

Revision 1

1 Effects of composition and pressure on 2 electronic states of iron in bridgmanite

3 Susannah M. Dorfman^{1,2}, Vasily Potapkin³, Mingda Lv¹, Eran Greenberg^{4,*}, Ilya Kupenko^{3,5},
4 Aleksandr I. Chumakov⁵, Wenli Bi^{6,7}, E. Ercan Alp⁶, Jiachao Liu¹, Arnaud Magrez⁸, Siân E.
5 Dutton^{9,†}, Robert J. Cava⁹, Catherine A. McCammon¹⁰, Philippe Gillet²

6 1: Department of Earth and Environmental Sciences, Michigan State University, East Lansing,
7 MI, USA.

8 2: Earth and Planetary Science Laboratory, Institute of Physics, École Polytechnique Fédérale de
9 Lausanne, CH-1015 Lausanne, Switzerland.

10 3: Institute of Mineralogy, University of Münster, Münster, Germany.

11 4: School of Physics & Astronomy, Tel-Aviv University, Tel-Aviv, Israel.

12 5: ESRF-The European Synchrotron, 71, Avenue des Martyrs, Grenoble, France.

13 6: Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA.

14 7: Department of Geology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801,
15 USA; Department of Physics, University of Alabama at Birmingham, Birmingham, Alabama
16 35294, USA.

17 8: Crystal Growth Facility, Institute of Physics, École Polytechnique Fédérale de Lausanne, CH-
18 1015 Lausanne, Switzerland.

1

Revision 1

19 9: Department of Chemistry, Princeton University, Princeton, NJ, USA.

20 10: Bayerisches Geoinstitut, University of Bayreuth, Bayreuth, Germany.

21 *now at Applied Physics Department, Soreq Nuclear Research Center (NRC), Yavne 81800,
22 Israel.

23 †now at Cavendish Laboratory, University of Cambridge, Cambridge, CB3 0HE, UK.

24 Abstract

25 Electronic states of iron in the lower mantle's dominant mineral, $(\text{Mg,Fe,Al})(\text{Fe,Al,Si})\text{O}_3$
26 bridgmanite, control physical properties of the mantle including density, elasticity, and electrical
27 and thermal conductivity. However, determination of electronic states of iron has been
28 controversial, in part due to different interpretations of Mössbauer spectroscopy results used to
29 identify spin state, valence state, and site occupancy of iron. We applied energy-domain
30 Mössbauer spectroscopy to a set of four bridgmanite samples spanning a wide range of
31 compositions: 10-50% Fe/total cations, 0-25% Al/total cations, 12-100% Fe^{3+} /total Fe.
32 Measurements performed in the diamond anvil cell at pressures up to 76 GPa below and above
33 the high to low spin transition in Fe^{3+} provide a Mössbauer reference library for bridgmanite and
34 demonstrate the effects of pressure and composition on electronic states of iron. Results indicate
35 that although the spin transition in Fe^{3+} in the bridgmanite B-site occurs as predicted, it does not
36 strongly affect the observed quadrupole splitting of 1.4 mm/s, and only decreases center shift for
37 this site to 0 mm/s at ~ 70 GPa. Thus center shift can easily distinguish Fe^{3+} from Fe^{2+} at high
38 pressure, which exhibits two distinct Mössbauer sites with center shift ~ 1 mm/s and quadrupole
39 splitting 2.4-3.1 and 3.9 mm/s at ~ 70 GPa. Correct quantification of Fe^{3+} /total Fe in bridgmanite

Revision 1

40 is required to constrain effects of composition and redox states in experimental measurements of
41 seismic properties of bridgmanite. In Fe-rich, mixed-valence bridgmanite at deep-mantle-
42 relevant pressures, up to ~20% of the Fe may be a Fe^{2.5+} charge transfer component, which
43 should enhance electrical and thermal conductivity in Fe-rich heterogeneities at the base of
44 Earth's mantle.

45 Keywords: bridgmanite, Mössbauer spectroscopy, iron oxidation state, lower mantle

46 Introduction

47 Iron-bearing bridgmanite, the most abundant material in the Earth's interior, is the dominant
48 mineral responsible for chemical and physical behavior of the lower mantle. Redox of iron in
49 bridgmanite buffers the mantle and thus has implications for formation of the atmosphere and
50 habitability of the planet, storage and transport of volatiles including water and carbon in the
51 deep interior, and interpretation of structures and dynamic processes observed by seismic
52 tomography (e.g. Frost and McCammon 2008; Gu et al. 2016; Liu et al. 2018). Heterogeneous
53 structures at the base of the mantle including large low shear velocity provinces and ultra-low
54 velocity zones have been suggested to be iron-rich relative to surrounding mantle based on
55 inversion of normal mode data (Ishii and Tromp 1999), tidal tomography (Lau et al. 2017), and
56 travel times of seismic waves reflected off the core-mantle boundary (Rost et al. 2005);
57 identifying these features and their role in the differentiation and mixing of the mantle depends
58 on accurate constraints on the physical properties of iron-rich bridgmanite. Because bridgmanite
59 samples from the lower mantle have not been recovered, redox conditions are inferred based on

Revision 1

60 remote geophysical observations and experimental and theoretical modeling of chemistry at
61 extreme pressures and temperatures.

62 Depth and composition both affect redox states of iron incorporated in the mantle's dominant
63 phase, but efforts to measure these changes have been complicated by the crystal chemistry of
64 (Mg,Fe,Al)(Fe,Al,Si)O₃ bridgmanite (e.g. McCammon et al. 2013; Shim et al. 2017).

65 Bridgmanite adopts the orthorhombic GdFeO₃-type perovskite structure, with a larger 8-12-fold
66 pseudo-dodecahedral "A" site and smaller 6-fold octahedral "B" site. Both Fe²⁺ and Fe³⁺
67 substitute for Mg in the A-site, while only the smaller Fe³⁺ ion may substitute for Si in the B-site.
68 At pressure/temperature conditions corresponding to the top of the lower mantle, bridgmanite
69 typically exhibits Fe³⁺/total Fe ratio at least 50%, even under reducing conditions in contact with
70 metallic iron (Frost et al. 2004; Shim et al. 2017). The Fe³⁺/total Fe ratio in bridgmanite
71 synthesized at pressures corresponding to the deep lower mantle has been observed to decrease
72 with pressure to ~15%, then increase again to ~50% (Shim et al. 2017). Variations in valence
73 states of iron with depth are inferred to be due to energetics of substitution mechanisms as local
74 structure and spin state of iron change with depth. Distortion of the perovskite structure due to
75 pressure and/or composition divides the A-site into A1- and A2-sites (Hsu et al. 2010; Hummer
76 and Fei 2012) and occurs at similar conditions as the observed decrease in Fe³⁺/total Fe. A spin-
77 pairing transition in Fe³⁺ in the B-site at ~48 GPa, corresponding to the mid-lower-mantle, may
78 also drive partitioning of Fe³⁺ into the B-site (Badro et al. 2004; Catalli et al. 2010, 2011; Hsu et
79 al. 2011; Liu et al. 2018). The presence of Al may also modify incorporation of Fe³⁺ in
80 bridgmanite through paired substitution of trivalent cations for Mg and Si (e.g. Frost and
81 Langenhorst 2002; Piet et al. 2016) and formation of vacancies in cation (Sinmyo et al. 2014;

Revision 1

82 Kuppenko et al. 2015) or oxygen sites (Grüninger et al. 2019; Liu et al. 2019). Based on
83 experiments (e.g. Potapkin et al. 2013) and computational modeling using density functional
84 theory (DFT) (Caracas 2010), paired substitution places Al in the B-site and Fe³⁺ in the A-site at
85 equilibrium, though some observations support migration of Al and Fe³⁺ between the two sites
86 (Catalli et al. 2011) and/or migration of Fe³⁺ from A to B site due to vacancy redistribution
87 (Kuppenko et al. 2015). In bridgmanite compositions with mixed valence states, Fe²⁺–Fe³⁺
88 electronic charge transfer may also create Fe^{2.5+} states (Mattson and Rossman 1987, Burns
89 1993). Because the separation distance between A and B sites is smaller than between A and
90 adjacent A sites, the activation energy related to the distance of electron migration was suggested
91 to be lower for A-B Fe²⁺–Fe³⁺ charge transfer (Fei et al. 1994). For the same reason, charge
92 transfer is generally expected to be promoted by pressure and impeded by temperature (Mattson
93 and Rossman 1987; Fei et al. 1994; Xu and McCammon 2002; Lobanov et al. 2017). In total, Fe
94 in bridgmanite in Earth's mantle may be distributed among a multitude of different combinations
95 of valence state (Fe²⁺, Fe^{2.5+}, Fe³⁺), crystallographic site (A1, A2, or B), and spin state (high or
96 low).

97 Controversy over the electronic states of iron in bridgmanite has also been drawn out by different
98 interpretations of a key observational technique, Mössbauer spectroscopy. The Mössbauer effect
99 allows each valence state, coordination environment, and spin state to be distinguished by
100 characteristic values for center shift (CS) and quadrupole splitting (QS) (Dyar et al. 2006).
101 Interpretation of CS and QS obtained at high pressures requires deconvolving poorly-constrained
102 effects of structural and electronic changes. Pressure generally distorts crystallographic sites of
103 bridgmanite, leading to higher QS with pressure (e.g. Lin et al. 2013; McCammon et al. 2013).

Revision 1

104 Although the existence of the spin transition in Fe^{3+} in the bridgmanite B-site is now well-
105 accepted (Lin et al. 2013; Badro 2014), the published values for Mössbauer parameters of low-
106 spin Fe^{3+} in bridgmanite range from CS~1 mm/s and QS ~3 mm/s similar to high-spin Fe^{2+}
107 (Catalli et al. 2010; Gu et al. 2012) to CS<0.5 mm/s and QS ~1-1.5 mm/s similar to high-spin
108 Fe^{3+} (Jackson et al. 2005; Kuppenko et al. 2015; Liu et al. 2018). Predictions by DFT support
109 higher QS values 2-3 mm/s due to asymmetrical electronic field gradient generated by spin-down
110 electrons in the B-site, but have not addressed CS of low-spin Fe^{3+} (Hsu et al. 2011). Depending
111 on which of these interpretations is correct, low-spin Fe^{3+} may be misidentified as high-spin Fe^{2+}
112 or high-spin Fe^{3+} , or vice versa. The conditions at which the spin transition is reported based on
113 these observations range from 13-24 GPa (Mao et al. 2015) to 50-70 GPa (Catalli et al. 2010,
114 2011). Other phenomena suggested to impact Mössbauer spectra of bridgmanite and related
115 compounds at high pressures include charge-transfer, which should result in enhanced electrical
116 and thermal conductivity in silicates/perovskites with a mixture of Fe^{2+} and Fe^{3+} (Fei et al. 1994;
117 Xu and McCammon 2002; Keppler et al. 2008; Long et al. 2009), and changes in glasses in
118 recoil-free fraction of Fe^{2+} and Fe^{3+} , causing shifts in the relative contributions of Fe^{2+} and Fe^{3+}
119 to spectral area (Prescher et al. 2014). In addition, spectra for complex materials such as
120 bridgmanite suffer from overlapping peaks and non-unique fitting. These issues may be
121 addressed by complementary techniques such as X-ray emission spectroscopy and X-ray
122 diffraction to independently constrain spin state and structure (e.g. Catalli et al. 2010) and
123 systematic analysis of a range of compositions (e.g. McCammon et al. 2013).

124 Previous attempts to prepare well-characterized bridgmanite rely on samples synthesized in the
125 multianvil press, which is typically limited to ~25 GPa. At these conditions, bridgmanite is stable

Revision 1

126 with only up to ~15-20% Fe (Fei et al. 1996; Tange et al. 2009), and typically exhibits a mixture
127 of Fe²⁺ and Fe³⁺ depending on composition and f_{O_2} (e.g. Frost and Langenhorst 2002; Frost et al.
128 2004). At pressures ~75-100 GPa in the diamond anvil cell, a wider range of compositions with
129 up to at least 75-90% FeSiO₃ and lower Fe³⁺/total Fe becomes stable (Tateno et al. 2007;
130 Dorfman et al. 2012, 2013; Ismailova et al. 2016). The goal of this study is to systematically
131 analyze electronic states of iron-rich bridgmanite using Mössbauer spectroscopy of well-
132 characterized end-member samples. These experiments resolve discrepancies in interpretation of
133 high-pressure Mössbauer spectra of bridgmanite by firmly constraining valence states of iron at 1
134 bar, where Mössbauer parameters CS and QS are unambiguous. Results address the conditions
135 and observable characteristics of possible spin transitions and charge transfer, and will be
136 important to future characterization of bridgmanite relevant to Earth's deep mantle
137 heterogeneities.

138 Methods

139 Four bridgmanite compositions were examined ranging from 12-100% Fe³⁺/total Fe and from
140 10-50% Fe/total cations. Bridgmanites were synthesized from the following starting materials:

- 141 • 50% enstatite, 50% ferrosilite (En50Fs50) pigeonite was synthesized at the Crystal
142 Growth Facility at EPFL in a gas-mixing furnace. A stoichiometric mixture of Fe₂O₃
143 (enriched to 48.3% ⁵⁷Fe), MgO and SiO₂ was ground in an agate mortar until
144 homogenous and cold-sintered in a 3-ton press at room temperature for 1 minute. The
145 resulting pellet was placed in an alumina crucible on a bed of unenriched powder mixture
146 of the same composition. The sample was first heated in air at 1000°C, then reduced

Revision 1

147 under an N₂/H₂ mixture bubbled through H₂O at 1100°-1200°C for 3 days, then rapidly
148 quenched to room temperature. Mössbauer analysis of the starting material was consistent
149 with complete reduction of ferric iron to ferrous iron, with a detection limit of a few
150 percent. X-ray diffraction and electron microprobe analysis (Table 1) confirmed that the
151 oxides transformed to monoclinic *P2₁/c* pigeonite with composition (Mg_{0.52}Fe_{0.48}²⁺)SiO₃
152 (0% ferric before bridgmanite synthesis).

153 • 90% enstatite, 10% hematite (En90Hem10) glass starting material was synthesized from
154 intimately mixed Fe₂O₃ (enriched to 96.6% ⁵⁷Fe), MgO and SiO₂ powders by
155 containerless laser-levitation (Weber et al. 1994) under compressed air at IPGP, Paris.
156 Mössbauer spectroscopy indicates total ferric iron content of the glass before bridgmanite
157 synthesis is ~30%. The homogeneity and composition of the glass were determined by
158 electron microprobe analysis (Table 1), yielding formula for this sample as follows:
159 Mg_{0.97}Fe_{0.14}²⁺Fe_{0.06}³⁺Si_{0.90}O₃. Oxygen deficiency in measured formula may be due to use
160 of Fe²⁺-rich standards and few-% uncertainty indicated by 97-98% oxide totals during
161 microprobe measurements.

162 • 50% enstatite, 50% hematite (En50Hem50) akimotoite synthesis and characterization
163 were described in (Liu et al. 2018). Based on microprobe analysis and Mössbauer
164 spectroscopy, the formula obtained for this sample is Mg_{0.46}Fe_{1.04}³⁺Si_{0.49}O₃ (100% ferric).

165 • 75% ferrosilite, 25% corundum (Fs75Co25, or almandine-composition) glass synthesis
166 and characterization were described in Dorfman et al. (2016). The composition of the
167 glass, normalized to 3 oxygens, is Fe_{0.55}²⁺Fe_{0.12}³⁺Al_{0.54}Si_{0.73}O₃ (20% ferric before
168 bridgmanite synthesis).

Revision 1

169 Starting materials were loaded as crystalline powder or glass chip in diamond anvil cells with
170 100-150-micrometer culet and 300-micrometer bevel. Each sample was contained in a 30-50-
171 micrometer hole drilled in a Re gasket. To insulate the samples during laser heating and transmit
172 quasi-hydrostatic stress, En50Fs50 and Fs75Co25 were loaded sandwiched between platelets of
173 NaCl; En90Hem10 was loaded in Ar gas at the EPFL; and En50Hem50 was loaded in Ne gas
174 using the COMPRES/GSECARS gas loading system (Rivers et al. 2008). Pressure during
175 experiments up to ~100 GPa was measured by Raman spectroscopy of the stressed diamond
176 anvil culet center (Akahama and Kawamura 2006), or for En50Hem50 a ruby sphere loaded with
177 the sample (Mao et al. 1986).

178 Bridgmanite was synthesized from Fs75Co25, En50Fs50, and En90Hem10 compositions as in
179 previous studies (Dorfman et al. 2012, 2013) by laser heating to 2000-2500 K for ~20-60 min
180 after compression at 300 K directly to ~75-100 GPa. The transformation and homogeneity of
181 each sample was confirmed by X-ray diffraction at beamlines ID27 and ID09 ($\lambda=0.3738$ Å and
182 0.4117 Å or 0.4155 Å, respectively) of the ESRF (Figure 1). Minor CaCl₂-type SiO₂ diffraction
183 peaks are also observed in some samples after laser heating. As described by Liu et al. (2018),
184 the En50Hem50 akimotoite starting material transforms reproducibly and reversibly to
185 bridgmanite at 300 K and 22-26 GPa, so this sample was simply compressed at 300 K.

186 Energy-domain Mössbauer spectroscopy was performed at the Nuclear Resonance beamline
187 ID18 of the European Synchrotron Radiation Facility (Rüffer and Chumakov 1996; Potapkin et
188 al. 2012) and the COMPRES/sector 3 offline Mössbauer spectroscopy laboratory at the
189 Advanced Photon Source at Argonne National Laboratory. At ID18, incident light is synchrotron
190 X-rays monochromatized by a ⁵⁷FeBO₃ single crystal to the ⁵⁷Fe resonant energy of 14.4 keV

Revision 1

191 with energy resolution of ~ 5.5 neV. The X-ray beam is focused to $\sim 9 \times 14$ micrometers full width
192 at half maximum. At the sector 3 offline Mössbauer laboratory, incident gamma-rays are
193 provided by a 400-micrometer-diameter radioactive ^{57}Co point source. To generate a range of
194 energies for absorption spectroscopy measurements, both the $^{57}\text{FeBO}_3$ monochromator at ID18
195 and the ^{57}Co at sector 3 are oscillated ± 5 mm/s (1 bar measurement at sector 3 used ± 10
196 mm/s). Source velocities are calibrated with an α -Fe foil standard at 300 K. Synchrotron source
197 line width and center shift are calibrated with a $\text{K}_2\text{Mg}^{57}\text{Fe}(\text{CN})_6$ standard before and after each
198 measurement. The linewidth for the conventional measurements was set to match a 6-month-old
199 radioactive point source. Synchrotron Mössbauer spectra were collected for ~ 2 -8 hrs at each
200 pressure. Conventional Mössbauer spectra were obtained for ~ 2 weeks each. Spectra were fit to
201 pseudo Voigt doublets using MossA software (Prescher et al. 2012). All spectra were fit using a
202 full transmission integral to account for thicknesses of radiation sources and samples.

203 Results and discussion

204 To ensure no change in valence states of Fe across the measured pressure range, all Mössbauer
205 spectroscopy measurements were performed at 300 K and no additional heating was applied to
206 samples after synthesis of bridgmanite. Upon laser heating, both structural transformation and
207 redox may occur. Although some previous studies assume $\text{Fe}^{3+}/\text{total Fe}$ does not change during
208 synthesis (e.g. Nishio-Hamane et al. 2007; Lundin et al. 2008; Dorfman et al. 2013), redox
209 during laser heating is confirmed by our data to result in differences in $\text{Fe}^{3+}/\text{total Fe}$ in
210 synthesized bridgmanite relative to starting materials. During 300 K compression and
211 decompression, we assume that kinetics do not permit site-site diffusion and redox reactions.
212 Therefore, $\text{Fe}^{3+}/\text{total Fe}$ for bridgmanites synthesized at high pressure may be fixed to values
10

Revision 1

213 observed after 300 K decompression to 1 bar (these Fe^{3+} /total Fe values are reported here in
214 figures and tables). Mössbauer spectra were measured for Fs75Co25, En50Fs50, and
215 En90Hem10 bridgmanites on decompression from ~75-100 GPa in ~25 GPa steps to 1 bar
216 (Figures 2-4 a-c). En50Hem50 akimotoite was observed upon compression from 1 bar to
217 bridgmanite at 32 and 70 GPa (Figures 2-4 d). Changes in the Mössbauer parameters of each
218 bridgmanite composition during 300 K compression/decompression (Table 2, Figure 5) may be
219 due to 1) electronic spin transitions, 2) pressure-induced structural changes including site
220 distortion or amorphization, or 3) charge transfer between nearby Fe ions.

221 The spin transition in Fe^{3+}
222 Effects of the high-to-low spin transition on Mössbauer parameters of Fe^{3+} in bridgmanite may
223 be clearly observed in En50Hem50 bridgmanite, for which the spin transition in the octahedral
224 site has been documented at ~48 GPa at 300 K by X-ray diffraction and X-ray emission
225 spectroscopy (Liu et al. 2018). En50Hem50 bridgmanite is 100% Fe^{3+} , with 50% Fe in the
226 pseudo-dodecahedral site, and 50% Fe in the octahedral site. Mössbauer spectra at high pressure
227 exhibit two closely-overlapping doublets, with absorption at ~-0.4-0.0 mm/s and ~0.6-1 mm/s
228 (Figure 3d, Figure 4d). Across the pressure-induced spin transition from 32 to 70 GPa, spectra
229 change slightly: average CS decreases by 0.15 mm/s and QS increases by 0.35 mm/s. Two
230 reasonable fits to these data are possible for a sample with pure Fe^{3+} : either Fe^{3+} in A- and B-
231 sites adopt CS differing by <0.05 mm/s with contrasting QS, 0.6-0.9 and 1.4-1.8 mm/s, or the
232 difference in CS is larger, ~0.4 mm/s, while QS is identical within ~0.5 mm/s. Neither option is
233 consistent with a large change across the spin transition to QS ~3 mm/s predicted in bridgmanite
234 by DFT (Hsu et al. 2011). At 32 GPa (Figure 3d), the fit with contrasting CS would produce

Revision 1

235 CS=0.45 mm/s for the higher CS component, which would be high for Fe³⁺ (Figure 5). We
236 therefore favor a fit with contrasting QS for high-spin Fe³⁺ in A-site vs. B-site, consistent with
237 the different asymmetry of the two sites in high-spin state. At 70 GPa (Figure 4d), the overall
238 decrease in CS allows a fit with contrasting CS with acceptable Mössbauer parameters for Fe³⁺
239 for both sites, where the low-spin B-site Fe³⁺ exhibits lower CS and higher QS relative to high-
240 spin B-site Fe³⁺ at lower pressure. In addition, recent data for well-characterized samples indicate
241 that pressure tends to increase QS (i.e. level of structural distortion around the iron ion
242 increases), and the principal change in Mössbauer parameters of octahedrally-coordinated Fe³⁺
243 across the spin transition is a decrease in CS (i.e. density of electrons around the iron nucleus
244 increases) (Pasternak et al. 2002; Kuppenko et al. 2015; Liu et al. 2018) (Table 3). We thus obtain
245 CS ~0.35 mm/s for high-spin Fe³⁺ in both sites at 32 GPa below the spin transition, and a lower
246 CS -0.07 mm/s for low-spin Fe³⁺ at 70 GPa (Table 2, Figure 5).

247 These results can be used to determine whether spin transitions occur in other compositions with
248 mixed valence states of iron. For less Fe³⁺-rich En50Fs50 and En90Hem10 compositions, Fe³⁺
249 doublets can be interpreted based on values observed at similar conditions for En50Hem50. The
250 fit uncertainty for Fe³⁺ doublets in En50Fs50 at 75 GPa is large (as much as ~1 mm/s) due to
251 overlap with other doublets, but the refined value 0.4 mm/s is consistent with high-spin Fe³⁺ in
252 the A-site, as expected with a (Mg+Fe)/Si ratio ~1 and B-site filled with Si. For En90Hem10,
253 with ~50% Fe³⁺, stronger, better-resolved Fe³⁺ exhibits a slight decrease in CS, from 0.34 mm/s
254 to 0.29 mm/s at 36 and 67 GPa, respectively. While this CS indicates a dominantly HS Fe³⁺
255 component, based on an assumption of linear mixing of CS values as much as ~20% of the Fe³⁺
256 (~10% total Fe) may be low-spin Fe³⁺ in the B-site at 67 GPa (Figure 6a). This partial spin

Revision 1

257 transition is consistent with the more Si-depleted composition with space available for Fe³⁺ in the
258 B-site.

259 Site distortion

260 All Fe²⁺-bearing bridgmanite compositions exhibit splitting at lower-mantle pressures consistent
261 with predictions of distortion of the A-site (Hsu et al. 2010). At pressures above 1 bar for Fe²⁺-
262 rich Fs75Co25 and En50Fs50 compositions, absorption at ~2-3 mm/s requires two Fe²⁺ sites
263 (Figure 3a,b, Figure 4a,b). QS of both sites increases with pressure (Figure 5) and the relative
264 weight of the higher-QS site increases, in accord with increasingly asymmetric A-sites. At ~75
265 GPa in these compositions, ~1/3 of the Fe²⁺ sites exhibit QS=3.8-3.9 mm/s, with the remaining
266 Fe²⁺ at QS=2.1-2.5 mm/s. For Fe³⁺ in the A-site, QS remains relatively constant with pressure.
267 However, spectral resolution does not allow us to either confirm or disprove development of
268 multiple Fe³⁺ A-sites due to site distortion (Hummer and Fei 2012).

269 Charge transfer (Fe^{2.5+})

270 The signature of charge transfer, i.e. increased delocalization of electrons between iron ions, is
271 observed in Fe compositions Fs75Co25 and En50Fs50 as an absorption peak at ~1.6 mm/s
272 (Figure 2a, Figure 3a, Figure 4a-b). This peak can be fitted with a doublet with CS ~0.8 and QS
273 ~1.6, intermediate between typical parameters observed for Fe²⁺ and Fe³⁺ and similar to Fe^{2.5+} as
274 previously identified in bridgmanite (Fei et al. 1994; Xu and McCammon 2002) (Figure 7). The
275 Fe^{2.5+} doublet intensity is interpreted to represent 50% Fe²⁺ and 50% Fe³⁺ when calculating
276 Fe³⁺/total Fe (Figure 6b). This assumption yields constant Fe³⁺/total Fe with 300 K
277 compression/decompression for all compositions within ~10% error entailed in fitting site
278 weights, indicating no change in total redox state with pressure.

Revision 1

279 In general, the favorability of charge transfer would be expected to depend on whether Fe^{2+} and
280 Fe^{3+} occupy neighboring sites (note that Fe-rich En50Hem50 does not exhibit charge transfer
281 because all Fe is Fe^{3+}) and how much energy is required for electrons to hop between these sites.
282 As noted in previous work (Fei et al. 1994), the shortest site-site distances for electron migration
283 in the bridgmanite structure are between face-sharing B-sites and A-sites. However, the iron-rich
284 compositions examined in this study incorporate at least enough Al and Si to fill the B-site, and
285 are expected to accommodate both Fe^{2+} and Fe^{3+} in the A-site. The face-sharing A-A site
286 distance in Fe-rich bridgmanite, based on lattice parameters determined by X-ray diffraction
287 (Dorfman et al. 2012, 2013), is ~10% larger than the face-sharing A-B site distance, but
288 comparable to edge-sharing octahedra in chain silicates at 1 bar known to exhibit Fe^{2+} - Fe^{3+}
289 charge transfer (Mattson and Rossman 1987).

290 In the Fs75Co25 composition, $\text{Fe}^{2.5+}$ completely replaces Fe^{3+} at all pressures at 300 K. Even at 1
291 bar, ~20% of the spectral weight is a component with $\text{CS}=0.6$ mm/s, too high for Fe^{3+} and
292 consistent with $\text{Fe}^{2.5+}$ (Figure 7). With increasing pressure, the intensity of the $\text{Fe}^{2.5+}$ component
293 is constant within uncertainty, though the Mössbauer parameters are more uncertain due to
294 overlap. Rietveld refinement of atomic positions (Dorfman et al. 2012) confirms that all Fe in
295 this composition resides in the A-site. As a result, charge transfer in this composition must take
296 place between face-sharing A-site Fe^{2+} and A-site Fe^{3+} .

297 For En50Fs50-composition bridgmanite, Fe^{2+} - Fe^{3+} neighboring A-sites will be diluted by Mg in
298 the A-site, and charge transfer appears to be possible but less favorable. A charge transfer
299 component accounting for ~1/3 of the Fe^{3+} is needed to fit data obtained at ~75 GPa (Figure 4b).
300 Although Fe^{2+} - Fe^{3+} neighboring A-sites would be expected to be nearly as common in En50Fs50

Revision 1

301 as in Fs75Co25, a separate Fe³⁺ doublet is still observed, and upon decompression to pressures
302 25 GPa and below the Fe^{2.5+} component disappears (Figure 3a,b). Weights of Fe^{2.5+} and Fe³⁺ sites
303 at all conditions are consistent with the 1 bar Fe³⁺/total Fe (Figure 6b). These observations
304 suggest a pressure-driven crossover in the stability of charge transfer in this composition.
305 Compression of adjoining sites is expected to lower energy required for electron transfer (Fei et
306 al. 1994; Xu and McCammon 2002). The mobility of electrons between A-sites appears to
307 increase accordingly between 25 and 75 GPa. Observations of charge transfer in En50Fs50
308 relative to Fs75Co25 bridgmanite these samples indicate that charge transfer is promoted by
309 pressure and high Fe concentration.

310 Evidence for charge transfer in En90Hem10-composition bridgmanite, which is also mixed-
311 valence but relatively Fe-poor and has (Mg+Fe)/(Al+Si) ratio greater than 1, is not clear (Figure
312 4c). A Fe²⁺ site with CS~0.8 at high pressures is observed in En90Hem10 composition, but broad
313 peaks, high QS, and no change in intensity of Fe³⁺ doublets when this doublet appears (Figure
314 6b, Table 2) all suggest the CS 0.8 mm/s doublet is more likely to represent Fe²⁺ in
315 untransformed glass starting material. In contrast to the Fe²⁺-rich compositions Fs75Co25 and
316 En50Fs50, in the En90Hem10 composition the ~50% Fe²⁺ and 50% Fe³⁺ are expected to occupy
317 the A- and B-sites respectively due to the higher (Mg+Fe)/(Al+Si) ratio, so charge transfer would
318 take place between A- and B-sites rather than two A-sites. Even for this lower Fe concentration,
319 Fe²⁺-Fe³⁺ neighboring sites would be expected to be common: the probability that none of the 8
320 B-sites surrounding Fe²⁺ in the A-site is Fe³⁺ should be ~50%. Under these conditions A-B site
321 charge transfer is not evident, though the presence of an overlapping Fe^{2.5+} doublet cannot be
322 ruled out. In contrast to intuition based on electron migration distance (Fei et al. 1994), charge

Revision 1

323 transfer appears to be more favorable between face-sharing A-sites than between face-sharing A-
324 and B-sites. Although the distance between A-sites is longer, the enthalpy cost of moving an
325 electron into the highly-compressed B-site (effectively, Fe^{2+} in B and Fe^{3+} in A) may provide an
326 explanation for a failure to observe A-B charge transfer.

327 Implications

328 If previous studies of physical properties of bridgmanite have misidentified or missed spin
329 transitions based on incorrect assignment of sites observed by Mössbauer spectroscopy,
330 predicted seismic velocities for iron-bearing lower mantle phase assemblages may be
331 systematically offset. The greatest effects of valence states of iron on geophysical properties are
332 likely to be observed in the shallow lower mantle due to softening during the spin transition for
333 Fe^{3+} -bearing compositions (Shukla et al. 2016) and higher contrast in bulk compressibility and
334 density between Fe^{2+} - and Fe^{3+} -rich bridgmanite at pressures at and below the Fe^{3+} spin
335 transition (Liu et al. 2018). At greater depths above the spin transition pressure range, seismic
336 velocities of Fe^{2+} - and Fe^{3+} -rich bridgmanite converge. While speciation of Fe will also affect
337 partitioning of Fe between bridgmanite and ferropericlase in the mantle (e.g. Piet et al. 2016), the
338 net effect of multiple orders of magnitude difference in bridgmanite-ferropericlase partition
339 coefficient on density contrast is only 0.1% (Ricolleau et al. 2009; Dorfman and Duffy 2014),
340 suggesting that effects of partitioning on elastic properties are too subtle to be observed via
341 seismology. Attempts to use seismology to map the redox conditions of the lower mantle should
342 focus on depths below the spin transition pressure, between 660 and 1000 km.

Revision 1

343 The dependence of charge transfer in mantle bridgmanite on composition and pressure may not
344 significantly affect elastic properties, but could result in regional- and depth-variation of
345 transport properties including electrical and thermal conductivity. A-A site charge transfer
346 should have no effect on density of the bridgmanite structure as the overall site occupancy
347 remains the same. A-B site charge transfer would decrease density by expanding the B-site, but
348 based on our data, we infer that this mechanism is not significant in Earth's mantle. Either
349 mechanism of charge transfer, along with other mechanisms including conductivity of vacancies
350 and ions, will contribute to electrical and thermal conductivity (Xu and McCammon 2002). Our
351 observations do support enhancement of charge transfer by Fe-enrichment and high pressures
352 corresponding to the deep lower mantle—both likely characteristics of dense heterogeneities
353 (Ishii and Tromp 1999; Lau et al. 2017) and basalt-rich slabs near the core-mantle boundary
354 (e.g. Grand 2002). In addition, the very deep lower mantle has been suggested to host mixed-
355 valence bridgmanite, even under reduced conditions in contact with metallic iron from the outer
356 core (Shim et al. 2017). Regions rich in subducted basalt will have higher Al- and Si-content,
357 which is more likely to stabilize mixed-valence iron in the bridgmanite A-site. Basalt graveyards
358 could thus more efficiently conduct heat from the outer core, with corresponding effects on the
359 formation of thermochemical plumes and entrainment of subducted material. As the densest
360 heterogeneities identified in the lower mantle, ULVZs resting on the core-mantle boundary are
361 likely Fe-rich (e.g. Rost et al. 2005; Brown et al. 2015), but their redox states are not well-
362 constrained by available geophysical data. Proposed compositions for ULVZs include
363 enrichment in metallic melt (Williams and Garnero 1996; Liu et al. 2016) or iron-rich oxide
364 (Wicks et al. 2010; Hu et al. 2016; Liu et al. 2017) or silicate (Mao et al. 2006). However, the

Revision 1

365 high temperatures expected at the base of the mantle may impede charge transfer (Mattson and
366 Rossman 1987, Xu and McCammon 2002), and additional mechanisms such as conductivity of
367 vacancies and ions will be increasingly important at high temperatures (Xu and McCammon
368 2002). Future experimental studies will also need to quantify charge transfer in lower-mantle
369 post-perovskite. If observed, enhanced electrical and thermal conductivity of ULVZs may
370 indicate either the presence of Fe metal or charge transfer due to mixed-valence Fe-rich
371 bridgmanite. Distinguishing these hypotheses is important to constraining redox evolution at the
372 core-mantle boundary.

373 Acknowledgements

374 The authors thank Susanne Seitz for assistance with microprobe analysis of starting materials at
375 the University of Lausanne. We thank Richard Gaal for assistance with gas loading at the EPFL
376 and Sergey Tkachev for assistance at the APS. Use of the COMPRES-GSECARS gas loading
377 system and the APS offline Mössbauer laboratory facilities was supported by COMPRES under
378 NSF Cooperative Agreement EAR-1606856 and by GSECARS through NSF grant EAR-
379 1634415 and DOE grant DE-FG02-94ER14466. ⁵⁷Co-source Mössbauer spectroscopy was
380 performed at the APS beamline 3-ID Mössbauer Laboratory. This research used resources of the
381 Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility
382 operated for the DOE Office of Science by Argonne National Laboratory under Contract No.
383 DE-AC02-06CH11357. We thank the European Synchrotron Radiation Facility (Grenoble,
384 France) for provision of synchrotron radiation at beamlines ID18 for synchrotron Mössbauer
385 spectroscopy, and beamlines ID09 and ID27 for synchrotron X-ray diffraction. Laser heating was
386 performed at beamline ID24 of the ESRF with assistance from Innokenty Kantor. S. M. Dorfman

Revision 1

387 acknowledges funding support from the Marie Heim-Vögtlin program of the Swiss National
388 Science Foundation through project PMPDP2_151256 and the National Science Foundation
389 project EAR-1664332.

390 Figure and table captions

391 Figure 1: X-ray diffraction patterns for bridgmanites obtained after laser heating and before
392 decompression with energy-domain SMS, with diffraction angle converted to lattice spacing (d)
393 to account for differences in diffraction wavelength. Diffraction peaks from medium (N=NaCl,
394 and Ar for En90Hem10 sample) and minor stishovite (St) are identified, and black sticks below
395 comprise bridgmanite reference pattern.

396 Figure 2: Observed Mössbauer spectra at 1 bar. For compositions in a) b) and c), synchrotron
397 Mössbauer spectra are obtained at ESRF ID18 from iron-bearing bridgmanite samples recovered
398 to 1 bar after 300 K decompression from high-pressure synthesis. In d), conventional ^{57}Co
399 Mössbauer spectrum is obtained at APS sector 3 offline lab from synthetic akimotoite before 300
400 K compression. Blue doublets= Fe^{2+} . Red doublets=high spin Fe^{3+} . Purple doublets= $\text{Fe}^{2.5+}$ charge
401 transfer component. Original data are black points, with total fit indicated by red curve and misfit
402 by red points.

403 Figure 3: Observed Mössbauer spectra for iron-bearing bridgmanite at high pressure ~ 27 GPa
404 below the spin transition in Fe^{3+} . Spectra shown in a) b) and c) use synchrotron Mössbauer
405 source at ESRF ID18 (total Fe^{3+} /total Fe listed for each composition is assumed to be same as 1
406 bar recovered sample), while d) uses conventional ^{57}Co Mössbauer source at APS sector 3
407 offline lab. Blue doublets= Fe^{2+} (where darker blue indicates distorted A-site with high QS, and

Revision 1

408 lighter blue Fe^{2+} in untransformed glass in En90Hem10 composition in c)). Red doublets=high
409 spin Fe^{3+} . Purple doublets= $\text{Fe}^{2.5+}$ charge transfer component. Original data are black points, with
410 total fit indicated by red curve and misfit by red points.

411 Figure 4: Observed Mössbauer spectra for iron-bearing bridgmanite at high pressure ~ 72 GPa
412 above the spin transition in Fe^{3+} . Spectra shown in a) b) and c) use synchrotron Mössbauer
413 source at ESRF ID18 (total Fe^{3+} /total Fe listed for each composition is assumed to be same as 1
414 bar recovered sample), while d) uses conventional ^{57}Co Mössbauer source at APS sector 3
415 offline lab. Blue doublets= Fe^{2+} (where darker blue indicates distorted A-site with high QS, and
416 lighter blue Fe^{2+} in untransformed glass in En90Hem10 composition in c)). Red doublets=high
417 spin Fe^{3+} , and pink=low spin Fe^{3+} . Purple doublets= $\text{Fe}^{2.5+}$ charge transfer component. Original
418 data are black points, with total fit indicated by red curve and misfit by red points.

419 Figure 5: Mössbauer parameters a) quadrupole splitting (QS) and b) center shift (CS) observed
420 for bridgmanite as a function of pressure for all sites in all compositions. Symbols indicate bulk
421 composition of each bridgmanite sample (diamonds: Fs75Co25, squares: En50Fs50, circles:
422 En90Hem10, triangles: En50Hem10), while colors indicate spin and valence state of iron (blue:
423 Fe^{2+} , purple: $\text{Fe}^{2.5+}$ (charge transfer), red: high-spin Fe^{3+} , light pink: low-spin Fe^{3+} , magenta:
424 mixed-spin Fe^{3+} (overlap between doublets impedes resolution of separate high- and low-spin
425 doublets).

426 Figure 6: a) Relative total amount of high-spin iron in each sample as a function of pressure,
427 based on sum of area of all high-spin Fe^{2+} , $\text{Fe}^{2.5+}$, and Fe^{3+} doublets. b) Relative total amount of
428 Fe^{3+} in each sample as a function of pressure, based on area of Fe^{3+} doublets plus half the area of

Revision 1

429 charge transfer component. Error bars represent 2σ obtained from fit of Mössbauer spectral
430 intensity.

431 Figure 7: Mössbauer parameters observed for Fe in bridgmanite and other compounds. Results
432 from this study for Fe^{2+} =blue circles, high-spin Fe^{3+} =red up-pointing triangles, low-spin
433 Fe^{3+} =pink down-pointing triangles, charge transfer ($\text{Fe}^{2.5+}$) component=purple diamonds. Error
434 bars represent fit uncertainty for each doublet. Predicted values for QS from density functional
435 theory for Fe^{2+} from (Hsu et al. 2010) and for Fe^{3+} from (Hsu et al. 2011). Shaded regions
436 comprise envelope of observations from previous studies: (Greenwood and Gibb 1971; Pasternak
437 et al. 2002; Hummer and Fei 2012; McCammon et al. 2013).

438 Table 1: Microprobe composition analysis of starting materials performed at the University of
439 Lausanne. Standards used to quantify SiO_2 , MgO , and FeO were forsterite, fayalite and
440 orthopyroxene. Oxide totals for glass were consistently less than 100%, potentially due to use of
441 Fe^{2+} -rich standards, higher Fe^{3+} -content in glass, and matrix effects. Measurements with totals
442 less than 97% were dropped. FeO vs. $\text{FeO}_{1.5}$ was determined by Mössbauer spectroscopy at
443 ambient conditions.

444 Table 2: Mössbauer parameters observed for bridgmanite. CS and QS in units of mm/s. *
445 indicates parameters constrained to equal values to aid fit convergence. Note that $\text{Fe}^{2.5+}$ fraction
446 can be assumed to represent 50% Fe^{2+} + 50% Fe^{3+} .

447 Table 3: Hyperfine parameters of high- and low-spin Fe^{3+} in perovskites obtained by energy-
448 domain Mössbauer spectroscopy.

Revision 1

449 Tables and figures

450 Table 1

	En50Fs50 (pigeonite)		En90Hem10 (glass)	
	Weight % oxides	Cations normalized to 3 O (3% Fe ³⁺)	Weight % oxides	Cations normalized to 3 O (30% Fe ³⁺)
SiO ₂	52.0(2)	0.996	49.2(2)	0.900
MgO	18.1(2)	0.519	35.4(4)	0.965
FeO	30.3(2)	0.478	13.31(18)	0.143
FeO _{1.5}		0.015		0.061
Total	100.4(4)	1.993	97.8(6)	2.069

451

Revision 1

452 Table 2

	Fs75Co25			En50Fs50			
	1 bar			1 bar			
	Fe ²⁺		Fe ^{2.5+}	Fe ²⁺		Fe ³⁺ HS	
CS (mm/s)	1.07(4)		0.60(8)	1.06(3)		0.39(3)	
QS (mm/s)	2.01(7)		1.06(20)	1.96(6)		0	
Weight	80(11)		20(11)	72(6)		28(6)	
	15 GPa			25 GPa			
	Fe ²⁺		Fe ^{2.5+}	Fe ²⁺		Fe ³⁺ HS	
CS	1.089* (18)	1.089* (18)	0.84(15)	1.21(5)	1.08(3)	0.2(3)	
QS	3.66(8)	2.34(2)	1.2(3)	2.69(11)	1.73(9)	1.0(4)	
Weight	6(9)	76(17)	17(16)	52(27)	26(21)	22(21)	
	76 GPa			75 GPa			
	Fe ²⁺		Fe ^{2.5+}	Fe ²⁺		Fe ^{2.5+}	Fe ³⁺ HS
CS	0.998(9)	1.0(3)	0.6(2)	0.985(8)	1.00(4)	0.9(9)	0.4 (10)
QS	3.926 (19)	2.4(4)	1.7(7)	3.90(2)	3.1(3)	1.6 (1.9)	0.7 (19)
Weight	28(14)	54(20)	18(19)	20(27)	43(28)	18(17)	18(18)
	En90Hem10			En50Hem50			
	1 bar			1 bar			
	Fe ²⁺		Fe ³⁺ HS	Fe ³⁺ HS			
CS	1.02(7)		0.42(9)	0.36(3)			
QS	1.96(19)		0.95(16)	0.73(5)			
Weight	47(9)		53(9)	100			
	36 GPa			32 GPa			
	Fe ²⁺		Fe ³⁺ HS	Fe ³⁺ A HS		Fe ³⁺ B HS	
CS	1.2(8)	0.8(7)	0.34(3)	0.35(2)		0.32(3)	
QS	3.1(1.7)	2.3(1.4)	1.02(6)	1.37(11)		0.59(10)	
Weight	22(14)	25(18)	52(16)	0.5*		0.5*	
	67 GPa			70 GPa			
	Fe ²⁺		Fe ³⁺ mixed	Fe ³⁺ A HS		Fe ³⁺ B LS	
CS	1.0(3)	0.81(13)	0.29(3)	0.38(9)		-0.07(10)	
QS	3.3(3)	2.3(7)	1.13(9)	1.35(4)		1.30(5)	
Weight	20(17)	31(16)	50(15)	0.5*		0.5*	

453

454

Revision 1

455 Table 3

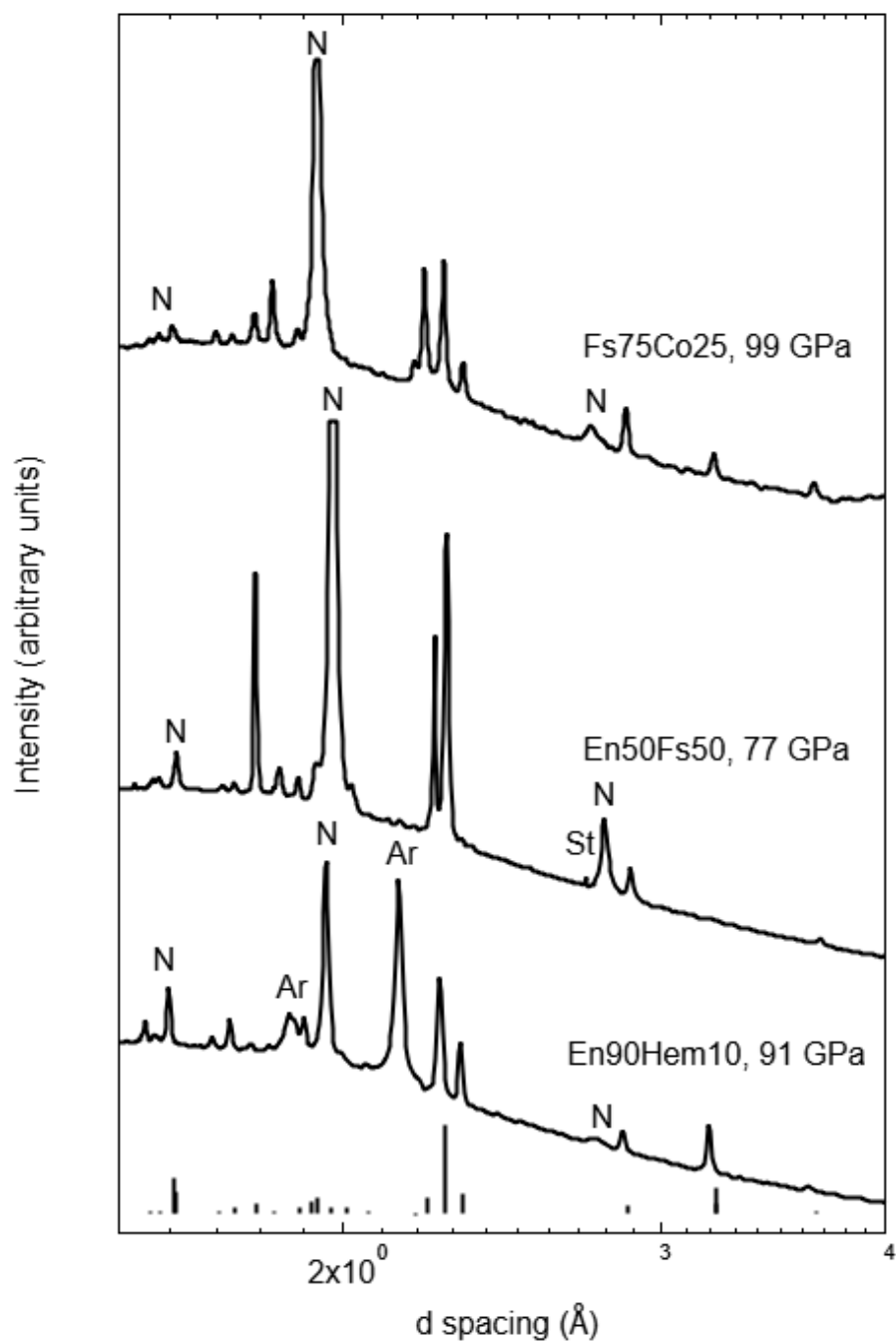
	HS CS (mm/s)	HS QS (mm/s)	LS CS (mm/s)	LS QS (mm/s)	Reference
Bridgmanite (Mg,Fe,Al) (Fe,Al,Si)O ₃	0.0-0.5	0.3-1.7	N/A	N/A	(Hummer and Fei 2012)
	0.4	1.2-1.5	N/A	N/A	(Potapkin et al. 2013)
	0.4	0.8-1.3	-0.1	0.9	(Kupenko et al. 2015)
	0.1-0.15 (Δ IS A-B)	1.1-1.2	0.3 (Δ IS A-B)	1.3-1.4	(Liu et al. 2018)
	0.2-0.4	0.6-1.4	0.0	1.3	This work
Perovskite-structured rare-earth orthoferrites	0.22-0.24	0.24-0.59	0.04-0.23	0.55-1.42	(Pasternak et al. 2002)

456

457

Revision 1

458 Figure 1



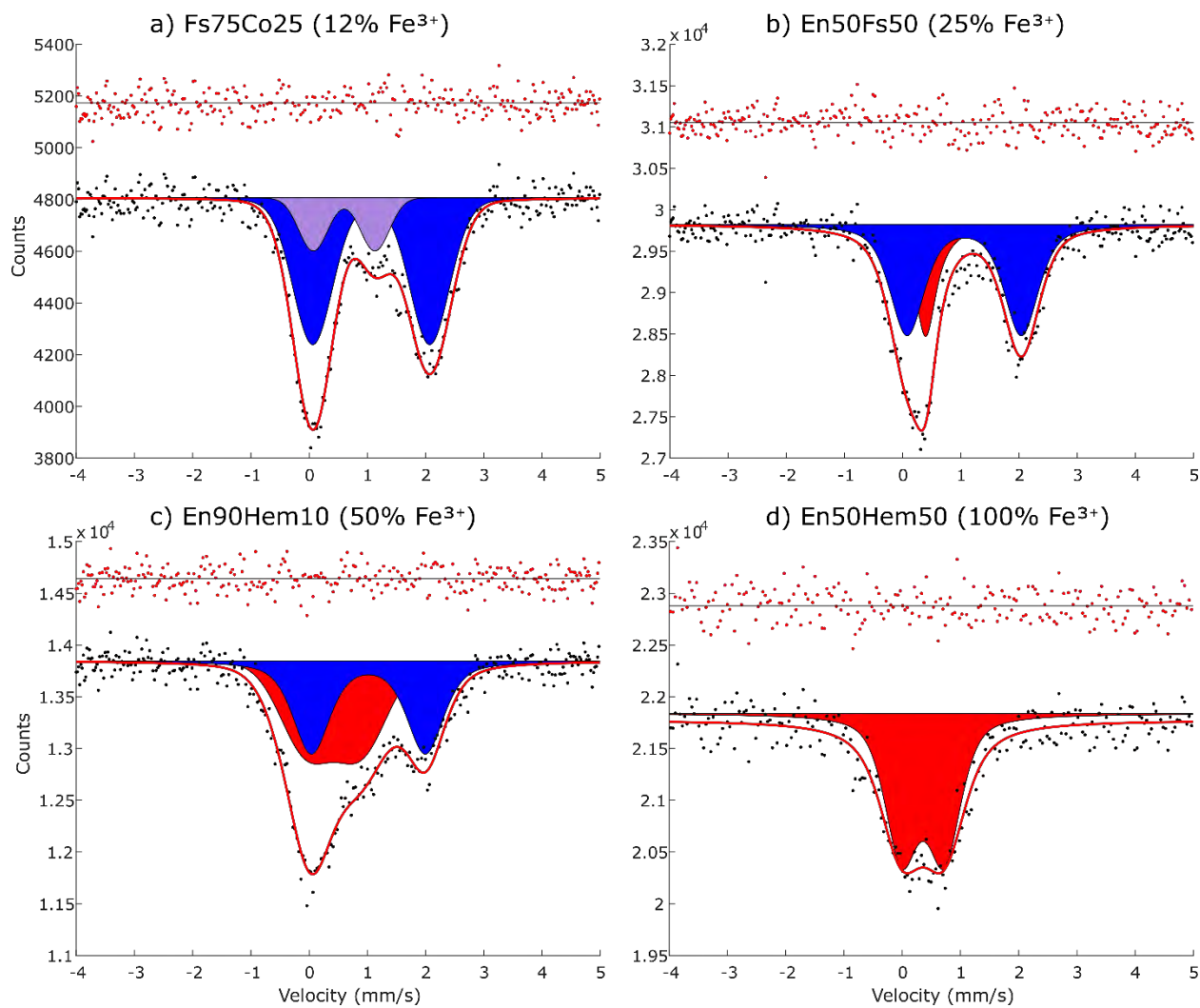
459

25

Revision 1

460 Figure 2

1 bar



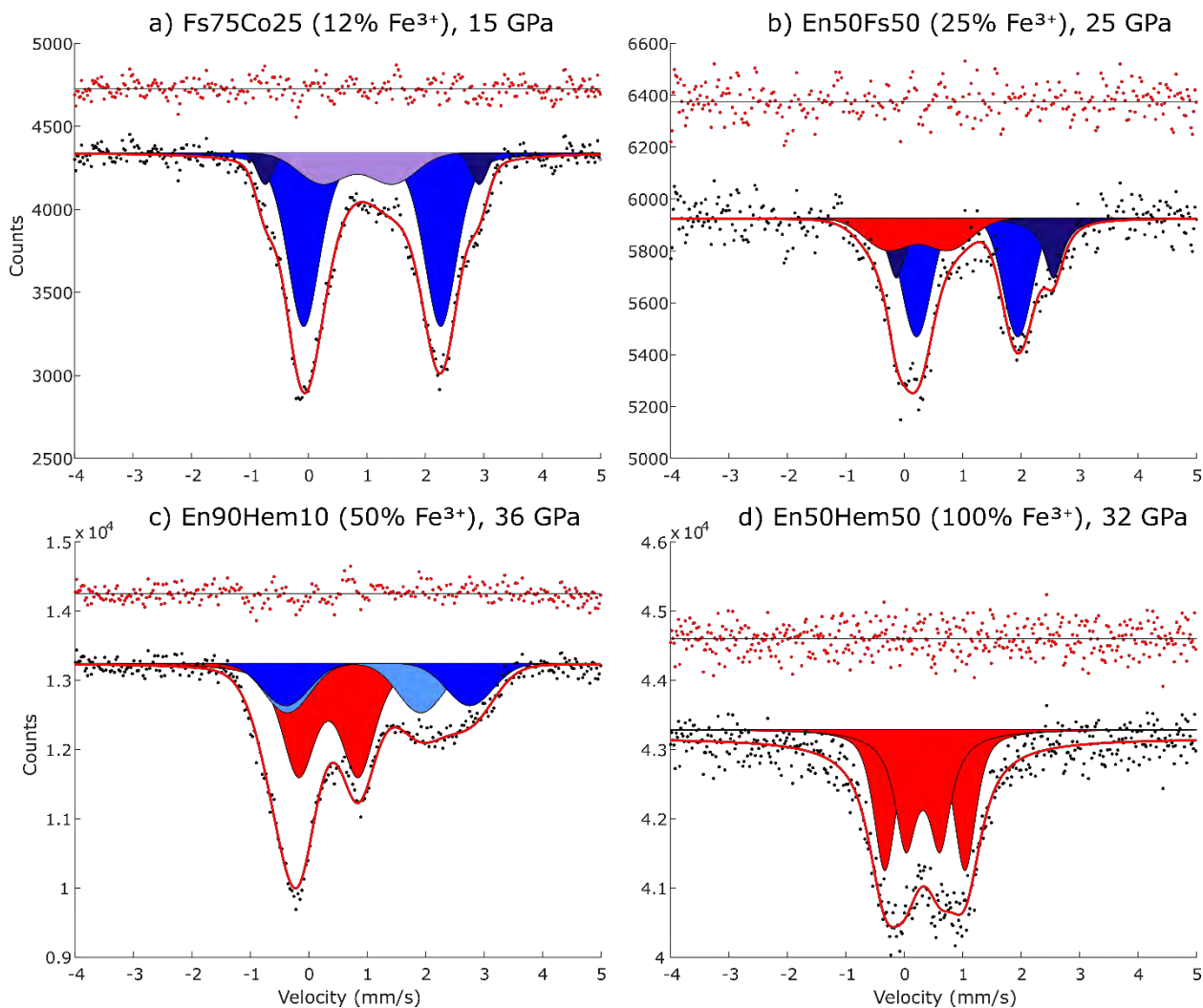
461

26

Revision 1

462 Figure 3

Below spin transition



463

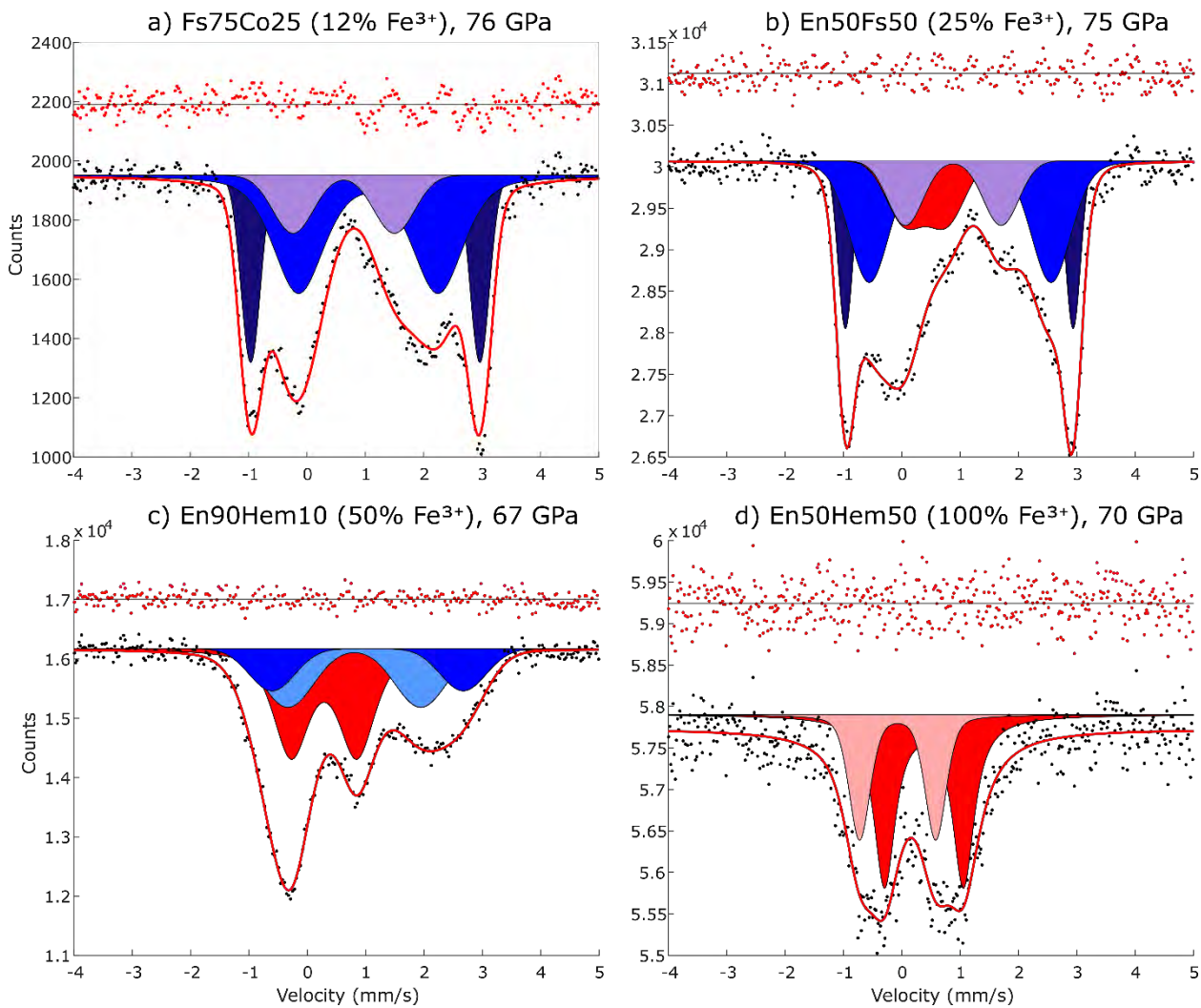
464

27

Revision 1

465 Figure 4

Above spin transition



466

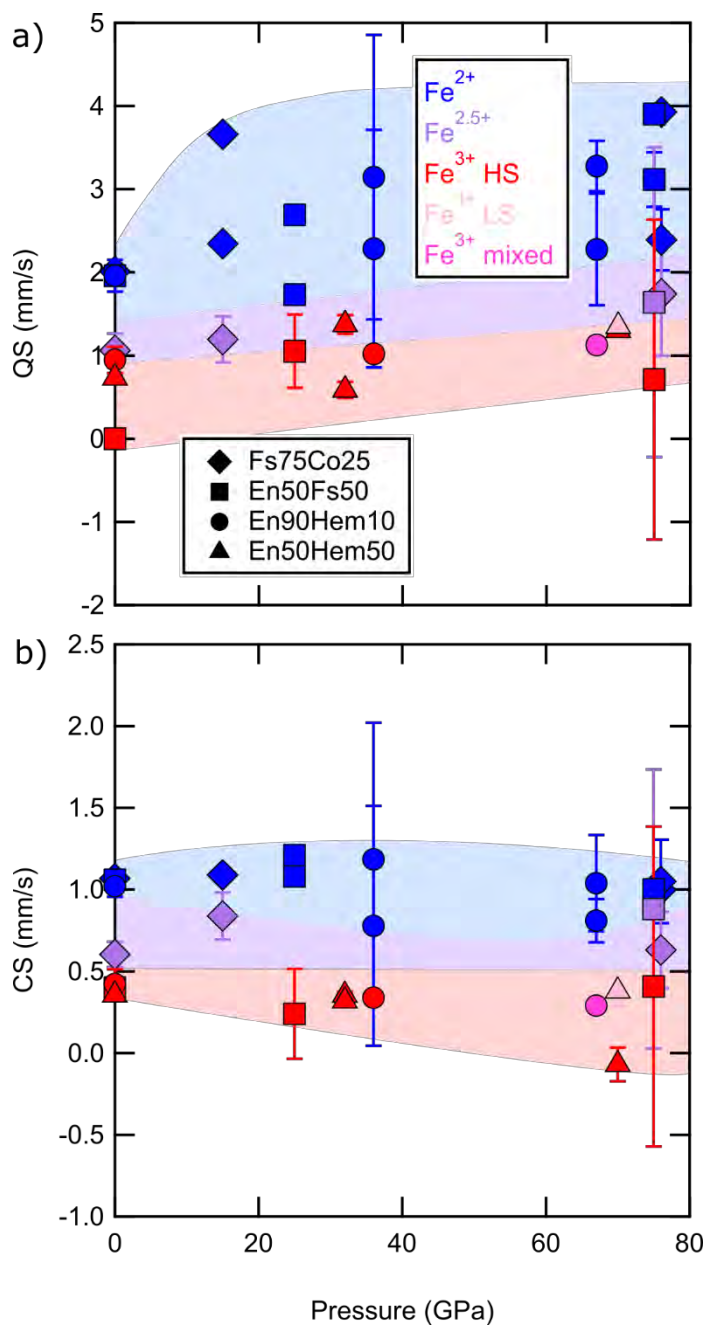
467

468

469

Revision 1

470 Figure 5

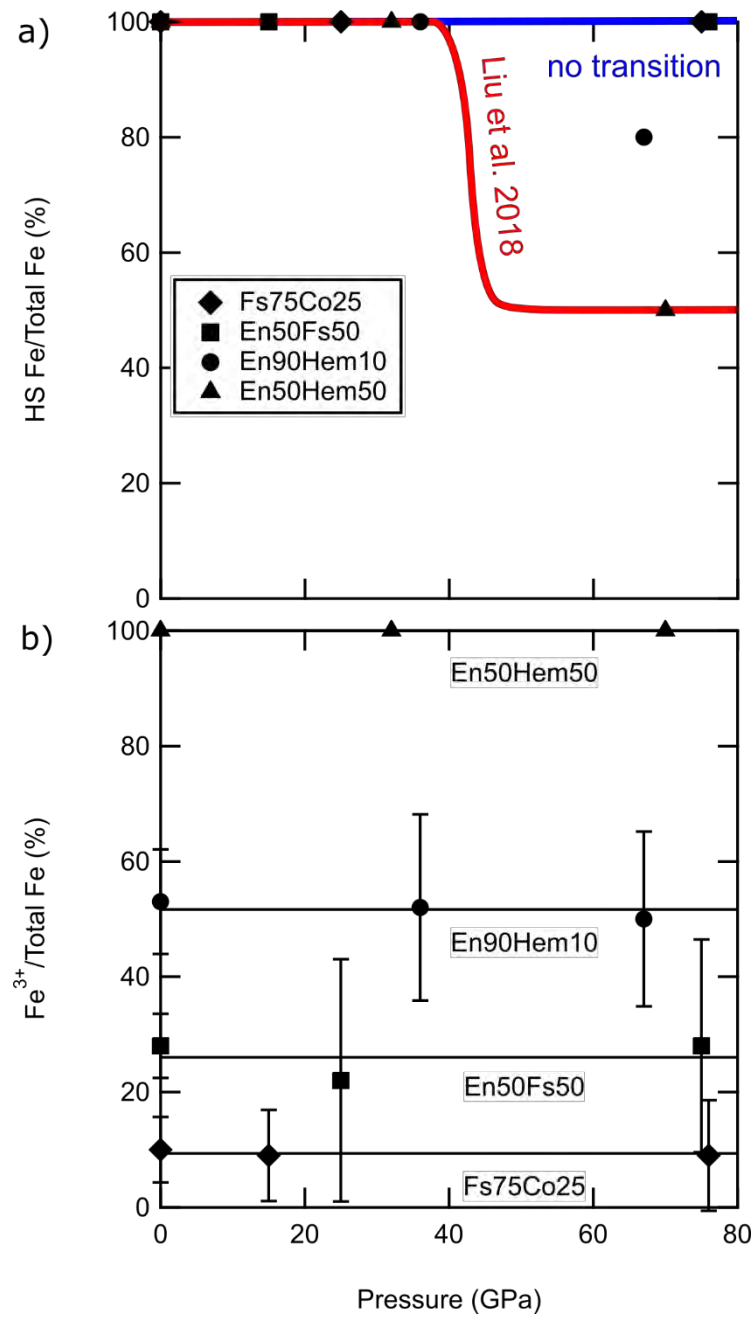


471

29

Revision 1

472 Figure 6



473

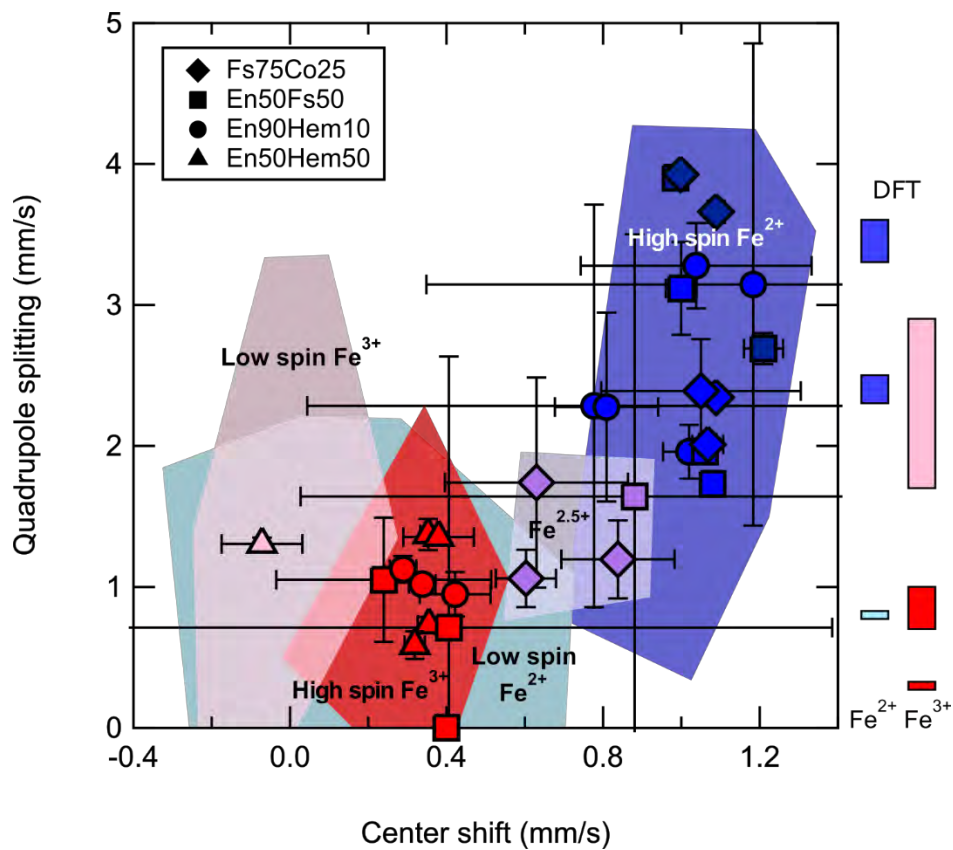
474

475

30

Revision 1

476 Figure 7



477

478

Revision 1

479 References

- 480 Akahama, Y., and Kawamura, H. (2006) Pressure calibration of diamond anvil Raman gauge to
481 310 GPa. *Journal of Applied Physics*, 100, 043516–4.
- 482 Badro, J. (2014) Spin Transitions in Mantle Minerals. *Annual Review of Earth and Planetary*
483 *Sciences*, 42, 231–248.
- 484 Badro, J., Rueff, J.-P., Vanko, G., Monaco, G., Fiquet, G., and Guyot, F. (2004) Electronic
485 Transitions in Perovskite: Possible Nonconvecting Layers in the Lower Mantle. *Science*,
486 305, 383–386.
- 487 Brown, S.P., Thorne, M.S., Miyagi, L., and Rost, S. (2015) A compositional origin to ultralow-
488 velocity zones. *Geophysical Research Letters*, 2014GL062097.
- 489 Burns, R.G. (1993) *Mineralogical Applications of Crystal Field Theory*, 563 p. Cambridge
490 University Press.
- 491 Caracas, R. (2010) Spin and structural transitions in AlFeO_3 and FeAlO_3 perovskite and post-
492 perovskite. *Physics of the Earth and Planetary Interiors*.
- 493 Catalli, K., Shim, S.-H., Prakapenka, V.B., Zhao, J., Sturhahn, W., Chow, P., Xiao, Y., Liu, H.,
494 Cynn, H., and Evans, W.J. (2010) Spin state of ferric iron in MgSiO_3 perovskite and its
495 effect on elastic properties. *Earth and Planetary Science Letters*, 289, 68–75.
- 496 Catalli, K., Shim, S.-H., Dera, P., Prakapenka, V.B., Zhao, J., Sturhahn, W., Chow, P., Xiao, Y.,
497 Cynn, H., and Evans, W.J. (2011) Effects of the Fe^{3+} spin transition on the properties of
498 aluminous perovskite—New insights for lower-mantle seismic heterogeneities. *Earth and*
499 *Planetary Science Letters*, 310, 293–302.
- 500 Dorfman, S.M., and Duffy, T.S. (2014) Effect of Fe-enrichment on seismic properties of
501 perovskite and post-perovskite in the deep lower mantle. *Geophysical Journal*
502 *International*, 197, 910–919.
- 503 Dorfman, S.M., Shieh, S.R., Meng, Y., Prakapenka, V.B., and Duffy, T.S. (2012) Synthesis and
504 equation of state of perovskites in the $(\text{Mg, Fe})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ system to 177 GPa. *Earth and*
505 *Planetary Science Letters*, 357–358, 194–202.
- 506 Dorfman, S.M., Meng, Y., Prakapenka, V.B., and Duffy, T.S. (2013) Effects of Fe-enrichment
507 on the equation of state and stability of $(\text{Mg,Fe})\text{SiO}_3$ perovskite. *Earth and Planetary*
508 *Science Letters*, 361, 249–257.
- 509 Dorfman, S.M., Dutton, S.E., Potapkin, V., Chumakov, A., Rueff, J.-P., Chow, P., Xiao, Y.,
510 Cava, R.J., Duffy, T.S., McCammon, C.A., and others (2016) Electronic transitions of
511 iron in almandine-composition glass to 91 GPa. *American Mineralogist*, 101.

32

Revision 1

- 512 Dyar, M.D., Agresti, D.G., Schaefer, M.W., Grant, C.A., and Sklute, E.C. (2006) Mössbauer
513 spectroscopy of Earth and planetary materials. *Annual Review of Earth and Planetary*
514 *Sciences*, 34, 83–125.
- 515 Fei, Y., Virgo, D., Mysen, B.O., Wang, Y., and Mao, H. -k. (1994) Temperature-dependent
516 electron delocalization in (Mg,Fe)SiO₃ perovskite. *American Mineralogist*, 79, 826–837.
- 517 Fei, Y., Wang, Y., and Finger, L.W. (1996) Maximum solubility of FeO in (Mg,Fe)SiO₃-
518 perovskite as a function of temperature at 26 GPa: Implication for FeO content in the
519 lower mantle. *Journal of Geophysical Research*, 101, 11525–11530.
- 520 Frost, D.J., and Langenhorst, F. (2002) The effect of Al₂O₃ on Fe–Mg partitioning between
521 magnesiowüstite and magnesium silicate perovskite. *Earth and Planetary Science Letters*,
522 199, 227–241.
- 523 Frost, D.J., and McCammon, C.A. (2008) The redox state of Earth’s mantle. *Annual Review of*
524 *Earth and Planetary Sciences*, 36, 389–420.
- 525 Frost, D.J., Liebske, C., Langenhorst, F., McCammon, C.A., Trønnes, R.G., and Rubie, D.C.
526 (2004) Experimental evidence for the existence of iron-rich metal in the Earth’s lower
527 mantle. *Nature*, 428, 409–412.
- 528 Grand, S.P. (2002) Mantle Shear–Wave Tomography and the Fate of Subducted Slabs.
529 *Philosophical Transactions of the Royal Society of London A*, 360, 2475–91.
- 530 Greenwood, N.N., and Gibb, T.C. (1971) Low-spin Iron(II) and Iron(III) Complexes. In
531 *Mössbauer Spectroscopy* pp. 169–193. Springer Netherlands.
- 532 Grüninger, H., Liu, Z., Siegel, R., Ballaran, T.B., Katsura, T., Senker, J., and Frost, D.J. (2019)
533 Oxygen Vacancy Ordering in Aluminous Bridgmanite in the Earth’s Lower Mantle.
534 *Geophysical Research Letters*, 46, 8731–8740.
- 535 Gu, C., Catalli, K., Grocholski, B., Gao, L., Alp, E., Chow, P., Xiao, Y., Cynn, H., Evans, W.J.,
536 and Shim, S.-H. (2012) Electronic structure of iron in magnesium silicate glasses at high
537 pressure. *Geophysical Research Letters*, 39.
- 538 Gu, T., Li, M., McCammon, C., and Lee, K.K.M. (2016) Redox-induced lower mantle density
539 contrast and effect on mantle structure and primitive oxygen. *Nature Geoscience*, 9, 723–
540 727.
- 541 Hsu, H., Umemoto, K., Blaha, P., and Wentzcovitch, R.M. (2010) Spin states and hyperfine
542 interactions of iron in (Mg,Fe)SiO₃ perovskite under pressure. *Earth and Planetary*
543 *Science Letters*, 294, 19–26.

Revision 1

- 544 Hsu, H., Blaha, P., Cococcioni, M., and Wentzcovitch, R.M. (2011) Spin-State Crossover and
545 Hyperfine Interactions of Ferric Iron in MgSiO₃ Perovskite. *Physical Review Letters*,
546 106, 118501.
- 547 Hu, Q., Kim, D.Y., Yang, W., Yang, L., Meng, Y., Zhang, L., and Mao, H.-K. (2016) FeO₂ and
548 FeOOH under deep lower-mantle conditions and Earth's oxygen-hydrogen cycles.
549 *Nature*, 534, 241–244.
- 550 Hummer, D.R., and Fei, Y. (2012) Synthesis and crystal chemistry of Fe³⁺-bearing
551 (Mg,Fe³⁺)(Si,Fe³⁺)O₃ perovskite. *American Mineralogist*, 97, 1915–1921.
- 552 Ishii, M., and Tromp, J. (1999) Normal-Mode and Free-Air Gravity Constraints on Lateral
553 Variations in Velocity and Density of Earth's Mantle. *Science*, 285, 1231–1236.
- 554 Ismailova, L., Bykova, E., Bykov, M., Cerantola, V., McCammon, C., Ballaran, T.B., Bobrov,
555 A., Sinmyo, R., Dubrovinskaia, N., Glazyrin, K., and others (2016) Stability of Fe,Al-
556 bearing bridgmanite in the lower mantle and synthesis of pure Fe-bridgmanite. *Science*
557 *Advances*, 2, e1600427.
- 558 Jackson, J.M., Sturhahn, W., Shen, G., Zhao, J., Hu, M.Y., Errandonea, D., Bass, J.D., and Fei,
559 Y. (2005) A synchrotron Mössbauer spectroscopy study of (Mg,Fe)SiO₃ perovskite up to
560 120 GPa. *American Mineralogist*, 90, 199–205.
- 561 Keppler, H., Dubrovinsky, L.S., Narygina, O., and Kantor, I. (2008) Optical Absorption and
562 Radiative Thermal Conductivity of Silicate Perovskite to 125 Gigapascals. *Science*, 322,
563 1529–1532.
- 564 Kuppenko, I., McCammon, C.A., Sinmyo, R., Cerantola, V., Potapkin, V., Chumakov, A.I.,
565 Kantor, A.P., Rüffer, R., and Dubrovinsky, L.S. (2015) Oxidation state of the lower
566 mantle: In situ observations of the iron electronic configuration in bridgmanite at extreme
567 conditions. *Earth and Planetary Science Letters*, 423, 78–86.
- 568 Lau, H.C.P., Mitrovica, J.X., Davis, J.L., Tromp, J., Yang, H.-Y., and Al-Attar, D. (2017) Tidal
569 tomography constrains Earth's deep-mantle buoyancy. *Nature*, 551, 321–326.
- 570 Lin, J.-F., Speziale, S., Mao, Z., and Marquardt, H. (2013) Effects of the electronic spin
571 transitions of iron in lower mantle minerals: Implications for deep mantle geophysics and
572 geochemistry. *Reviews of Geophysics*, 51.
- 573 Liu, J., Li, J., Hrubiak, R., and Smith, J.S. (2016) Origins of ultralow velocity zones through
574 slab-derived metallic melt. *Proceedings of the National Academy of Sciences*, 113, 5547–
575 5551.
- 576 Liu, J., Hu, Q., Kim, D.Y., Wu, Z., Wang, W., Xiao, Y., Chow, P., Meng, Y., Prakapenka, V.B.,
577 Mao, H.-K., and others (2017) Hydrogen-bearing iron peroxide and the origin of
578 ultralow-velocity zones. *Nature*, 551, 494.

Revision 1

- 579 Liu, J., Dorfman, S.M., Zhu, F., Li, J., Wang, Y., Zhang, D., Xiao, Y., Bi, W., and Alp, E.E.
580 (2018) Valence and spin states of iron are invisible in Earth's lower mantle. *Nature*
581 *Communications*, 9, 1284.
- 582 Liu, Z., Boffa Ballaran, T., Huang, R., Frost, D.J., and Katsura, T. (2019) Strong correlation of
583 oxygen vacancies in bridgmanite with Mg/Si ratio. *Earth and Planetary Science Letters*,
584 523, 115697.
- 585 Lobanov, S.S., Holtgrewe, N., Lin, J.-F., and Goncharov, A.F. (2017) Radiative conductivity and
586 abundance of post-perovskite in the lowermost mantle. *Earth and Planetary Science*
587 *Letters*, 479, 43–49.
- 588 Long, Y.W., Hayashi, N., Saito, T., Azuma, M., Muranaka, S., and Shimakawa, Y. (2009)
589 Temperature-induced A–B intersite charge transfer in an A-site-ordered LaCu₃Fe₄O₁₂
590 perovskite. *Nature*, 458, 60–63.
- 591 Mao, H.-k., Xu, J., and Bell, P.M. (1986) Calibration of the Ruby Pressure Gauge to 800 kbar
592 Under Quasi-Hydrostatic Conditions. *Journal of Geophysical Research*, 91, 4673–4676.
- 593 Mao, W.L., Mao, H., Sturhahn, W., Zhao, J., Prakapenka, V.B., Meng, Y., Shu, J., Fei, Y., and
594 Hemley, R.J. (2006) Iron-rich post-perovskite and the origin of ultralow-velocity zones.
595 *Science*, 312, 564–565.
- 596 Mao, Z., Lin, J.-F., Yang, J., Inoue, T., and Prakapenka, V.B. (2015) Effects of the Fe³⁺ spin
597 transition on the equation of state of bridgmanite. *Geophysical Research Letters*, 42,
598 2015GL064400.
- 599 Mattson, S.M., and Rossman, G.R. (1987) Identifying characteristics of charge transfer
600 transitions in minerals. *Physics and Chemistry of Minerals*, 14, 94–99.
- 601 McCammon, C., Glazyrin, K., Kantor, A., Kantor, I., Kuppenko, I., Narygina, O., Potapkin, V.,
602 Prescher, C., Sinmyo, R., Chumakov, A., and others (2013) Iron spin state in silicate
603 perovskite at conditions of the Earth's deep interior. *High Pressure Research*, 0, 1–10.
- 604 Pasternak, M.P., Xu, W.M., Rozenberg, G.Kh., and Taylor, R.D. (2002) Electronic, Magnetic
605 and Structural Properties of the RFeO₃ Antiferromagnetic-Perovskites at Very High
606 Pressures. In *Symposium D – Perovskite Materials Vol. 718*.
- 607 Piet, H., Badro, J., Nabiei, F., Dennenwaldt, T., Shim, S.-H., Cantoni, M., Hébert, C., and Gillet,
608 P. (2016) Spin and valence dependence of iron partitioning in Earth's deep mantle.
609 *Proceedings of the National Academy of Sciences*, 201605290.
- 610 Potapkin, V., Chumakov, A.I., Smirnov, G.V., Celse, J.-P., Rüffer, R., McCammon, C., and
611 Dubrovinsky, L. (2012) The ⁵⁷Fe Synchrotron Mössbauer Source at the ESRF. *Journal of*
612 *Synchrotron Radiation*, 19, 559–569.

Revision 1

- 613 Potapkin, V., McCammon, C.A., Glazyrin, K.D., Kantor, A.P., Kuppenko, I., Prescher, C.,
614 Sinmyo, R., Smirnov, G.V., Chumakov, A.I., Ruffer, R., and others (2013) Effect of iron
615 oxidation state on the electrical conductivity of the Earth's lower mantle. *Nature*
616 *Communications*, 4, 1427.
- 617 Prescher, C., McCammon, C., and Dubrovinsky, L. (2012) MossA: a program for analyzing
618 energy-domain Mössbauer spectra from conventional and synchrotron sources. *Journal of*
619 *Applied Crystallography*, 45, 329–331.
- 620 Prescher, C., Weigel, C., McCammon, C.A., Narygina, O., Potapkin, V., Kuppenko, I., Sinmyo,
621 R., Chumakov, A.I., and Dubrovinsky, L.S. (2014) Iron spin state in silicate glass at high
622 pressure: Implications for melts in the Earth's lower mantle. *Earth and Planetary Science*
623 *Letters*, 385, 130–136.
- 624 Ricolleau, A., Fei, Y., Cottrell, E., Watson, H., Deng, L., Zhang, L., Fiquet, G., Auzende, A.-L.,
625 Roskosz, M., Morard, G., and others (2009) Density profile of pyrolite under the lower
626 mantle conditions. *Geophysical Research Letters*, 36, L06302.
- 627 Rivers, M., Prakapenka, V., Kubo, A., Pullins, C., Holl, C.M., and Jacobsen, S.D. (2008) The
628 COMPRES/GSECARS gas-loading system for diamond anvil cells at the Advanced
629 Photon Source. *High Pressure Research*, 28, 273–292.
- 630 Rost, S., Garnero, E.J., Williams, Q., and Manga, M. (2005) Seismological constraints on a
631 possible plume root at the core-mantle boundary. *Nature*, 435, 666–669.
- 632 Ruffer, R., and Chumakov, A.I. (1996) Nuclear Resonance Beamline at ESRF. *Hyperfine*
633 *Interactions*, 97–98, 589–604.
- 634 Shim, S.-H., Grocholski, B., Ye, Y., Alp, E.E., Xu, S., Morgan, D., Meng, Y., and Prakapenka,
635 V.B. (2017) Stability of ferrous-iron-rich bridgmanite under reducing midmantle
636 conditions. *Proceedings of the National Academy of Sciences*, 201614036.
- 637 Shukla, G., Cococcioni, M., and Wentzcovitch, R.M. (2016) Thermoelasticity of Fe³⁺- and Al-
638 bearing bridgmanite: Effects of iron spin crossover. *Geophysical Research Letters*, 43,
639 5661–5670.
- 640 Sinmyo, R., Pesce, G., Greenberg, E., McCammon, C., and Dubrovinsky, L. (2014) Lower
641 mantle electrical conductivity based on measurements of Al, Fe-bearing perovskite under
642 lower mantle conditions. *Earth and Planetary Science Letters*, 393, 165–172.
- 643 Tange, Y., Takahashi, E., Nishihara, Y., Funakoshi, K., and Sata, N. (2009) Phase relations in
644 the system MgO-FeO-SiO₂ to 50 GPa and 2000°C: An application of experimental
645 techniques using multianvil apparatus with sintered diamond anvils. *Journal of*
646 *Geophysical Research*, 114, B02214.

Revision 1

- 647 Tateno, S., Hirose, K., Sata, N., and Ohishi, Y. (2007) Solubility of FeO in (Mg,Fe)SiO₃
648 perovskite and the post-perovskite phase transition. *Physics of the Earth and Planetary*
649 *Interiors*, 160, 319–325.
- 650 Weber, J.K.R., Hampton, D.S., Merkle, D.R., Rey, C.A., Zatarski, M.M., and Nordine, P.C.
651 (1994) Aero-acoustic levitation: A method for containerless liquid-phase processing at
652 high temperatures. *Review of Scientific Instruments*, 65, 456–465.
- 653 Wicks, J.K., Jackson, J.M., and Sturhahn, W. (2010) Very low sound velocities in iron-rich
654 (Mg,Fe)O: Implications for the core-mantle boundary region. *Geophysical Research*
655 *Letters*, 37, 5 PP.
- 656 Williams, Q., and Garnero, E.J. (1996) Seismic Evidence for Partial Melt at the Base of Earth's
657 Mantle. *Science*, 273, 1528–1530.
- 658 Xu, Y., and McCammon, C.A. (2002) Evidence for ionic conductivity in lower mantle
659 (Mg,Fe)(Si,Al)O₃ perovskite. *Journal of Geophysical Research*, 107.
- 660