(2)	1.086(12)	0.423				
15	87(4)	2.247(19)	1.035(13)	0.557				
41	88(4)	2.24(2)	0.959(10)	0.765				
54	89(5)	2.18(4)	0.890(14)	0.826				
NaCl medium								
7	87.6(1.9)	2.05(2)	1.066(9)	0.339				
18	84(3)	2.319(14)	1.036(12)	0.491				
30	85(5)	2.30(3)	0.99(2)	0.682				
42	84(5)	2.26(3)	0.94(2)	0.785				
57	86(6)	2.20(4)	0.86(3)	0.773				
70	84(6)	2.13(4)	0.86(4)	0.967				
91	86(5)	2.05(3)	0.81(3)	0.859				
High spin Fe ³⁺					Low spin Fe ³⁺			
Pressure (GPa)	Weight (%)	QS (mm/s)	IS (mm/s)	FWHM (mm/s)	Weight (%)	QS (mm/s)	IS (mm/s)	FWHM (mm/s)
Ambient								
0.0001	18(3)	1.23(11)	0.39(5)	0.63(13)				
Ne medium								
0.2	19(8)	1.18(9)	0.43(5)	0.58(12)	--	--	--	--
5	13(6)	1.20(18)	0.46(10)	0.53(15)	--	--	--	--
15	9(3)	0.74(13)	0.57(5)	0.36(16)	4(4)	1.74(10)	0.48(5)	0.2(2)
41	--	--	--	--	12(4)	1.82(7)	0.36(3)	0.33(10)
54	--	--	--	--	11(4)	1.83(6)	0.35(3)	0.36(13)
NaCl medium								
7	12.4(1.9)	1.17(13)	0.41(7)	0.50(12)	--	--	--	--
18	9.1(1.7)	0.90(7)	0.64(3)	0.32(7)	7(3)	1.97(5)	0.53(3)	0.23(10)
30	5(3)	0.90(8)	0.61(4)	0.25(12)	9(5)	1.88(7)	0.42(3)	0.31(13)
42	4(3)	0.92(8)	0.62(3)	0.24(13)	12(5)	1.93(7)	0.41(3)	0.35(11)
57	4(3)	0.99(7)	0.62(3)	0.20(14)	10(5)	2.00(7)	0.38(3)	0.33(12)
70	--	--	--	--	16(6)	1.88(6)	0.34(3)	0.39(11)
91	--	--	--	--	14(5)	1.84(6)	0.30(3)	0.40(11)

649

650

651 Table 2

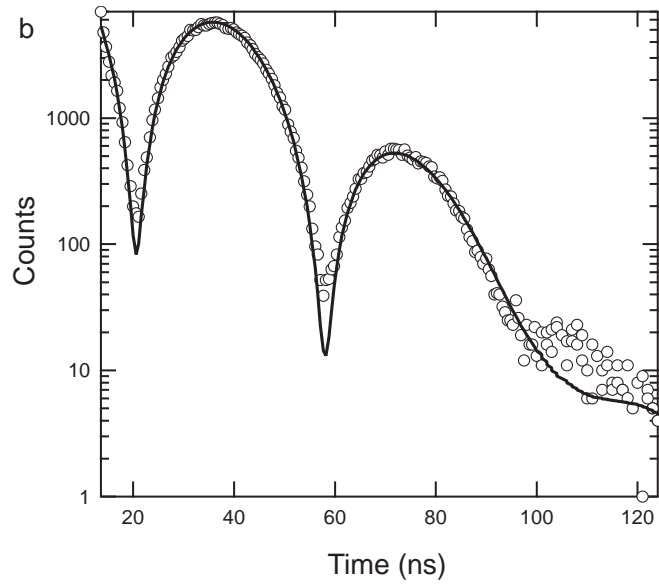
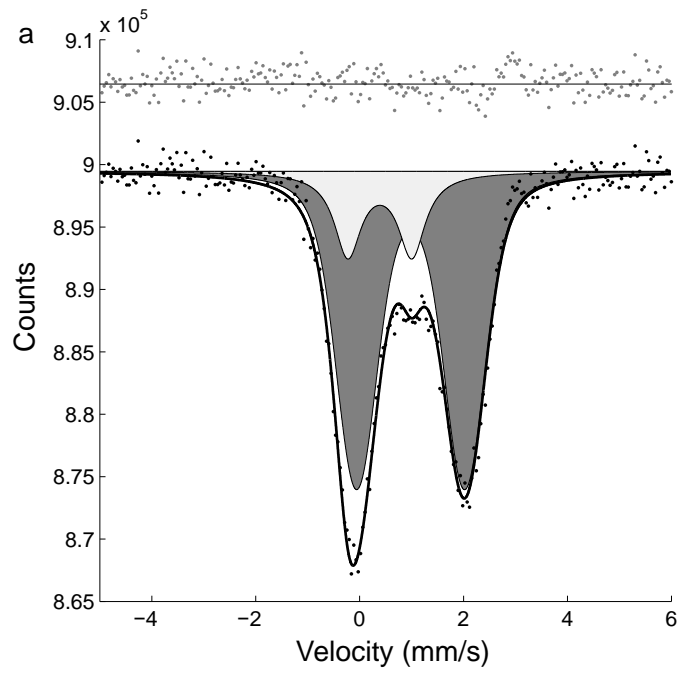
Fe ²⁺								
Pressure (GPa)	Weight (%)	QS (mm/s)	Δ IS (mm/s)	FWHM (mm/s)	Weight (%)	QS (mm/s)	Δ IS (mm/s)	FWHM (mm/s)
0.0001	83	2.10	0.56	0.63				
6	40*	1.90	0.55	0.68	40*	2.25	0.66	0.79
17	40*	2.07	0.55	0.70	40*	2.34	0.83	0.74
26	40*	1.99	0.57	0.69	40*	2.64	0.69	0.75
37	40*	2.02	0.54	0.71	40*	2.66	0.75	0.76
47	40*	1.95	0.54	0.72	40*	2.67	0.77	0.74
56	40*	2.02	0.51	0.71	40*	2.66	0.78	0.77
65	40*	2.01	0.50	0.69*	40*	2.66	0.79	0.78*
76	40*	1.91	0.51	0.69	40*	2.66	0.77	0.78
85	40*	1.88	0.54	0.69*	40*	2.66	0.80	0.78*
Fe ³⁺								
Pressure (GPa)	Weight (%)	QS (mm/s)	FWHM (mm/s)					
0.0001	17	1.17	0.77					
6	20*	1.14	0.64					
17	20*	1.58	0.63					
26	20*	1.72	0.59					
37	20*	1.81	0.54					
47	20*	1.81	0.53					
56	20*	1.84	0.51					
65	20*	1.83	0.48*					
76	20*	1.77	0.48					
85	20*	1.77	0.48*					

652

653

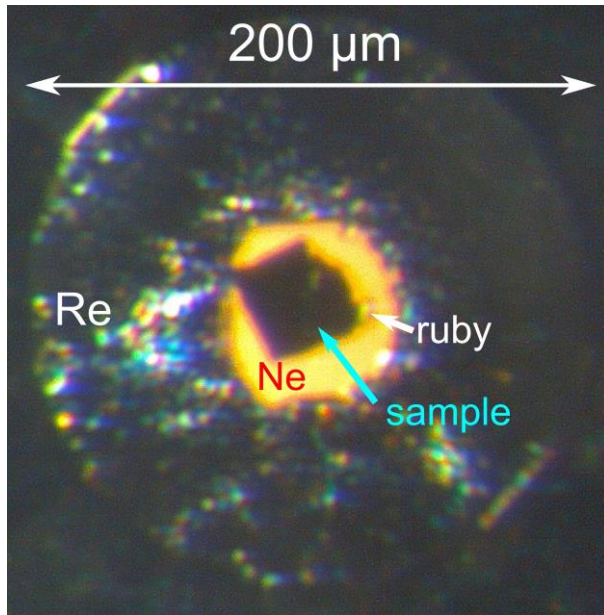
654

655 **Figures**



656

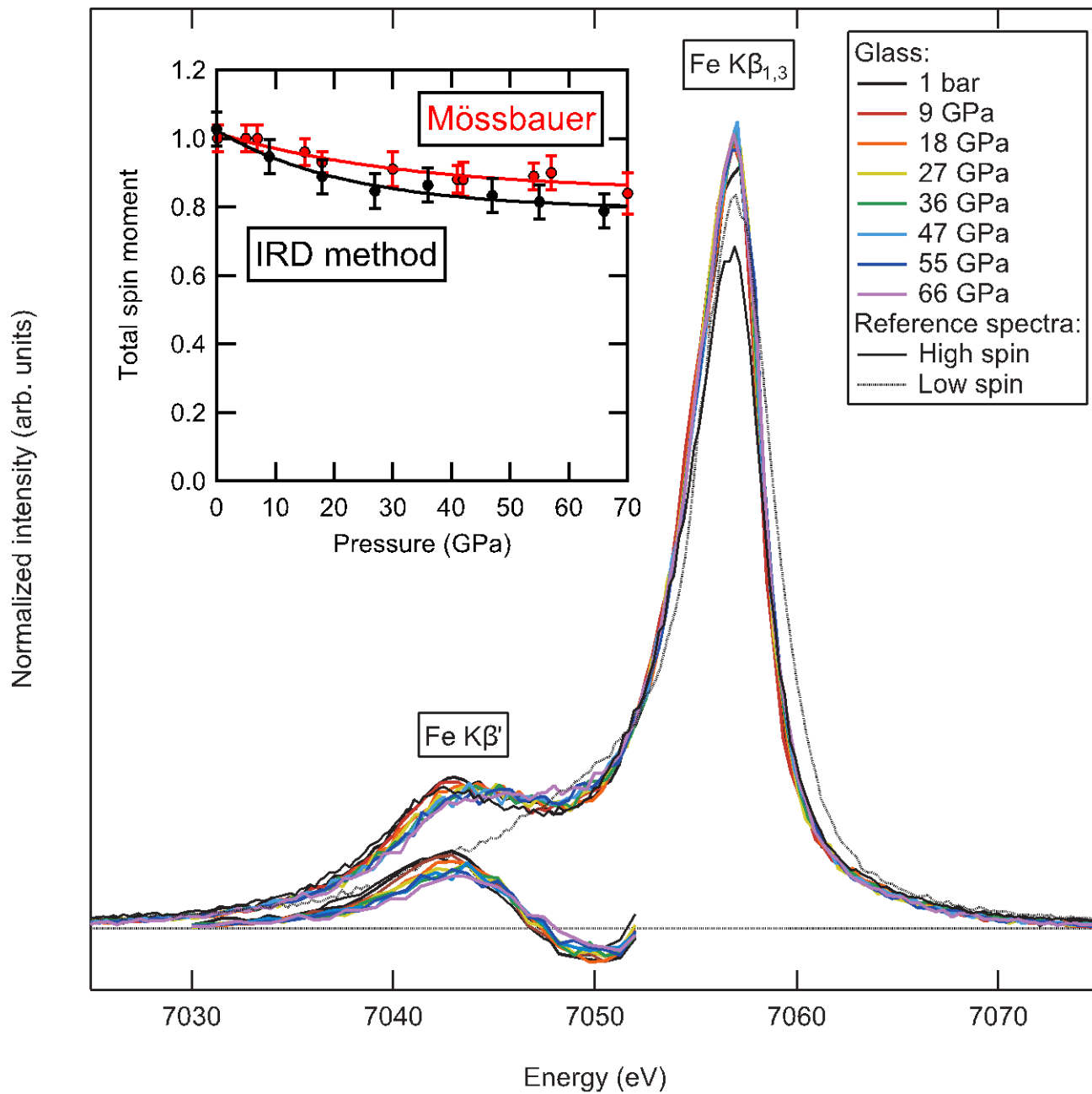
657 **Figure 1**



658

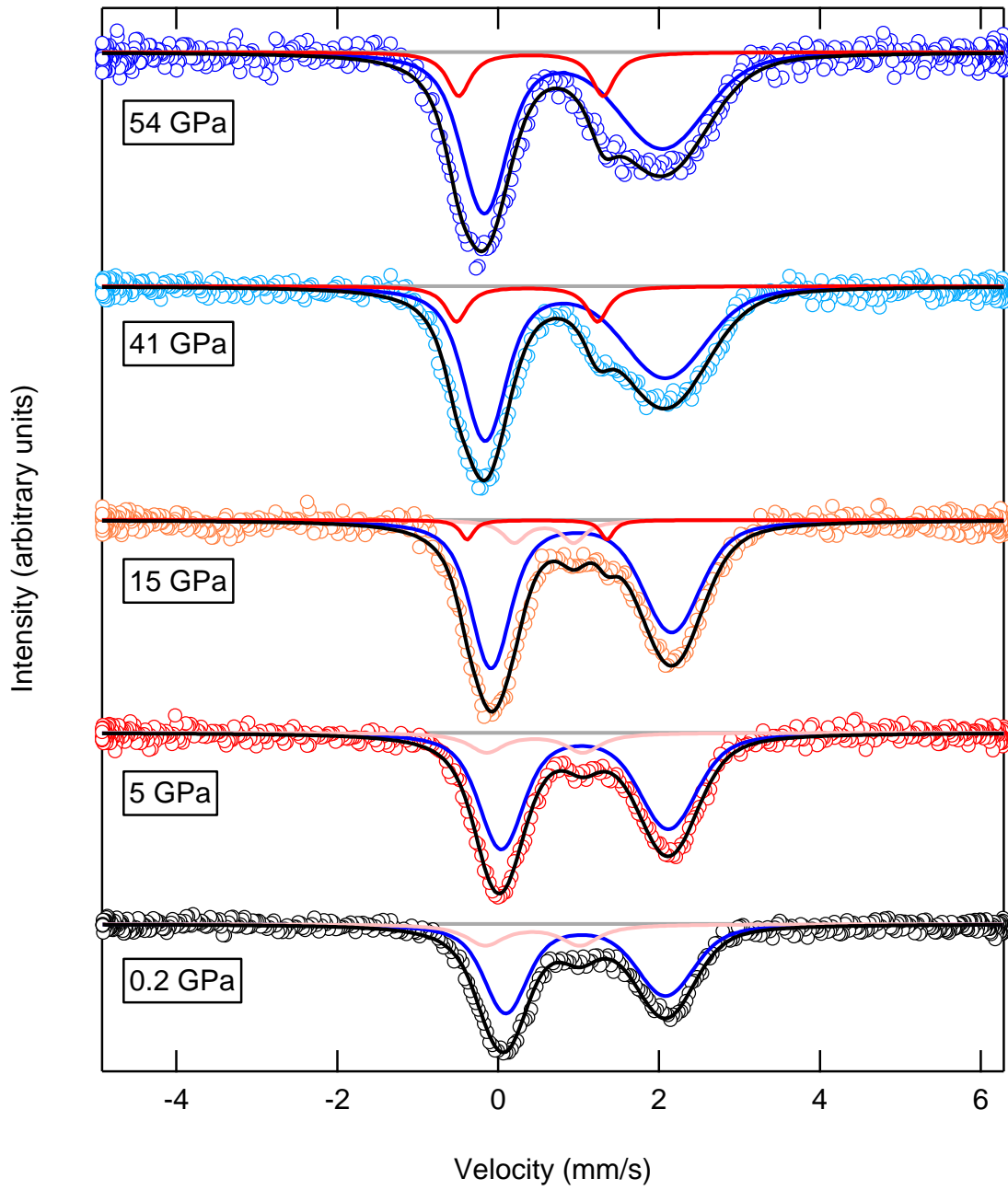
659 **Figure 2**

660



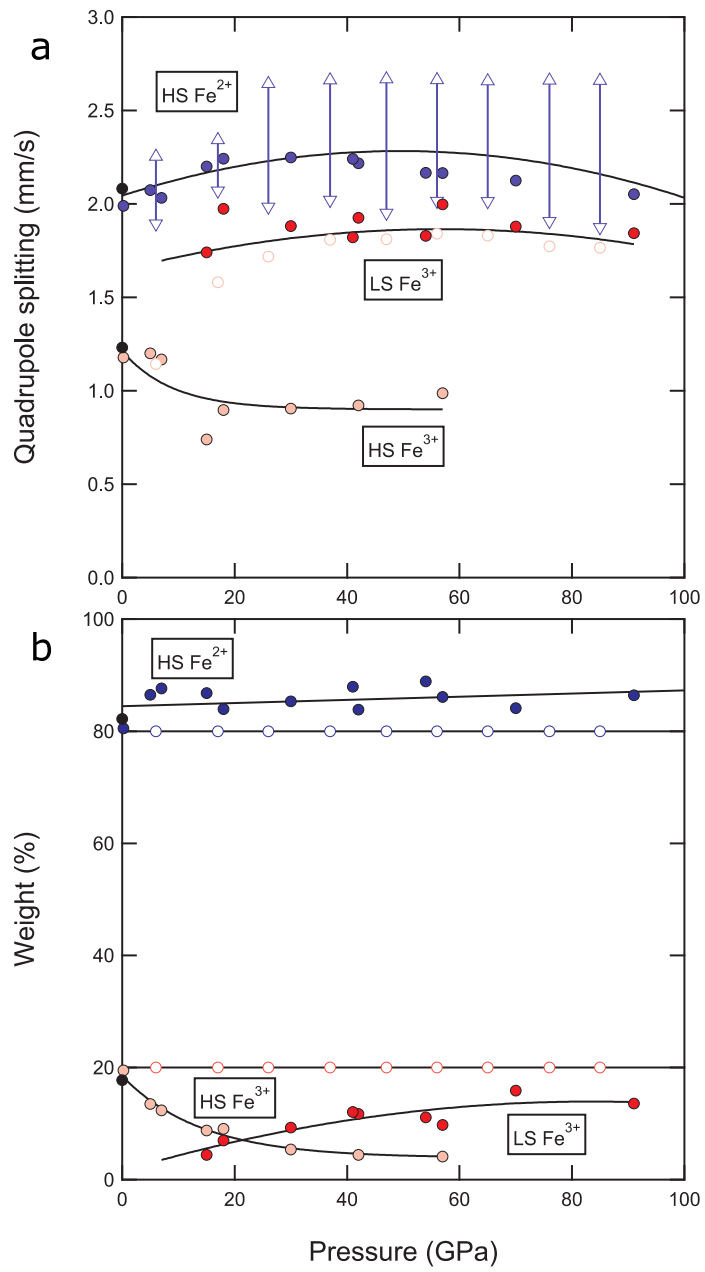
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662 **Figure 3**



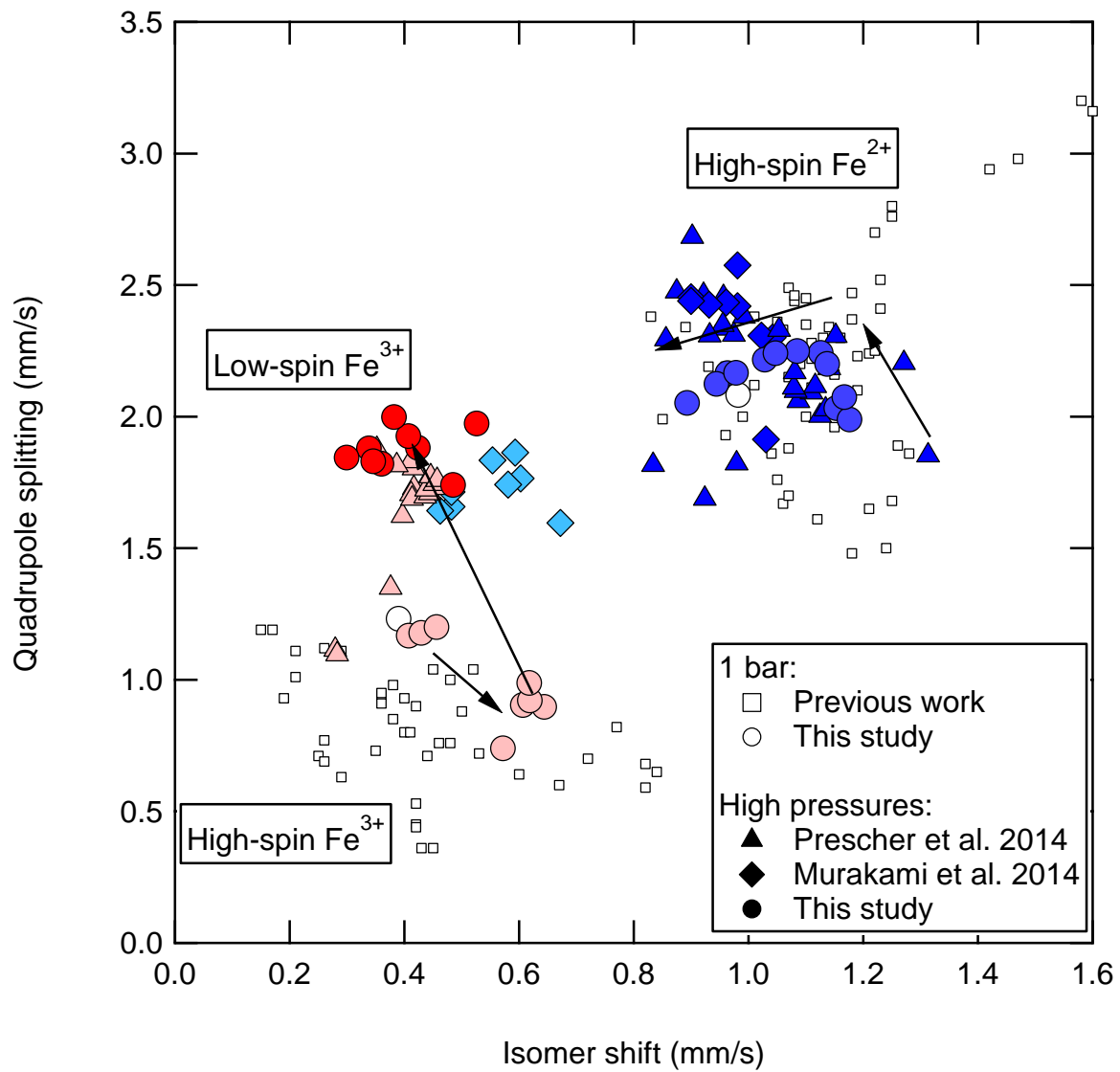
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664 **Figure 4**



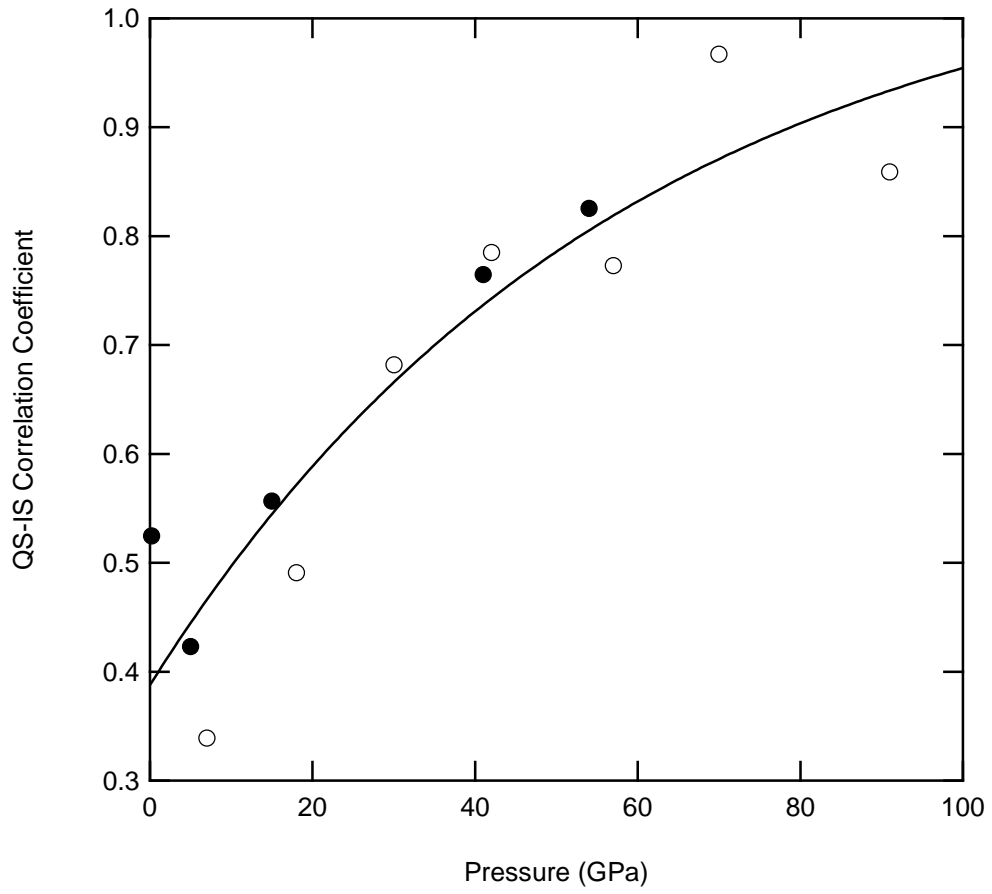
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666 **Figure 5**



667

668 **Figure 6**



669

670 **Figure 7**