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► To cite this version:

C. Mccammon, L. Dubrovinsky, O. Narygina, I. Kantor, X. Wu, et al.. Low-spin Fe in silicate perovskite and a possible layer at the base of the lower mantle. *Physics of the Earth and Planetary Interiors*, 2010, 180 (3-4), pp.215. 10.1016/j.pepi.2009.10.012 . hal-00644709

HAL Id: hal-00644709

<https://hal.science/hal-00644709>

Submitted on 25 Nov 2011

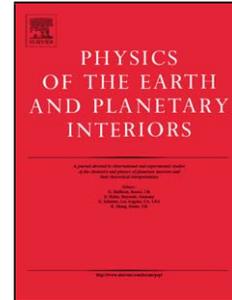
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Accepted Manuscript

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PII: S0031-9201(09)00222-2
DOI: doi:10.1016/j.pepi.2009.10.012
Reference: PEPI 5220

To appear in: *Physics of the Earth and Planetary Interiors*

Received date: 2-6-2009
Revised date: 6-10-2009
Accepted date: 29-10-2009

Please cite this article as: McCammon, C., Dubrovinsky, L., Narygina, O., Kantor, I., Wu, X., Glazyrin, K., Sergueev, I., Chumakov, A.I., Low-spin Fe²⁺ in silicate perovskite and a possible layer at the base of the lower mantle, *Physics of the Earth and Planetary Interiors* (2008), doi:10.1016/j.pepi.2009.10.012

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1 **Low-spin Fe²⁺ in silicate perovskite and a possible layer at the base of the lower**
2 **mantle**

3

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15

16 **Abstract**

17 We investigated the spin state of iron in Mg_{0.82}Fe_{0.18}SiO₃ silicate perovskite using
18 Mössbauer spectroscopy and nuclear forward scattering (NFS) at pressures up to 130
19 GPa and temperatures up to 1000 K. Majorite starting material was loaded into
20 diamond anvil cells in three separate experiments, and transformed to silicate
21 perovskite through laser heating. We found, in agreement with previous work, the
22 predominance of a component with high isomer shift (~ 1 mm/s relative to α -Fe) and
23 high quadrupole splitting (QS) (> 4 mm/s) in Mössbauer and NFS spectra up to 115
24 GPa at room temperature, and in accordance with previous work this component was
25 assigned to intermediate-spin Fe²⁺. At higher pressures, the intensity of the high QS
26 component in the silicate perovskite spectrum decreased, while the intensity of a new
27 component with low isomer shift (~ 0 mm/s relative to α -Fe) and low quadrupole
28 splitting (< 0.5 mm/s) increased. This new component was assigned to low-spin Fe²⁺,
29 and its intensity increased with both increasing pressure and increasing temperature:
30 at 120 GPa and 1000 K all Fe²⁺ was in the low-spin state. X-ray diffraction data
31 showed well crystallised perovskite in all runs, and although the stable phase above ~
32 110 GPa is expected to be post-perovskite, sluggish transition kinetics likely
33 preserved the perovskite phase in a metastable state. Our results combined with data
34 in the literature and thermodynamic and topological considerations suggest that there

35 may be a region where silicate perovskite containing low-spin Fe^{2+} is stable, which
36 coincides with predicted pressure-temperature conditions near the D'' layer.

37

38 Keywords: spin transition; D'' layer; perovskite; post-perovskite; Mössbauer
39 spectroscopy, nuclear forward scattering

40

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41 1. Introduction

42 The base of the lower mantle shows many anomalous properties, a number of
43 which have been explained by the transition of $(\text{Mg,Fe})(\text{Si,Al})\text{O}_3$ perovskite to a post-
44 perovskite structure (e.g., Hirose, 2006). Other properties, however, remain
45 unexplained (e.g., large P-wave velocity discontinuities, the sharpness of the D''
46 discontinuity in some regions, high electrical conductivity and the nature of ultralow
47 velocity layers). One possibility that has been considered to account for these
48 observations is lateral variations in chemistry at the base of the lower mantle (Hirose
49 et al., 2006). However there is another mechanism that can change physical and
50 chemical properties of minerals, namely spin-pairing transitions of iron. Such
51 transitions were predicted to occur within the Earth's interior nearly 50 years ago, but
52 only in the past few years has direct experimental evidence for such transitions at
53 lower mantle conditions been reported. For $(\text{Mg,Fe})\text{O}$, both experimental and
54 computational results confirm a high-spin to low-spin transition of Fe^{2+} that is
55 expected to occur in the middle part of the lower mantle (e.g., Lin and Tsuchiya, 2008
56 and references therein). For $(\text{Mg,Fe})(\text{Si,Al})\text{O}_3$ perovskite, previous experimental
57 results show a high-spin to intermediate-spin transition of Fe^{2+} that is expected to
58 occur at the top of the lower mantle, with Fe^{2+} remaining in the intermediate-spin state
59 throughout the bulk of the lower mantle (McCammon et al., 2008; Lin et al., 2008).
60 Fe^{2+} in $(\text{Mg,Fe})(\text{Si,Al})\text{O}_3$ post-perovskite is also observed to be in the intermediate-
61 spin state (Lin et al., 2008). However Badro et al. (2004) observed that iron in
62 $(\text{Mg,Fe})\text{SiO}_3$ perovskite was in the low-spin state above 120 GPa at room
63 temperature, although since the post-perovskite phase had not been discovered when
64 the experiments were performed, the structure of the sample was not investigated. To
65 address the question of whether low-spin Fe^{2+} is stable in silicate perovskite, we
66 conducted a combined nuclear forward scattering (NFS) and conventional Mössbauer
67 experiment on $(\text{Mg,Fe})\text{SiO}_3$ perovskite at high pressure and high temperature.

68

69 2. Experimental methods

70 The starting material for the present study was polycrystalline majorite with
71 composition $\text{Mg}_{0.82}\text{Fe}_{0.18}\text{SiO}_3$ (~ 90% enriched in ^{57}Fe) (sample U1219; McCammon
72 and Ross, 2003). The majorite sample was synthesised using a multianvil press;
73 further details of synthesis conditions and sample characterisation can be found in
74 McCammon and Ross (2003). We synthesised silicate perovskite from majorite using

75 a laser-heated diamond anvil cell (DAC) in three different experiments, and carried
76 out Mössbauer spectroscopy and/or NFS measurements over a range of different
77 pressures and temperatures. The run conditions are summarised in Table 1.

78 Run #1 was carried out at the European Synchrotron Radiation Facility (ESRF)
79 during experiment HE-2750. The majorite sample was loaded together with a small
80 ruby chip and a small (about 5 μm in diameter) piece of gold (used as a pressure
81 marker) with thin layers of SiO_2 (which act as a thermal insulator during laser
82 heating) into a Be gasket indented to $\sim 20 \mu\text{m}$ thickness and drilled with a $\sim 80 \mu\text{m}$
83 hole. The gasket was mounted within a panoramic-type DAC, designed and
84 constructed at Bayerisches Geoinstitut for nuclear inelastic scattering (NIS)
85 experiments, and equipped with bevelled 120 μm diameter culet gem-quality
86 diamonds. The majorite sample was compressed to 33 GPa, and then heated with a
87 double-sided near infrared laser ($\lambda = 1064 \text{ nm}$) at temperatures between 1800 and
88 2000 K to transform the sample to silicate perovskite. Pressure was increased
89 incrementally, with annealing after each increase of pressure using an infrared laser at
90 low power (temperature peak around 1500 K) to relieve stress. The pressure was
91 measured after each NFS spectrum using an online MAR CCD detector and
92 calculated based on the equation of state of gold (Fei et al., 2007). NIS data were also
93 collected during this experiment, but the results will be reported elsewhere.

94 Run #2 was carried out mainly at Bayerisches Geoinstitut, but with laser heating at
95 ESRF and X-ray diffraction collected at the Advanced Photon Source (APS), USA.
96 The majorite sample with thin layers of SiO_2 was loaded with a small ruby chip into a
97 Re gasket preindented to about 30 μm thickness and drilled with a $\sim 60 \mu\text{m}$ diameter
98 hole, and mounted in a four-pin modified Merrill-Bassett DAC with 120 μm diameter
99 culet gem-quality bevelled diamonds. The majorite sample was compressed in several
100 steps to a pressure within the post-perovskite stability field, with annealing after each
101 increase of pressure using an infrared laser at low power to relieve stress. At the
102 highest pressure ($145 \pm 10 \text{ GPa}$ according to ruby fluorescence and the Raman shift of
103 diamond) the sample was heated with a Nd:YLF laser ($\lambda = 1064 \text{ nm}$) to transform the
104 sample to silicate perovskite. X-ray diffraction data collected on beamline IDD-13D
105 at APS showed the sample to consist entirely of silicate perovskite at a pressure of
106 $125 \pm 5 \text{ GPa}$ (based on the equation of state of silicate perovskite determined using
107 the same methods; McCammon et al., 2008), with no evidence for a post-perovskite
108 phase.

109 Run #3 was carried out primarily at ESRF during experiment HE-2750. Majorite
110 was loaded together with a small ruby chip, a small piece of gold and layers of SiO₂
111 into a Re gasket as for run #1, and mounted in a four-pin modified Merrill-Bassett
112 DAC with 200 μm diameter culet gem-quality bevelled diamonds that was fitted with
113 an external resistive heater (Dubrovinskaia and Dubrovinsky, 2003). The majorite
114 sample was compressed directly to 120 ± 5 GPa, where it was then heated with a near
115 infrared laser to transform the sample to silicate perovskite. Subsequently the
116 temperature was increased using the resistive heater, and the tension screws of the
117 DAC were tightened to maintain the pressure at ~ 120 GPa during heating.
118 Temperature was measured continuously using a S-type thermocouple mounted next
119 to the diamonds, while pressure was measured both before and after the NFS data
120 collection using ruby fluorescence corrected for temperature (Rekhi et al., 1999). A
121 final NFS spectrum was collected after cooling to room temperature, and a Mössbauer
122 spectrum was collected after return to Bayerisches Geoinstitut. High-resolution X-ray
123 diffraction data were recorded on beam line ID09 at ESRF, and showed the sample to
124 consist only of silicate perovskite plus a small amount of gold and SiO₂ (Fig. 1). The
125 pressure was calculated from the X-ray diffraction pattern to be 130 ± 5 GPa based on
126 the gold equation of state (Fei et al., 2007). The higher pressure on cooling likely
127 resulted from the tightening of the tension screws during heating to maintain the
128 pressure.

129 ⁵⁷Fe Mössbauer spectra were recorded at room temperature in transmission mode
130 on a constant acceleration Mössbauer spectrometer with a nominal 370 MBq ⁵⁷Co
131 high specific activity source in a 12 μm thick Rh matrix. The methodology of high-
132 pressure Mössbauer measurements is further described in McCammon et al. (1992)
133 and Kantor et al. (2004). The velocity scale was calibrated relative to 25 μm thick α-
134 Fe foil using the positions certified for (former) National Bureau of Standards
135 standard reference material no. 1541; line widths of 0.36 mm/s for the outer lines of
136 α-Fe were obtained at room temperature. The dimensionless effective thickness for
137 the majorite sample measured in air was 2 (~ 5 mg unenriched Fe/cm²), while for the
138 majorite/perovskite in the DAC it was 24 (~ 52 mg unenriched Fe/cm²). Spectra took
139 4 to 10 days each to collect. Mössbauer spectra were fitted to Lorentzian lineshapes in
140 the thin-absorber approximation using conventional constraints (equal quadrupole
141 component widths and areas) using the commercially available fitting program
142 NORMOS written by R.A. Brand (distributed by Wissenschaftliche Elektronik

143 GmbH, Germany). To explore the influence of thickness effects, we additionally used
144 a full transmission integral to fit the Mössbauer data, but found that hyperfine
145 parameters and relative areas were unchanged within experimental uncertainty.

146 NFS data were collected on beamline ID18 at the ESRF during operation in 4-
147 bunch mode, with the beam focused to ca. $8 \mu\text{m} \times 13 \mu\text{m}$ using a Kirkpatrick-Baez
148 mirror. Further details of the beamline are given in Ruffer and Chumakov (1996). All
149 of the NFS spectra in run #3 and several of the spectra in run #1 were taken with the
150 DAC in “vertical” geometry, i.e., with the plane of the gasket perpendicular to the X-
151 ray beam. For the NFS spectra in run #1 that were taken in “horizontal” geometry, the
152 X-ray beam passed through the Be gasket before reaching the sample. Each NFS
153 spectrum took 1-2 hours to collect, and data were fitted using the program MOTIF
154 (Shvyd’ko, 2000).

155 High-resolution X-ray diffraction data were collected at beamline ID09 at ESRF
156 and beamline 13-ID-D at APS using the methods described in McCammon et al.
157 (2008). X-ray patterns were analysed by Rietveld refinement using the GSAS package
158 (Larsen and von Dreele, 1985).

159

160 **3. Results**

161 The NFS and Mössbauer spectra are illustrated in Figs. 2-4. In fitting the NFS
162 spectra, our goal was to extract only the parameters that could be robustly derived
163 from the data. We therefore restricted the number of sites to two, and varied only the
164 following parameters during the fit (number of parameters indicated in parentheses):
165 vertical scaling factor (1), Lorentzian broadening of all transitions (1), relative site
166 proportion (1), relative isomer shift between sites (1), and quadrupole splitting of each
167 site (2). Despite the limited parameter set, we were able to obtain reasonable fits for
168 all spectra. Our goal was the same in fitting the Mössbauer spectra, but the energy-
169 domain experiment enabled a larger number of parameters to be robustly determined
170 from the data (although energy resolution of NFS is formally ideal, in practice it is
171 limited by the time window of the 4-bunch mode = 704 ns, providing $\Delta E = \sim 0.1 \Gamma_0$).
172 The parameters determined from the Mössbauer spectra were: baseline (2); linewidth,
173 isomer shift, quadrupole splitting and relative area for each site (4 for each site).

174 The zero-pressure NFS spectrum of majorite (Fig. 2a) is dominated by quantum
175 beats with high frequency that arise from high-spin Fe^{2+} on the dodecahedral site,
176 which is seen in the zero-pressure Mössbauer spectrum as a quadrupole doublet with

177 large splitting (Fig. 3a). The minor quadrupole doublets in the Mössbauer spectrum
178 corresponding to high-spin Fe^{2+} on the octahedral site ($\sim 10\%$) and to high-spin Fe^{3+}
179 ($15\text{-}20\%$) (Fig. 3a) cause small modulations of the dominant quantum beats in the
180 NFS spectrum (Fig. 2a), but the overall structure of the spectrum remains the same.
181 The transition from majorite to silicate perovskite causes a significant change in the
182 NFS spectrum (Fig. 2c), which resembles those reported at similar conditions by
183 McCammon et al. (2008). There are several contributions dominated by a mixture of
184 high-spin Fe^{2+} and intermediate-spin Fe^{2+} , both occupying the A site (McCammon et
185 al., 2008). Since the high-spin Fe^{2+} contribution consists of more than one component,
186 the use of only two components (one high-spin Fe^{2+} and one intermediate-spin Fe^{2+})
187 to fit the spectrum produces only a moderately good fit to the data (Fig. 2c). However
188 the fit improves as the relative proportion of the high-quadrupole splitting component
189 assigned to intermediate-spin Fe^{2+} increases with pressure (Fig. 2d), and at 115 GPa
190 intermediate-spin Fe^{2+} accounts for nearly all of the spectrum (Fig. 2e). There is likely
191 still a minor contribution from Fe^{3+} , which for this composition is estimated to be 15-
192 20% $\text{Fe}^{3+}/\Sigma\text{Fe}$ (McCammon et al., 2004). However previous work has shown that the
193 proportion of Fe^{3+} does not change significantly with pressure (Jackson et al., 2005;
194 McCammon et al., 2008), and the results of the current study are also consistent with
195 this observation.

196 The Mössbauer spectrum for majorite in the DAC is significantly reduced in
197 quality from the zero-pressure spectrum (Fig. 3a) due to solid angle reduction and
198 absorption by the diamonds; however the dominant quadrupole doublet due to high-
199 spin Fe^{2+} on the dodecahedral site can still be resolved (Fig. 3b). After laser heating at
200 ~ 145 GPa to transform the sample to silicate perovskite (structure confirmed by X-
201 ray diffraction), there is a clear change in the spectrum (Fig. 3c). The quadrupole
202 splitting of the dominant doublet increases, consistent with the presence of
203 intermediate-spin Fe^{2+} , and a second component appears with significantly lower
204 quadrupole splitting and isomer shift.

205 The presence of the low quadrupole splitting component is also observed when
206 majorite is transformed through laser heating to silicate perovskite at 120 GPa (Fig.
207 4). In the NFS spectra the presence of the high frequency quantum beats
208 corresponding to intermediate-spin Fe^{2+} can still be observed (Fig. 4a), but they are
209 superimposed on a relatively monotonous downward slope arising from a component
210 with nearly zero quadrupole splitting. The proportion of the low quadrupole splitting

211 component grows with increasing temperature (as seen by the disappearance of the
212 high frequency quantum beats), and at 1000 K the spectrum consists of only low
213 quadrupole splitting components. With the disappearance of intermediate-spin Fe^{2+} in
214 Figs. 4d and 4e, the presence of a minor amount of a second component with low
215 quadrupole splitting can be resolved, which likely corresponds to Fe^{3+} . The
216 Mössbauer spectrum taken of the same sample at the same conditions as Fig. 4e
217 shows the low quadrupole splitting component as a singlet with extremely low isomer
218 shift (Fig. 3d), where the data scatter is too high for a Fe^{3+} component with ~ 20%
219 abundance to be resolved. The X-ray diffraction pattern taken of the same sample as
220 Fig. 3d shows only the *Pbnm* perovskite structure, confirming that the new component
221 arises only from an electronic transition (Fig. 1).

222 The variation of hyperfine parameters with pressure shows consistent trends for the
223 different components in the Mössbauer and NFS spectra (Fig. 5). The most notable
224 feature is the appearance above 120 GPa of the component with low isomer shift and
225 quadrupole splitting. The proportion of this component increases correspondingly
226 with the decrease of intermediate-spin Fe^{2+} , and there is a large difference in isomer
227 shift between this component and intermediate-spin Fe^{2+} (Fig. 5). The most plausible
228 assignment for this component is low-spin Fe^{2+} in the A site of silicate perovskite,
229 which is predicted to have both low isomer shift and low quadrupole splitting (e.g., Li
230 et al., 2006 and references therein). The proportion of low-spin Fe^{2+} in silicate
231 perovskite increases with both increasing pressure and increasing temperature (Fig.
232 6).

233 The assignment of the low quadrupole splitting component to low-spin Fe^{2+} is also
234 consistent with X-ray emission data which show a nearly complete disappearance of
235 the $K\beta'$ satellite peak above 120 GPa, indicating the complete spin pairing of $3d$
236 electrons (the residual intensity can be accounted for by a small amount of Fe^{3+})
237 (Badro et al., 2004). Electrical conductivity data of $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$ perovskite also
238 support the interpretation of low-spin Fe^{2+} . The conductivity drop of more than two
239 orders of magnitude between 58 and 104 GPa (Ohta et al., 2008) follows the expected
240 behaviour of a transition from two unpaired electrons (intermediate-spin Fe^{2+}) to none
241 (low-spin Fe^{2+}).

242 Low-spin Fe^{2+} has similar isomer shift and quadrupole splitting values to Fe^{3+} (Fig.
243 5), suggesting an alternative interpretation, namely that the low quadrupole splitting
244 component in Fig. 4 could be due to Fe^{3+} . We consider such a possibility to be

245 unlikely, however. The growth in intensity of the low quadrupole splitting component
 246 is proportional to the decrease of the intermediate-spin Fe^{2+} component, indicating
 247 that both take part in the transition. We can rule out that oxidation of Fe^{2+} to Fe^{3+}
 248 takes place as part of a chemical reaction, because we found the transition to be fully
 249 reversible with both pressure and temperature. It is also unlikely that intervalence
 250 charge transfer takes place, such as in FeTiO_3 at high pressure ($\text{Fe}^{2+} + \text{Ti}^{4+} \leftrightarrow \text{Fe}^{3+} +$
 251 Ti^{3+} ; Seda and Hearne, 2004) or $(\text{Mg,Fe,Cr})\text{O}$ at high temperature ($\text{Fe}^{2+} + \text{Cr}^{3+} \leftrightarrow$
 252 $\text{Fe}^{3+} + \text{Cr}^{2+}$; Eeckhout et al., 2007), since there are no other species in our experiments
 253 that could participate in coupled electron transfer. We can also rule out that the low
 254 quadrupole splitting component could arise through the reaction $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{Fe}^0$ as
 255 recently reported by Jackson et al. (2009) for laser-heated DAC experiments with
 256 $(\text{Mg,Fe})\text{SiO}_3$ post-perovskite, because we found the transition to be fully reversible
 257 with both pressure and temperature.

258 Previous NFS studies of $(\text{Mg,Fe})\text{SiO}_3$ and $(\text{Mg,Fe})(\text{Si,Al})\text{O}_3$ perovskite have
 259 suggested that Fe^{3+} may undergo a pressure-induced spin transition (Jackson et al.,
 260 2005; Li et al., 2006). However the samples used in these studies contained
 261 appreciable amounts of Fe^{3+} ($\text{Fe}^{3+}/\Sigma\text{Fe} \sim 0.4$ and 0.5 for the Jackson et al. and the Li
 262 et al. samples, respectively) compared to the present study ($\text{Fe}^{3+}/\Sigma\text{Fe} \sim 0.15$ - 0.2). Due
 263 to the low intensity of the Fe^{3+} component in our data, we cannot resolve the
 264 behaviour of Fe^{3+} unambiguously; hence the question of a spin transition in Fe^{3+} must
 265 remain open. We note, however, that our conclusions are independent of the
 266 behaviour of Fe^{3+} , and they would not change if there were a spin transition in that
 267 component.

268 Umemoto et al. (2008) suggested that sample annealing could enhance cation
 269 diffusion and clustering of irons at high pressure, which would promote the stability
 270 of low-spin Fe^{2+} in silicate perovskite. However since our experiment involving
 271 external heating (run #3) was conducted after the sample was laser heated *at the same*
 272 *pressure* to synthesise silicate perovskite, the degree of cation order would not have
 273 changed significantly during external heating. We therefore maintain that the spin
 274 state recorded by our measurements at 120 GPa and 1000 K represents close to
 275 equilibrium for those conditions.

276 Recent computational studies of iron in silicate perovskite have reported a
 277 pressure-induced high-spin to low-spin transition of Fe^{2+} in the A site (e.g.,
 278 Stackhouse et al., 2007; Bengston et al., 2008; Umemoto et al., 2008). Pressure

279 determinations for the spin transition of silicate perovskite for the iron composition
280 used in the present study range from ~ 60 GPa to ~ 200 GPa, depending on
281 parameters such as the exchange correlation method used and the atomic
282 configuration of iron atoms in the supercell.

283

284 **4. Discussion**

285 Our results show that an intermediate- to low-spin transition involving Fe^{2+} on the
286 A site takes place in $\text{Mg}_{0.82}\text{Fe}_{0.18}\text{SiO}_3$ perovskite around 120 GPa. At this pressure the
287 stable structure is expected to be post-perovskite (e.g., Hirose, 2006, and references
288 therein); however the well known sluggish reaction kinetics of the perovskite to post-
289 perovskite phase transition (e.g., Mao et al., 2004) likely preserved the perovskite
290 structure in a metastable state in our experiments. The important question is,
291 therefore, whether silicate perovskite with low-spin Fe^{2+} is thermodynamically stable
292 in any region of the phase diagram.

293 Our experimental data demonstrate that increasing temperature increases the
294 stability of low-spin Fe^{2+} in silicate perovskite, reaching 100% low-spin Fe^{2+} at 1000
295 K and 120 GPa (Fig. 6). It follows, therefore, that higher temperatures will preserve
296 the low-spin state. If the phase boundary between perovskite and post-perovskite were
297 shifted to higher pressures as a consequence of the intermediate- to low-spin transition
298 of Fe^{2+} in silicate perovskite, there would be a region in which low-spin Fe^{2+} would be
299 stable (Fig. 7). The slope of the phase boundary depends on the relative contribution
300 of the entropy and volume terms to the free energy. Our observation that temperature
301 stabilises the low-spin state relative to intermediate-spin Fe^{2+} implies that the P,T
302 slope of the transition in the perovskite field is negative, which means that the low-
303 spin Fe^{2+} perovskite to post-perovskite phase boundary must have a less steep slope
304 than the intermediate-spin Fe^{2+} perovskite to post-perovskite phase boundary based on
305 Schreinemakers' Rules (Schreinemakers, 1916).

306 Our proposed phase diagram is consistent with existing data on the spin state of
307 Fe^{2+} in silicate perovskite (Fig. 7). Lin et al. (2008) collected X-ray emission spectra
308 for $\text{Mg}_{0.6}\text{Fe}_{0.4}\text{SiO}_3$ perovskite at high pressure and temperature, and found a spin
309 number (S) close to one up to 3200 K at 108 GPa, which is consistent with the nuclear
310 forward scattering data of McCammon et al. (2008) for $\text{Mg}_{0.88}\text{Fe}_{0.12}\text{SiO}_3$ perovskite
311 which showed intermediate-spin Fe^{2+} ($S = 1$) to be present at 110 GPa and 300 K. X-
312 ray emission spectra of Badro et al. (2004) for $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$ perovskite showed a

313 spin number near one at 120 GPa, but near zero at 132 and 145 GPa. Lin et al. (2008)
314 suggest that an iron content below $x_{\text{Fe}} = 0.4$ is likely below the percolation threshold
315 where iron-iron interactions could significantly influence the spin transition pressure;
316 hence no strong difference in spin behaviour would be predicted within the
317 composition range of data shown in Fig. 7.

318 The pressure interval over which low-spin Fe^{2+} perovskite could occur coincides
319 with predicted P,T conditions near D'', raising the possibility of a layer at the base of
320 the lower mantle containing low-spin Fe^{2+} . Lateral temperature variations change the
321 depth of the perovskite to post-perovskite transition, which would also affect the
322 relative abundance of different spin-state populations. In hot regions the intermediate-
323 to low-spin transition would occur well above the core-mantle boundary (CMB),
324 while in cold regions silicate perovskite with intermediate-spin Fe^{2+} would transform
325 directly to post-perovskite (Fig. 8). Hernlund et al. (2005) proposed that in cold
326 regions above the core-mantle boundary a double crossing of the perovskite to post-
327 perovskite transition could occur, accounting for double seismic discontinuities and
328 allowing an estimate of heat flow out of the core. In our scenario a double crossing
329 would still occur, but the layer of silicate perovskite adjoining the CMB would
330 contain low-spin Fe^{2+} , not intermediate spin, which would influence physical and
331 chemical properties in that region.

332 The double-crossing model has been used in conjunction with geophysically
333 consistent estimates of deep mantle and inner core boundary temperatures to define
334 plausible ranges for the Clapeyron slope of the perovskite to post-perovskite transition
335 (Hernlund and Labrosse, 2007). In their analysis the higher estimates of the Clapeyron
336 slope from experiment and theory gave the best agreement with estimates of core
337 melting temperatures, while lower estimates such as those based on the gold pressure
338 scale (e.g., Hirose, 2006) were judged to be inconsistent. According to our results,
339 however, low-spin Fe^{2+} would increase the Clapeyron slope of the perovskite to post-
340 perovskite transition significantly (Fig. 7), favouring lower inner core boundary
341 temperatures and strengthening plausibility arguments for the double-crossing model
342 (Hernlund and Labrosse, 2007).

343

344 **5. Conclusions and outlook**

345 Our work has shown that low-spin Fe^{2+} is stable in silicate perovskite above ~ 120
346 GPa, and that increasing temperature increases the stability of the low-spin state,

347 raising the possibility of a layer containing low-spin Fe^{2+} silicate perovskite in the
348 lower mantle. The style of mantle convection is highly influenced by the chemical and
349 physical properties of materials at the CMB; hence low-spin Fe^{2+} may play a role in
350 mantle dynamics. Unfortunately little is known about the properties of silicate
351 perovskite with low-spin Fe^{2+} , which means that assessment of geophysical
352 implications must wait for the results of *in situ* studies, since spin transitions are
353 reversible with respect to both pressure and temperature. An initial wish list includes
354 measurements at conditions of D'' of the spin state of iron in silicate perovskite as
355 well as the Clapeyron slope of the perovskite to post-perovskite transition (Fig. 7),
356 and the density change and sharpness of the intermediate- to low-spin transition in
357 silicate perovskite.

358

359 **Acknowledgements**

360 We acknowledge the European Synchrotron Radiation Facility for provision of
361 synchrotron radiation facilities (ID18 and ID09) and we would like to thank R. Rüffer
362 and M. Hanfland for additional assistance. Use of the Advanced Photon Source
363 (beamline 13-ID-D) was supported by the U.S. Department of Energy, Office of
364 Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357,
365 and we would like to thank Vitali Prakapenka for additional assistance. The project
366 was partly supported by funds from the German Science Foundation (DFG) Priority
367 Programme SPP1236 under project Mc 3/16-1.

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Accepted Manuscript

490 **Figure Captions**

491 Figure 1. X-ray diffraction pattern of silicate perovskite at room temperature and 130
 492 (5) GPa collected at the end of run #3. The solid line through the data points indicates
 493 the fit derived from Rietveld refinement, and the line positions of Au (pressure
 494 marker), CaCl₂-structured SiO₂ (thermal insulator) and silicate perovskite with *Pbnm*
 495 space group are indicated by blue, red and black ticks, respectively.

496

497 Figure 2. Room temperature NFS spectra collected during run #1: (a) majorite in air at
 498 0 GPa; (b) majorite in DAC at 33 GPa; (c-e) sample transformed to silicate perovskite
 499 by laser heating. The pressures for the spectra are as follows: (c) 40 GPa; (d) 62 GPa;
 500 (e) 115 GPa. The red lines indicate the theoretical fit obtained using MOTIF.

501

502 Figure 3. Room temperature Mössbauer spectra collected for (a) majorite in air (run
 503 #1); (b) majorite in the DAC (run #2); (c) (d) silicate perovskite in the DAC (runs #2
 504 and #3). The pressures for the spectra are as follows: (a) 0 GPa; (b) 61 GPa; (c) 125
 505 GPa; and (d) 130 GPa. The solid lines indicate the theoretical fit obtained using
 506 NORMOS, and the residual is indicated above each spectrum. The doublets are
 507 shaded as follows: high-spin Fe²⁺ (yellow); intermediate-spin Fe²⁺ (green); low-spin
 508 Fe²⁺ (blue); Fe³⁺ (red).

509

510 Figure 4. NFS spectra of silicate perovskite during run #3 (at P = 120 GPa unless
 511 otherwise noted): (a) T = 300 K; (b) T = 380 K; (c) T = 830 K; (d) T = 1000 K; (e) P
 512 = 130 GPa, T = 300 K. The NFS spectrum in Fig. 4e was collected for the same
 513 sample at the same conditions as the Mössbauer spectrum in Fig. 3d. The red lines
 514 indicate the theoretical fit obtained using MOTIF.

515

516 Figure 5. Hyperfine parameter variation with pressure for majorite and silicate
 517 perovskite derived from room temperature NFS (squares) and Mössbauer (circles)
 518 spectra. The trends for individual species are linked by solid and dashed lines in their
 519 regions of stability and metastability, respectively, for high-spin Fe²⁺ in majorite
 520 (yellow); intermediate-spin Fe²⁺ in perovskite (green); low-spin Fe²⁺ in perovskite
 521 (blue) and Fe³⁺ (red).

522

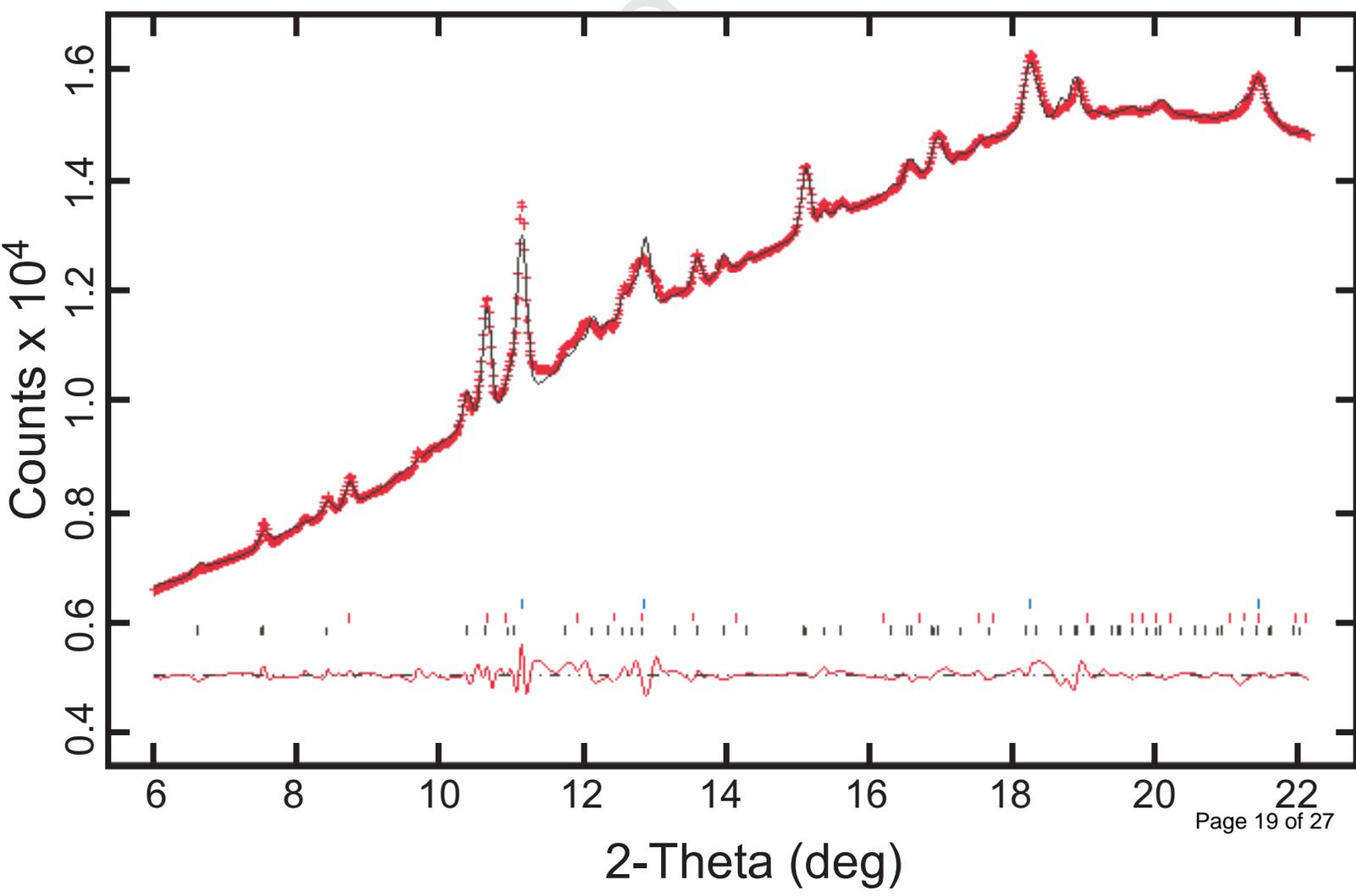
523 Figure 6. Proportion of low-spin Fe^{2+} relative to total Fe^{2+} in silicate perovskite as a
524 function of temperature at high pressure based on NFS (squares) and Mössbauer
525 (circles) spectra. The line joins the data for 120 GPa, while the pressures for the other
526 data points are indicated.

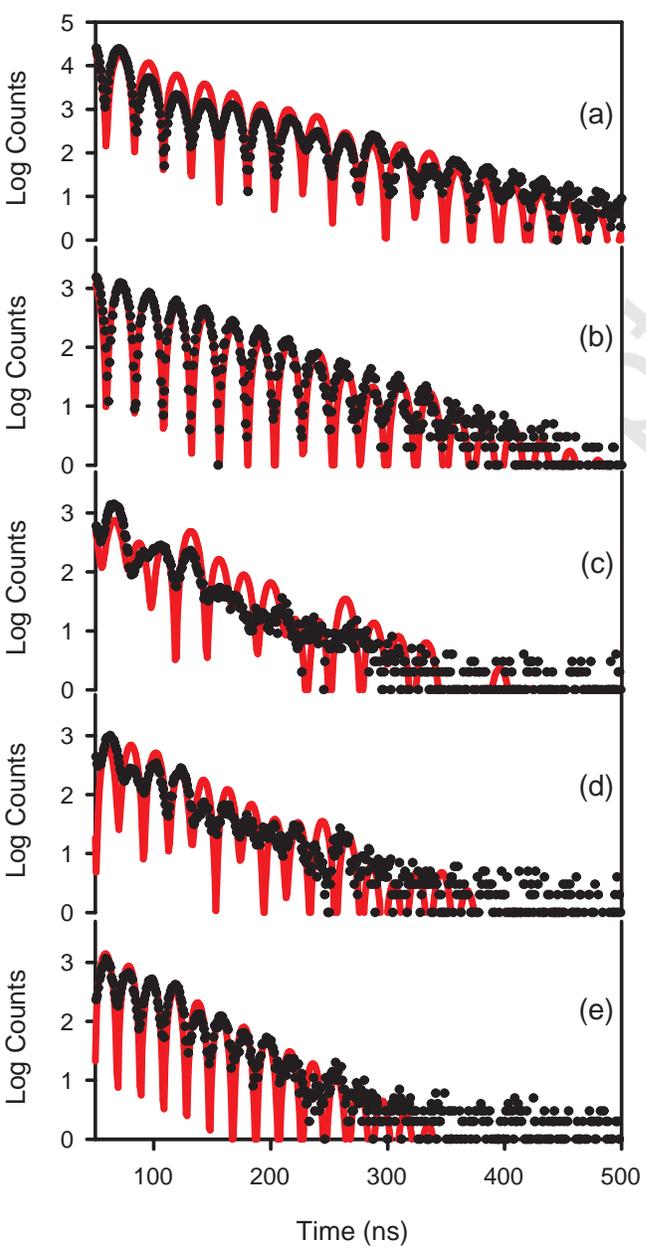
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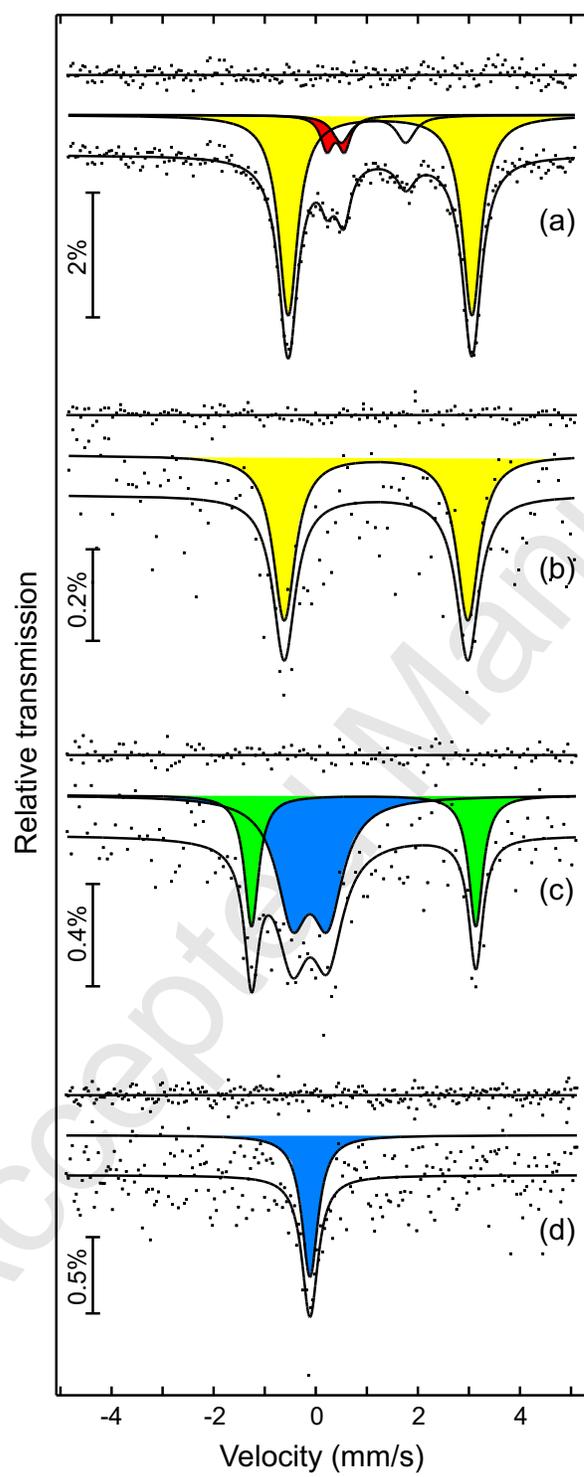
528 Figure 7. Proposed phase boundary for $(\text{Mg,Fe})(\text{Si,Al})\text{O}_3$ between perovskite (pv) and
529 post-perovskite (ppv). The thick solid line indicates the phase boundary summarised
530 from data in the literature (Hirose, 2006), which may be shifted to higher pressures
531 due to an intermediate-spin (IS) to low-spin (LS) transition in the perovskite phase,
532 creating a region where silicate perovskite containing low-spin Fe^{2+} is stable (blue).
533 The region where IS Fe^{2+} is stable in the perovskite structure is shaded yellow, while
534 the region where IS Fe^{2+} is stable in the post-perovskite structure is shaded purple.
535 Symbols indicate the spin state determined for Fe^{2+} in silicate perovskite, where green
536 indicates intermediate spin and blue indicates low spin: large circles (this work); small
537 circle (McCammon et al., 2008); diamonds (Lin et al., 2008); squares (Badro et al.,
538 2004). The estimated depth range of the D'' discontinuity is indicated by the black bar
539 (e.g., Wyssession et al., 1998), and the green and blue dashed lines are a guide for the
540 eye.

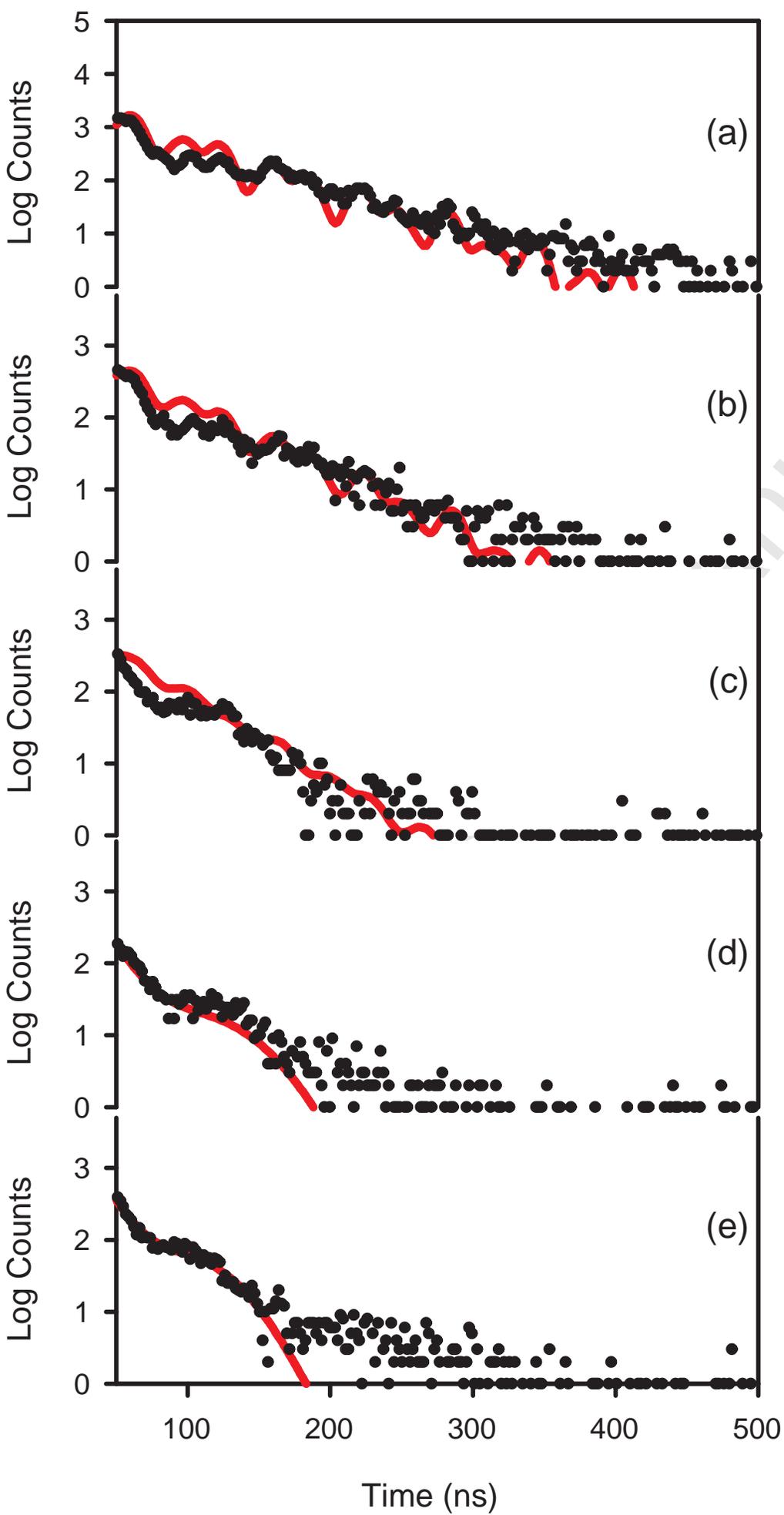
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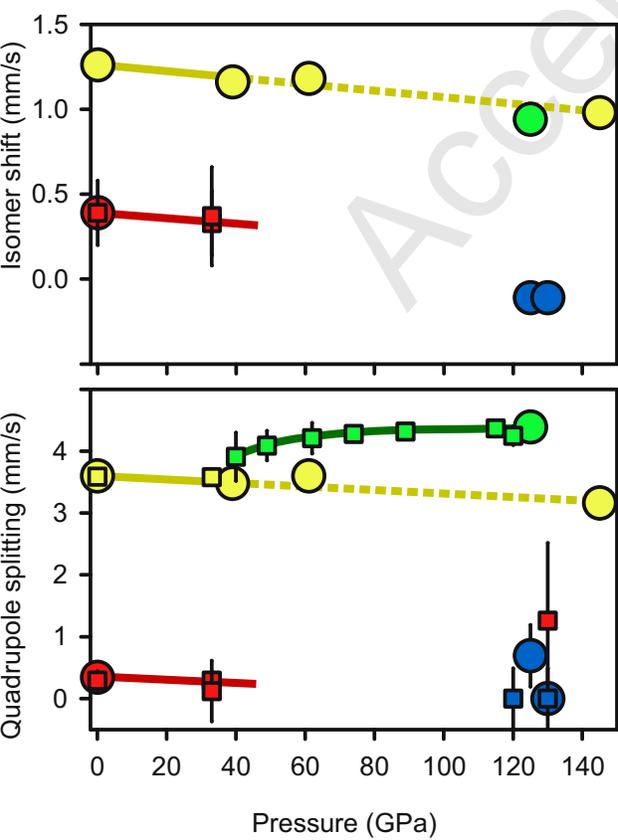
542 Figure 8. The estimated thermal structure of D'' adapted from Hernlund et al. (2005).
543 The perovskite to post-perovskite transition is shown by the thick solid (existing data)
544 and dashed (our proposed boundary) lines, and various geotherms are shown in red.
545 The region where IS Fe^{2+} is stable in the perovskite structure is shaded yellow, while
546 the region where IS Fe^{2+} is stable in the post-perovskite structure is shaded purple.
547 The blue region is where silicate perovskite containing low-spin Fe^{2+} would be stable,
548 which leads to the presence of post-perovskite lenses in cold regions (as already
549 proposed by Hernlund et al., 2005), but with intermediate-spin Fe^{2+} silicate perovskite
550 above and low-spin Fe^{2+} silicate perovskite below.

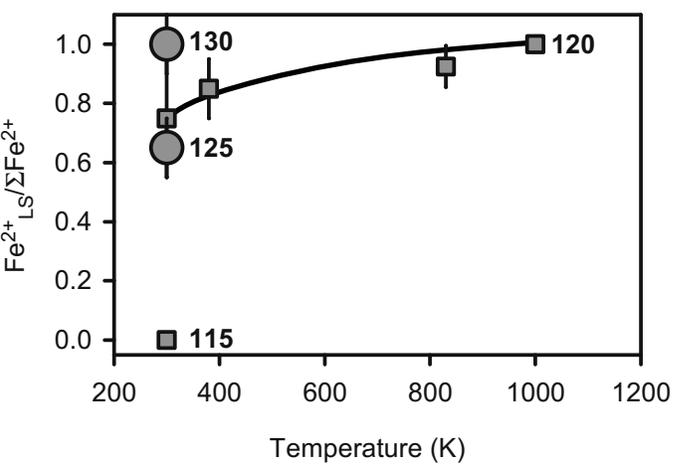












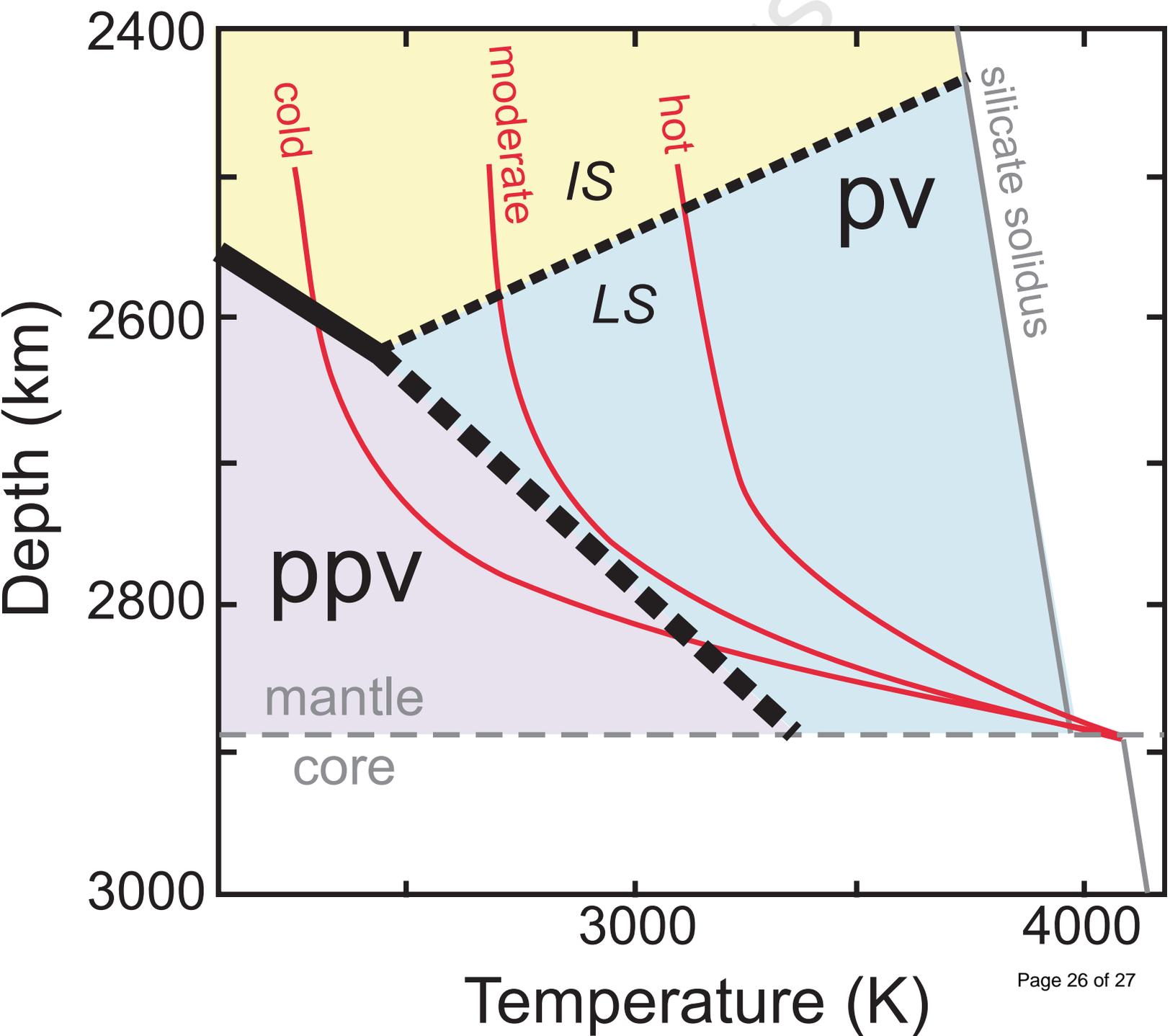


Table 1. Summary of run conditions and data collection

Run #	phase	P GPa	T K	NFS	Möss	comments	
1	mj	0	300	x	x		
		33	300	x		LH at high power after data collection	
	pv	33	300	x			
		40	300	x			
		49	300	x			
		62	300	x			
		74	300	x			
		89	300	x			
	115	300	x				
2	mj	0	300		x		
		39	300		x		
		61	300		x		
		145	300		x	LH at high power after data collection; P decreased during LH	
	pv	125	300		x		
3	pv	120	300	x			
		120	380	x			DAC screws were tightened during heating to maintain constant P
		120	830	x			“ “
		120	1000	x		“ “	
		130	300	x	x	P increased during quenching to room temperature	

Notes:

mj: majorite; pv: perovskite; NFS: nuclear forward scattering; Möss: Mössbauer spectroscopy; LH: laser heating

During runs #1 and #2, the sample was annealed after each increase of pressure using an infrared laser at low power to relieve stress