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1
2 **Direct observation of shock-induced disordering of enstatite below the melting**
3 **temperature**

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27
28 **Key Points:**

- 29
- 30 • We performed ultrafast X-ray diffraction of orthoenstatite crystals shock compressed up
31 to 337±55 GPa on the Hugoniot.
 - 32 • A disordered structure was observed from 80±13 GPa along the Hugoniot, well below the
33 melting temperature.
 - 34 • The degree of polymerization strongly influences the kinetics of recrystallization in
35 shocked silicates.

Abstract

We report *in situ* structural measurements of shock-compressed single crystal orthoenstatite up to 337±55 GPa on the Hugoniot, obtained by coupling ultrafast X-ray diffraction (XRD) to laser-driven shock-compression. Shock compression induces a disordering of the crystalline structure evidenced by the appearance of a diffuse XRD signal at nanosecond time scales at 80±13 GPa on the Hugoniot, well below the equilibrium melting pressure (> 170 GPa). The formation of bridgmanite and post-perovskite have been indirectly reported in microsecond-scale plate-impact experiments. Therefore, we interpret the high-pressure disordered state we observed at nanosecond-scale as an intermediate structure from which bridgmanite and post-perovskite crystallize at longer timescales. This evidence of a disordered structure of MgSiO₃ on the Hugoniot indicates that the degree of polymerization of silicates is a key parameter to constrain the actual thermodynamics of shocks in natural environments.

Plain language summary

The study of silicate materials at extreme pressures and temperatures provides insight on the evolution of planetary bodies evolution during Solar System formation. During their accretion, rocky bodies have undergone several collisions and possibly planetary impacts that have transformed their minerals. The microscopic processes occurring during such events are not fully understood. In this study, we used high-power lasers to generate shock-waves into MgSiO₃ enstatite crystals, creating conditions comparable to the deepest part of the early Earth mantle and large planetary impacts. During the shock-wave transit, within few nanoseconds, we probed the structure of shocked enstatite between 14±3 GPa and 337±55 GPa using intense X-ray pulses from LCLS X-ray free electron laser facility. We found that, when shocked between 80±13 GPa and the conditions of equilibrium melting (above 170 GPa), enstatite transforms into a disordered structure instead of forming bridgmanite or post-perovskite – the expected equilibrium phases. This disordered structure is similar to MgSiO₃ glass or liquid and is observed up to 337±55 GPa. This study provides the first direct measurement of shocked enstatite structure and suggests that the observed disordered state is an intermediate phase on the transformation pathway of bridgmanite in natural impacts.

64

65 **1 Introduction**

66 The abundance of (Mg,Fe)SiO₃ compounds in planetary mantles and the geochemical similarities
67 between the Earth, enstatite-rich chondrites (Dauphas 2017, Boyet et al. 2018) and/or
68 carbonaceous chondrites (Drake and Righter 2002) requires an understanding of how space-
69 related processes affect these meteorites before falling on Earth. In addition to space weathering
70 and/or hydrous alteration, most meteorites have undergone multiple collisions and present
71 evidence of shock metamorphism. These minerals can possess specific textures (e.g. mosaicism),
72 amorphous material (e.g. formation of maskeleynite in shocked plagioclase feldspar, Jaret et al.
73 2015) and high-pressure polymorphs (e.g. (Mg,Fe)₂SiO₄ ringwoodite; MgSiO₃ akimotoite,
74 majorite and bridgmanite, Binns et al., 1969, Putnis and Price 1979, Sharp et al. 1997, Zhang et
75 al. 2006, Tschauner et al. 2014).

76 Structural analysis of shock-compressed enstatite recovered from gas-gun or detonation
77 experiments (Hörz and Quaide 1973, Kozlov and Sazonova 2012) compared to minerals found in
78 natural impacts has established impact condition indicators in enstatite chondrites (Rubin et al.
79 1997, Izawa et al. 2011). However, during the shock wave transit, these samples have undergone
80 both dynamic compression up to a peak pressure and the subsequent release phase. Both loading
81 and unloading paths induce different transformation mechanisms and their deconvolution is
82 critical to constrain the impact history. Together with sample recovery, the acquisition of *in situ*
83 structural data is required to identify the relevant microscopic mechanisms occurring during the
84 different stages of the shock and their kinetics. This approach has long been prevented by
85 technical limitations due to the short time-scales involved in laser (nanosecond) and gas-gun
86 (microsecond) experiments.

87 Multiple attempts to infer the structure of shocked MgSiO₃ have been pursued by comparing
88 equation of state measurements (pressure, density and temperature above 4000 K) and optical
89 properties (Ahrens et al. 1971, Watt et al. 1986, Akins et al. 2004, Luo et al. 2004, Mosenfelder
90 et al. 2009, Frantanduno et al. 2018) with predicted MgSiO₃ Hugoniot paths from atomistic
91 simulations based on the equilibrium phase diagram (Akins et al. 2004, Militzer 2013, Soubiran
92 et al. 2018). However, this approach is limited by the accuracy on density measurements
93 currently achievable in shock experiments. Moreover, atomistic simulations are generally based

94 on equilibrium phase diagrams, while it is not well established if such equilibrium is effectively
95 achieved at the time-scales of these experiments.

96 In this context, the recent coupling of ultrafast (fs) *in situ* XRD and shock compression allows
97 direct investigation of transition mechanisms at short-time scales relevant to both gas-gun (few
98 hundred of ns) and laser-driven (few ns) experiments. These new experimental opportunities
99 have led to outstanding discoveries with major impacts on our understanding of shock
100 metamorphism. Notable findings include the evidence of nanosecond scale formation of
101 polycrystalline stishovite in shocked SiO₂ glass (Gleason et al. 2015, Tracy et al. 2018).
102 Unfortunately, to date very few data have been reported for more complex silicates (Newman et
103 al. 2018), and in particular for enstatite, with a higher relevance for natural environments
104 found in shocked meteorites.

105 We report direct structural measurements of laser-shocked MgSiO₃ enstatite between 14±3 GPa
106 and 337±55 GPa from ultrafast *in situ* XRD.

107 **2 Materials and Methods**

108 The experiment was performed at the Matter in Extreme Conditions (MEC) end-station of the
109 Linac Coherent Light Source (LCLS, Stanford, USA) by combining ultrafast XRD from the X-
110 ray free electron laser (XFEL) at 9 keV and laser-driven shock-compression (Figure S1) of single
111 crystals of enstatite along the [100] direction. We recorded two-dimensional XRD images in
112 transmission geometry on four Cornell-SLAC Pixel Array Detectors (CSPADs). We determined
113 the uniaxial pressure by measuring fluid and/or mean shock velocities using a velocity
114 interferometer system for any reflector (VISAR) and existing refractive index and equation of
115 state measurements of shocked enstatite on the principal Hugoniot (Luo et al. 2004, Akins et al.
116 2004, Mosenfelder et al. 2009, Fratanduono et al. 2018). By varying the drive laser energies and
117 by adjusting the delay between the drive lasers and the 60 fs (pulse width) XFEL pulse, we
118 captured quasi-instantaneous snapshots of the structure of uniformly shocked enstatite between
119 14±3 GPa and 337±55 GPa.

120

121 **2.1 Target preparation**

122 Planar multilayered targets (Figure S1b) were composed of a 50 μm -thick polystyrene (PS)
123 ablator glued to the enstatite sample. We first coated both the ablator and the sample with 300
124 nm Ti on the drive laser side prior gluing. The Ti coating on the ablator prevented the drive laser
125 from shining through it. On the sample, it acts as a reflective layer for optical diagnostics.
126 Natural orthoenstatite single crystals of gem quality (loc. Mogok, Myanmar) were first cut into
127 2×2 mm plates perpendicular to the [100] direction and polished down to a thickness of 50-60
128 μm . Two groups of orthoenstatite crystals were used with initial densities of 3.219 and 3.259
129 $\text{g}\cdot\text{cm}^{-3}$ (respective compositions of $\text{Mg}_{0.98}\text{Fe}_{0.02}\text{SiO}_3$ and $\text{Mg}_{0.93}\text{Fe}_{0.07}\text{SiO}_3$). Using confocal
130 imagery and interferometry we measured the thickness and the planarity of each sample with
131 accuracy <100 nm and selected only those thinner than 57 ± 1 μm . We optimized the PS and
132 enstatite thicknesses for shock stationarity in concert with hydrodynamic simulations made with
133 the Lagrangian one-dimensional code MULTI (Ramis et al. 1988). We designed additional targets
134 with a LiF window behind the sample (see section S1) to verify that steady conditions are
135 maintained during the shock transit through the sample.

136

137 **2.2 Laser-driven dynamic compression**

138 Uniaxial dynamic compression was achieved by launching a shock wave using two frequency-
139 doubled Nd-glass MEC laser beams with 10 ns square pulses operating at 527 nm (Figure S1a).
140 The flatness and uniformity of the 250 μm -diameter focal spot was achieved by using continuous
141 phase plates. In this configuration we obtained a maximum intensity on target of $I_L\sim 10^{13}$ $\text{W}\cdot\text{cm}^{-2}$.
142 In order to reach higher intensities, required to melt enstatite, we removed the phase plates and
143 focused the two laser beams into smaller Gaussian spot profiles. In this case, we carefully
144 checked the shock planarity and the overlap between the drive laser and the X-ray beam focal
145 spots.

146 Characteristic velocities of shock-compressed enstatite were measured using VISAR with a
147 probe laser operating at a wavelength of 532 nm. Space-time images were recorded on an
148 ultrafast streak camera with ~ 100 ps time resolution. The velocity changes of the reflecting
149 interface(s) were detected from interference fringe shifts. VISAR channel sensitivities were
150 4.658 $\text{km}\cdot\text{s}^{-1}\cdot\text{fringe}^{-1}$ and 1.814 $\text{km}\cdot\text{s}^{-1}\cdot\text{fringe}^{-1}$. Shock-compressed enstatite remains transparent
151 on the principal Hugoniot at least up to 164 GPa (Fratanduono et al. 2018). In this pressure range
152 we measured the velocity of the Ti/enstatite interface (by reflecting off the thin Ti coating),

153 which corresponds to the apparent fluid velocity of the shocked enstatite. We deduced the true
154 fluid velocity (U_p) by correcting the apparent velocity for the change of refractive index in the
155 shocked enstatite according to the linear dependence on density given in Fratanduono et al.
156 (2018). The shock breakout also induces a fringe shift due to the large change of refractive index
157 between the vacuum and the shock front on the rear side of the target. The delay between the
158 shock entrance in the enstatite and the shock breakout determines the mean shock velocity (U_s).
159 For high intensity shots, the shocked enstatite became opaque and the thermodynamic conditions
160 were deduced from the measured mean shock velocity U_s and the Hugoniot relation of
161 Fratanduono et al. (2018). Pressure and density are then determined from U_s and U_p via Rankine-
162 Hugoniot relations.

163

164 **2.4 Ultrafast X-ray diffraction**

165 *In situ* XRD was performed using quasi-monochromatic ($dE/E = 0.2-0.5\%$) 9 keV X-ray pulses
166 of 60 fs duration with an average intensity of $\sim 10^{12}$ photons per pulse. The XFEL beam had a
167 normal incidence on the target surface and a 20° angle with the drive laser arms. LCLS XFEL
168 spot diameter was set to 50 μm , which is much smaller than the flat-compressed region so as to
169 avoid probing regions affected by pressure and temperature gradients. As X-rays probe the bulk
170 sample, special attention was paid to ensure uniform thermodynamic conditions in the shocked
171 part, both by optimizing target design and probing times. Two-dimensional XRD images were
172 recorded in transmission geometry on the four CSPADs. CSPADs were calibrated with powders
173 of CeO₂ 674a and LaB₆ 660a NIST standard reference materials. For each target, a reference
174 XRD pattern of the unshocked sample was acquired prior to shock compression. Additional
175 details about the azimuthal integration procedure are given in Section S3.

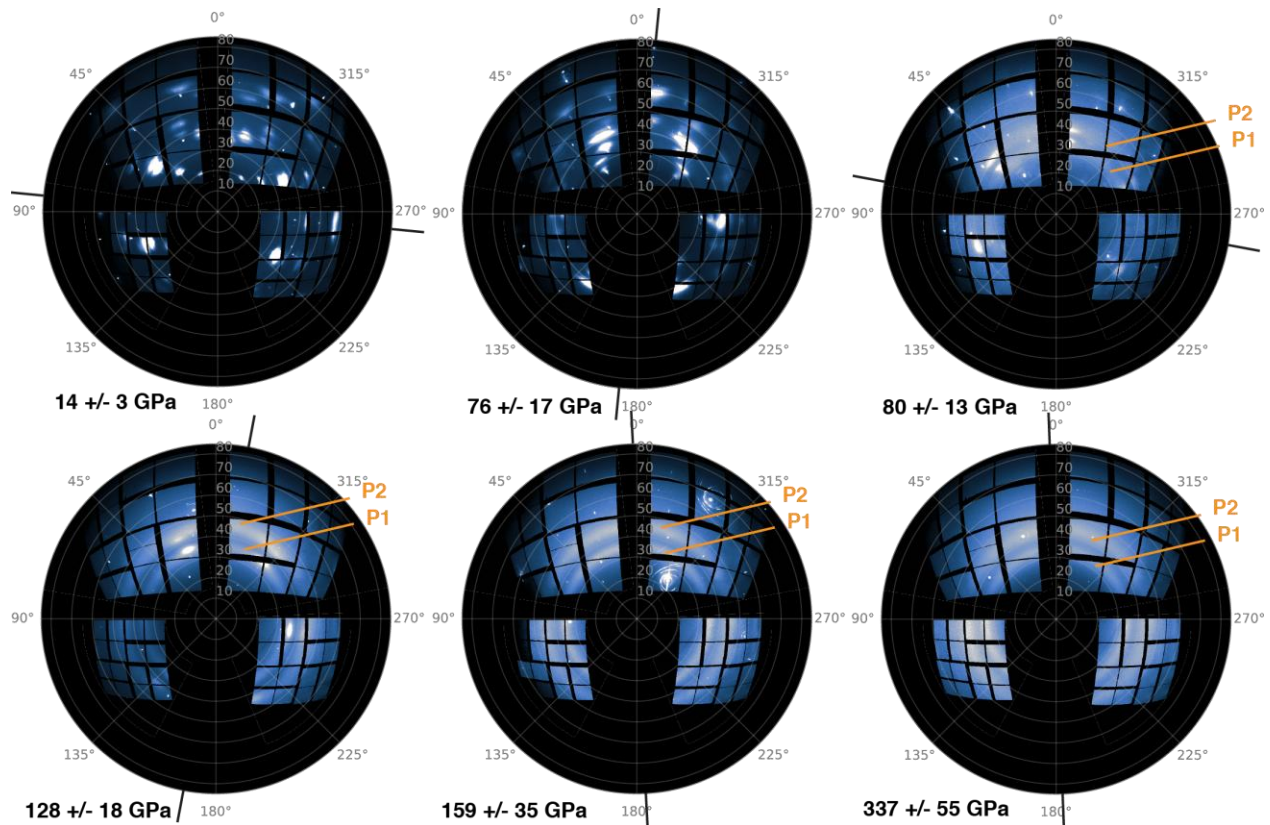
176

177 **3 Results**

178 **3.1 *In situ* X-ray diffraction of shock-compressed orthoenstatite**

179 Figure 1 shows the evolution of the XRD patterns obtained at different pressures along the
180 principal Hugoniot of enstatite 1.7-6 ns after the shock entrance in the sample and before the
181 shock breakout. Between 14 ± 3 GPa and 79 ± 26 GPa, i.e. above the Hugoniot elastic limit of
182 enstatite and within the so-called mixed phase region (MPR, Akins et al. 2004), only single

183 crystal patterns attributed to pyroxenoid (i.e. pyroxene-like) structures, are recorded at
 184 nanosecond time-scale during the shock (e.g. Figure 1, 14 ± 3 GPa and 76 ± 17 GPa). The different
 185 single crystal XRD patterns were tentatively attributed to metastable structures described by
 186 Finkelstein et al. (2015) such as compressed enstatite and β -post-orthopyroxene (β -popx, see
 187 section S4).



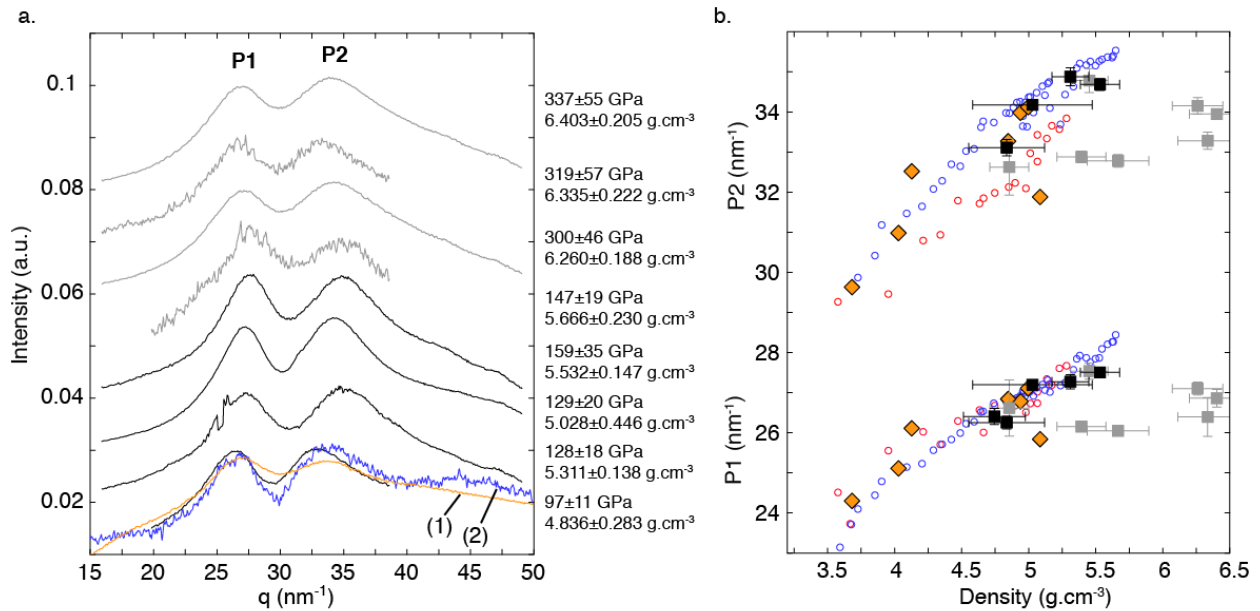
188 **Figure 1:** Experimental *in situ* XRD data recorded at peak pressure in laser-shocked single crystal enstatite oriented
 189 along [100]. Images from the four CSPAD are projected in the $(2\theta, \phi)$ coordinate system. Black ticks indicate
 190 sample relative rotations along the shock and XFEL axis. The intense few pixel-wide diffraction spots present on all
 191 images come from the unshocked part of the enstatite sample; wide spots with variable intensities visible up to
 192 128 ± 18 GPa originate from the shocked sample and can be reproduced considering two pyroxenoids (Figure S4).
 193 Enstatite transformation toward a disordered structure begins at 80 ± 13 GPa, well below melting conditions, with the
 194 appearance of two diffuse rings, labelled P1 and P2. Above 128 ± 18 GPa, the diffraction spots of dense pyroxenoid
 195 structures disappear and only features P1 and P2 remain. At 337 ± 55 GPa, enstatite is shocked in the liquid state.

196
 197
 198 Between 80 ± 13 GPa and 128 ± 18 GPa, pyroxenoid structures persist and coexist with two diffuse
 199 rings at $20\sim 35^\circ$ and $20\sim 44^\circ$, respectively denoted P1 and P2, whose intensities increase with

200 pressure. For all shocks above 129 ± 20 GPa, only the diffuse rings come from the shocked
201 enstatite (see shocks at 159 ± 35 and 337 ± 55 GPa in Figure 1).

202 Azimuthal integration of the diffuse signal was done as a function of pressure and density along
203 the Hugoniot (Figure 2). We first investigate the possibility that the diffuse pattern is produced
204 by bridgmanite (Bd) or post-perovskite (Ppv), the thermodynamically stable phases between
205 80 ± 13 GPa and the equilibrium melting line (i.e. above 170 GPa). The comparison of our spectra
206 with simulated diffraction patterns (Figure S5) of both polycrystalline Bd and Ppv with 3 nm-
207 large crystals (twice smaller than first stishovite crystals observed in laser-shocked silica glass,
208 Gleason et al. 2015) excludes the formation of these high-pressure polymorphs at nanosecond
209 scale. Then, the spectra and the positions of P1 and P2 were compared, and found to be similar to
210 the ones obtained in both static and dynamic compression experiments performed on MgSiO_3
211 glass (Kono et al, 2018, Morard et al. 2020). Fourier transform analyses of these compressed
212 glasses have shown that both the appearance of P2, and the shift toward higher q-values of P1,
213 are attributed to the continuous change from 4-fold to 6-fold Si-O coordination (Ghosh et al.
214 2014, Kono et al. 2018). By analogy, we suggest that enstatite transforms into a disordered phase
215 under shock-compression at nanosecond-scale between 80 ± 13 GPa and 179 ± 37 GPa, which
216 changes continuously toward a six-fold Si-O structure. Complete refinement at the atomic scale
217 would require larger q-range. Based on our previous measurements on MgSiO_3 glass (Morard et
218 al. 2020) we find a striking agreement for peak positions of diffuse signal from cold compressed
219 glass and shocked disordered enstatite at similar densities (Figure 2), suggesting the
220 transformation of crystalline enstatite into a six-fold Si-O disordered structure under shock
221 compression.

222



(1) Shocked MgSiO₃ glass, 80 GPa, 4.847 g.cm⁻³ (Morard et al. 2020)

(2) MgSiO₃ glass at 300 K and 76 GPa, 4.831 g.cm⁻³ (Morard et al. 2020)

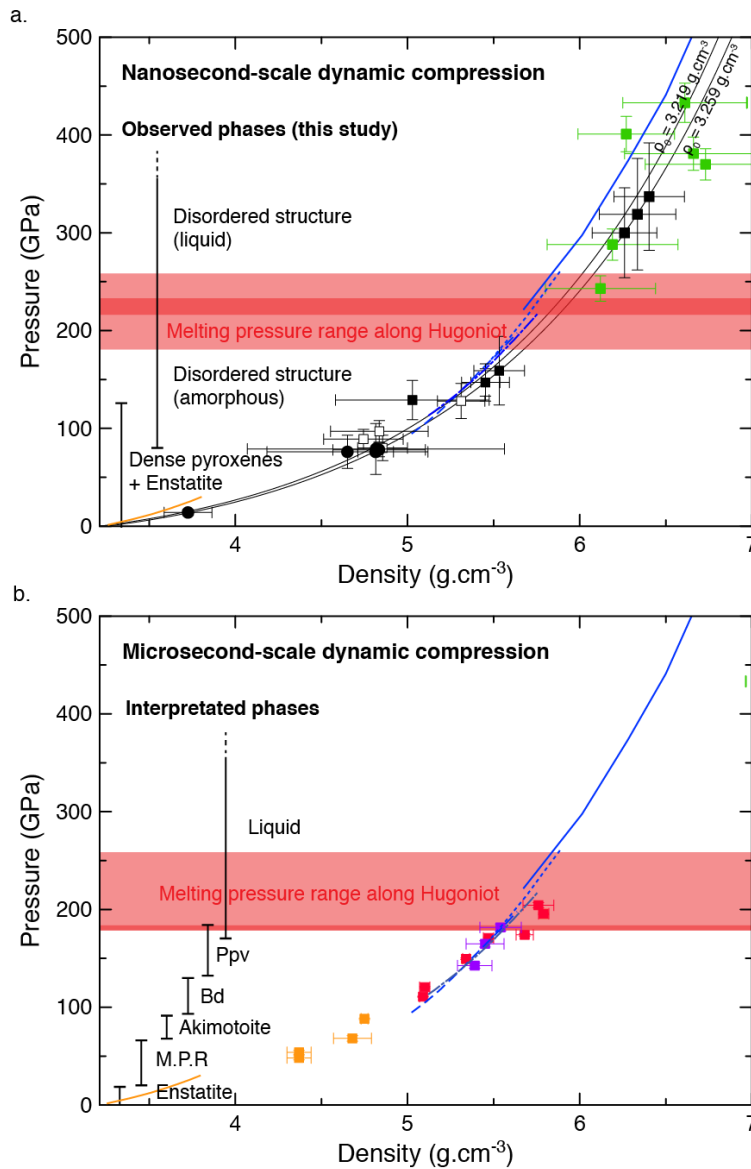
Figure 2: **a.** Azimuthal integration of the disordered component observed in shocked orthoenstatite between 97±11 GPa and 337±55 GPa (black and grey lines respectively indicate shots with and without phase plate). Diffraction spots coming either from the unshocked part of the target or from dense pyroxenoids have been masked before the integration. The norm of the scattering vector q is related to the Bragg angle by $q = 4\pi \sin(\theta) / \lambda$. All spectra are normalized with respect to their area. The spectrum at 97±11 GPa is compared to two spectra obtained from statically compressed MgSiO₃ glass at 300 K (blue) and from laser-shocked MgSiO₃ glass (orange) at comparable density (Morard et al. 2020). Our data show that all three spectra are similar and demonstrate the typical of 6-fold Si-O coordinated features in silicates with P2 arising under compression above several GPa (Sanloup et al. 2013, Ghosh et al. 2014, Zeidler and Salmon 2016, Prescher et al. 2017, Kono et al. 2018, Morard et al. 2020). **b.** Positions of P1 and P2 as function of density. Squares represent the data obtained in the present shock experiment, where the density is determined from VISAR measurements. Empty circles correspond to statically compressed MgSiO₃ at 300 K (red: from Kono et al. 2018, blue: from Morard et al. 2020). Corresponding densities have been derived from pressures based on the equation of state of Petitgirard et al. (2015). Orange diamonds refer to shocked MgSiO₃ glass (Morard et al. 2020).

The presence of diffuse rings on the XRD patterns does not allow us to discriminate between a hot metastable amorphous or a liquid phase. Consensus on the exact melting pressure on the shock Hugoniot does not exist, however, all theoretical and experimental studies place it above 170-180 GPa (Akins et al. 2004, Belonoshko et al. 2005, Stixrude et al. 2005, De Koker et al. 2009, Mosenfelder et al. 2009). Recent laser experiments suggest a complete melting pressure as high as 227±10 GPa from a slope change in the thermal emission of the sample in a decaying

245 shock experiment (Fratanduono et al. 2018). In addition, VISAR images show that at 128 ± 18
246 GPa and 159 ± 35 GPa, shocked MgSiO_3 presents a large absorption length of ~ 20 μm at 532 nm,
247 in good agreement with Fratanduono et al. (2018) at sub-melting conditions (see Figure S6). On
248 the contrary, the VISAR data for the experiment above 300 ± 46 GPa (Figure S6) only show only
249 ghost fringes due to an interfering reflection on the rear side of the silicate (no anti-reflection
250 coating), indicating that MgSiO_3 is opaque or weakly reflecting. This is consistent with the
251 properties predicted for the equilibrium liquid in Soubiran et al. (2018).

252 Figure 3.a shows the pressures and densities of shocked enstatite deduced from our velocity
253 measurements with the corresponding lattice structure probed by XRD at nanosecond timescales.
254 Figure 3.b shows existing pressure-density measurements obtained in gas-gun experiments at the
255 microsecond scale and the interpreted phases from velocimetry. The pressure range in which we
256 observe crystalline XRD patterns corresponds to three different regimes on the microsecond
257 scale Hugoniot: compressed enstatite up to 15 GPa; a mixed phase region that is expected to
258 contain multiple phases (Akins et al. 2004) and extend up to 70 GPa; akimotoite (70-90 GPa).
259 The disordering of enstatite observed in our experiment occurs at conditions where Bd and Ppv
260 are considered to form at microsecond scale, and leads us to consider disordered MgSiO_3 as a
261 reaction intermediate in the formation of Bd and Ppv from shocked enstatite.

262



263
 264 **Figure 3:** Pressure-density diagrams of shock-compressed enstatite at nanosecond-scale (a.) and microsecond-scale
 265 (b.). a. We distinguish the shots in which only compressed enstatite and a dense pyroxene-like structure have been
 266 observed (black dots) from those in which they coexist with disordered MgSiO_3 (white squares). Filled squares
 267 correspond to the shots where the signal of the disordered structure only comes from the shocked part of the target.
 268 Green squares represent measurements from Frantanduono et al. (2018). b. Squares correspond to data from gas-gun
 269 experiments: orange, Akins et al. (2004); red, Akins et al. (2004) data reanalyzed by Mosenfelder et al. (2009);
 270 purple; Luo et al. (2004) data reanalyzed by Mosenfelder et al. (2009). The black line corresponds to the linear fit of
 271 all shock versus fluid velocity as done in Frantanduono et al. (2018). Blue curves represent calculated Hugoniot paths
 272 from atomistic simulations at thermodynamic equilibrium based on density functional theory (continuous, liquid
 273 from Militzer 2013; dotted, Ppv from Militzer 2013; dash-dotted, glass from Wolf et al. 2019 based on data from
 274 DeKoker and Stixrude 2009; dashed, Bd from Akins et al. 2004). The orange line is the Hugoniot of enstatite (Akins
 275 2003). In panel a., the dark red area corresponds to the melting pressure of shocked enstatite (227 ± 10 GPa)

276 estimated from laser decaying shock experiments from Frantanduono et al. (2018). In panel b., it represents the
277 melting pressure estimated from gas-gun experiments in Mosenfelder et al. (2009). The pale red area indicates the
278 melting pressure range along the enstatite Hugoniot considering DFT-MD simulations from Militzer et al. (2013).
279

280 **4 Discussion**

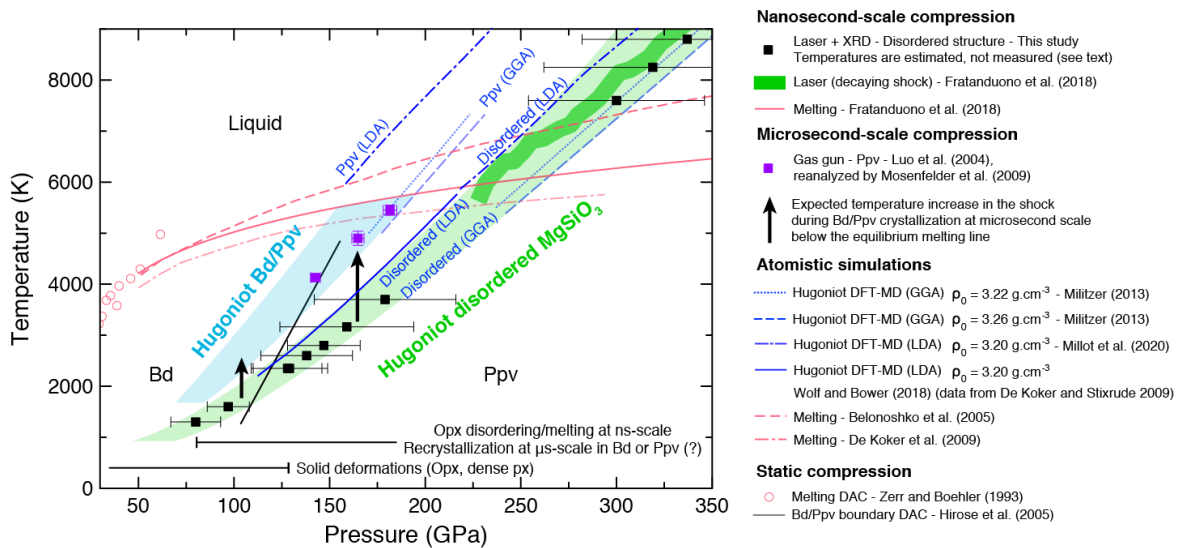
281 In order to understand transformation kinetics in shocked enstatite and to overcome the
282 limitations inherent to the pressure-density diagram, we investigate possible temperature
283 differences between MgSiO₃ enstatite shocked state formed in gas gun (microsecond
284 equilibration at peak pressure) and in laser experiments (nanosecond equilibration at peak
285 pressure). The following interpretation is based on an analogy with recent results on shocked
286 SiO₂ (Shen et al. 2016a, 2016b, Gleason et al. 2015, Gleason et al. 2017) and assumes that Bd or
287 Ppv actually form in gas gun experiments as interpreted in Akins et al. (2003), Luo et al. (2004)
288 and Mosenfelder et al. (2009).

289 In shocked SiO₂, polycrystalline stishovite nucleates and grows within few nanoseconds from a
290 6-fold Si-O coordinated amorphous phase that has the same structure as the melt obtained at
291 higher pressures (Shen et al. 2016a, 2016b; Gleason et al. 2015). Hundred picoseconds behind
292 the shock front, the thermodynamic conditions in the high-pressure amorphous state lay on the
293 extension of the liquid state Hugoniot below the equilibrium melting line (Figure S7). During
294 crystallization, temperature increases by ~1000 K up to the Hugoniot of stishovite (Shen et al.
295 2016a, 2016b) although pressure and density do not change significantly compared to the
296 reachable experimental accuracy. We propose that such mechanism occurs in shocked MgSiO₃
297 but at longer time scales.

298 Since optical emission of shocked enstatite was not recorded in our experiment, we estimated the
299 temperature of our shots – in which disordered MgSiO₃ has formed – based on existing Hugoniot
300 measurements of liquid MgSiO₃ (Frantanduono et al. 2018) and Hugoniot predictions for both
301 liquid and glassy MgSiO₃ from atomistic simulations (DeKoker and Stixrude 2009, Militzer
302 2013 and Millot et al. 2020), which all use an initial density of 3.22-3.26 g.cm⁻³ (Figure 4). The
303 resulting temperatures at 80±13 GPa and at 159±35 GPa differ by 500-1500 K with existing gas
304 gun measurements (Luo et al. 2004), and *a contrario*, are in an excellent agreement with the
305 Hugoniot of Ppv deduced from equilibrium atomistic simulations (Militzer et al. 2013). This
306 difference between the shock temperature estimated in our ns-scale experiment (with *in situ*

307 observation of disordered MgSiO_3) and the shock temperature measured in μs -scale experiments
 308 (which compressed state is interpreted as Bd or Ppv based on compression curves) suggests
 309 that shocked orthoenstatite first amorphizes and recrystallizes into Bd or Ppv within few
 310 microseconds. Therefore, the crystallization kinetics of high-pressure polymorphs in shocked
 311 MgSiO_3 would be 2-3 orders of magnitude slower than the one occurring in SiO_2 . This reveals
 312 that the degree of polymerization of shocked silicates may be a key parameter to understand
 313 recrystallization kinetics in natural environment, e.g. shock veins in meteorites for example.
 314 We mention that the crystalline state of the unshocked sample does not influence the kinetics of
 315 crystallization since we observed the same behavior when starting from MgSiO_3 glass (Morard et
 316 al. 2020).

317



318

319 **Figure 4:** Phase diagram of MgSiO_3 . Hugoniot measurements are all performed from shock-compressed enstatite.
 320 Assuming that MgSiO_3 behaves similarly as SiO_2 when shocked, i.e. high-pressure polymorphs crystallize from a
 321 high-pressure amorphous metastable phase similar to the equilibrium melt, we estimate the temperature of the
 322 amorphous and melt samples (probed in this study by *in situ* XRD) based on the extrapolation of the melt Hugoniot
 323 measured by decaying shock at nanosecond timescales (Fratanduono et al. 2018). The resulting temperature
 324 difference between the amorphous material formed after a few ns and the gas-gun microsecond timescale
 325 measurements may indicate the crystallization of MgSiO_3 bridgmanite or post-perovskite at microsecond timescales.
 326 As such, the equilibrium Hugoniot (as calculated from DFT assuming a Ppv structure) would be reached after a few
 327 microseconds.

328

329 **5 Conclusions**

330 We studied the structure of shocked [100] orthoenstatite using ultrafast XRD. We found that
331 orthoenstatite densifies while keeping crystalline pyroxene-like structures up to 76 ± 17 GPa. At
332 80 ± 13 GPa and above, it amorphizes into a dense disordered phase with the same structure as
333 observed in statically compressed MgSiO_3 glass. Between 80 ± 13 GPa and 128 ± 18 GPa, the
334 signal of the disordered phase coexists with diffraction spots from pyroxene-like structures,
335 indicating that disordering is incomplete or occurs after first crystalline transformations. Between
336 128 ± 18 GPa and the melting conditions, only the disordered phase is observed. The liquid,
337 sampled between 300 ± 46 GPa and 337 ± 55 GPa, presents a similar structure. We propose that the
338 disordered state is a reaction intermediate on the transition pathway towards dense MgSiO_3
339 polymorphs, such as akimotoite, bridgmanite and post-perovskite, that would crystallize from it
340 at peak pressure. As these high-pressure polymorphs have been indirectly shown to form in
341 microsecond scale shock experiments (Akins et al. 2004, Luo et al. 2004, Mosenfelder et al.
342 2009), and are absent from our nanosecond scale measurements, we expect their crystallization
343 to occur within 0.01-1 μs . This differs significantly from the crystallization kinetics of stishovite
344 in shocked SiO_2 which occurs at (sub-)nanosecond scale (Gleason et al. 2015, Shen et al. 2016a).
345 Future XRD measurements should investigate the formation of Bd and Ppv at microsecond scale
346 in shock-compressed enstatite, i.e. using a gas gun facility.

347

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