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

Supporting Information:
- Supporting Information S1

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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 to laser-driven shock compression. Shock compression induces a disordering of the crystalline structure evidenced by the appearance of a diffuse X-ray diffraction signal at nanosecond timescales 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 and 337 ± 55 GPa using intense X-ray pulses from Linac Coherent Light Source 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.

1. Introduction

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

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

Multiple attempts to infer the structure of shocked MgSiO3 have been pursued by comparing equation of state measurements (pressure, density, and temperature above 4000 K) and optical properties (Ahrens & Gaffney, 1971; Akins et al., 2004; Fratanduono et al., 2018; Luo et al., 2004; Mosenfelder et al., 2009; Watt & Ahrens, 1986) with predicted MgSiO3 Hugoniot paths from atomistic simulations based on the equilibrium phase diagram (Akins et al., 2004; Militzer, 2013; Soubiran & Militzer, 2018). However, this approach is limited by the accuracy on density measurements currently achievable in shock experiments. Moreover, atomistic simulations are generally based on equilibrium phase diagrams, while it is not well established if such equilibrium is effectively achieved at the timescales of these experiments.

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

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

2. Materials and Methods

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

2.1. Target Preparation

Planar multilayered targets (Figure S1b) were composed of a 50 μm thick polystyrene ablator glued to the enstatite sample. We first coated both the ablator and the sample with 300 nm Ti on the drive laser side prior gluing. The Ti coating on the ablator prevented the drive laser from shining through it. On the sample, it acts as a reflective layer for optical diagnostics. Natural orthoenstatite single crystals of gem quality (loc. Mogok, Myanmar) were first cut into 2 × 2 mm plates perpendicular to the [100] direction and polished down to a thickness of 50–60 μm. Two groups of orthoenstatite crystals were used with initial densities of 3.219 and
3.259 g·cm⁻³ (compositions of Mg₀.₉₈Fe₀.₀₂SiO₃ and Mg₀.₉₃Fe₀.₀₇SiO₃, respectively). Using confocal imagery and interferometry, we measured the thickness and the planarity of each sample with accuracy <100 nm and selected only those thinner than 57 ± 1 μm. We optimized the polystyrene and enstatite thicknesses for shock stationarity in concert with hydrodynamic simulations made with the Lagrangian one-dimensional code MULTI (Ramis et al., 1988). We designed additional targets with a LiF window behind the sample (see section S1) to verify that steady conditions are maintained during the shock transit through the sample.

2.2. Laser-Driven Dynamic Compression

Uniaxial dynamic compression was achieved by launching a shock wave using two frequency-doubled Nd glass Mater in Extreme Conditions laser beams with 10 ns square pulses operating at 527 nm (Figure S1a). The flatness and uniformity of the 250 μm diameter focal spot was achieved by using continuous phase plates. In this configuration we obtained a maximum intensity on target of I_L ~ 10¹³ W·cm⁻². In order to reach higher intensities, required to melt enstatite, we removed the phase plates and focused the two laser beams into smaller Gaussian spot profiles. In this case, we carefully checked the shock planarity and the overlap between the drive laser and the X-ray beam focal spots. Characteristic velocities of shock-compressed enstatite were measured using VISAR with a probe laser operating at a wavelength of 532 nm. Space-time images were recorded on an ultrafast streak camera with ~100 ps time resolution. The velocity changes of the reflecting interface(s) were detected from interference fringe shifts. VISAR channel sensitivities were 4.658 and 1.814 km·s⁻¹·fringe⁻¹. Shock-compressed enstatite remains transparent on the principal Hugoniot at least up to 164 GPa (Fratanduono et al., 2018). In this pressure range we measured the velocity of the Ti/enstatite interface (by reflecting off the thin Ti coating), which corresponds to the apparent fluid velocity of the shocked enstatite. We deduced the true fluid velocity (U_p) by correcting the apparent velocity for the change of refractive index in the shocked enstatite according to the linear dependence on density given in Fratanduono et al. (2018). The shock breakout also induces a fringe shift due to the large change of refractive index between the vacuum and the shock front on the rear side of the target. The delay between the shock entrance in the enstatite and the shock breakout determines the mean shock velocity (U_s). For high intensity shots, the shocked enstatite became opaque, and the thermodynamic conditions were deduced from the measured mean shock velocity U_s and the Hugoniot relation of Fratanduono et al. (2018). Pressure and density are then determined from U_s and U_p via Rankine-Hugoniot relations.

2.3. Ultrafast XRD

In situ XRD was performed using quasi-monochromatic (dE/E = 0.2–0.5%) 9 keV X-ray pulses of 60 fs duration with an average intensity of ~10¹² photons per pulse. The XFEL beam had a normal incidence on the target surface and a 20° angle with the drive laser arms. Linac Coherent Light Source XFEL spot diameter was set to 50 μm, which is much smaller than the flat-compressed region so as to avoid probing regions affected by pressure and temperature gradients. As X-rays probe the bulk sample, special attention was paid to ensure uniform thermodynamic conditions in the shocked part, both by optimizing target design and probing times. Two-dimensional XRD images were recorded in transmission geometry on the four CSPADs. CSPADs were calibrated with powders of CeO₂ 674a and LaB₆ 660a NIST standard reference materials. For each target, a reference XRD pattern of the unshocked sample was acquired prior to shock compression. Additional details about the azimuthal integration procedure are given in section S3.

3. Results

3.1. In situ XRD of Shock-Compressed Orthoenstatite

Figure 1 shows the evolution of the XRD patterns obtained at different pressures along the principal Hugoniot of enstatite 1.7–6 ns after the shock entrance in the sample and before the shock breakout. Between 14 ± 3 and 79 ± 26 GPa, that is, above the Hugoniot elastic limit of enstatite and within the so-called mixed phase region (Akins et al., 2004), only single crystal patterns attributed to pyroxenoid (i.e., pyroxene-like) structures are recorded at nanosecond timescale during the shock (e.g., Figure 1; 14 ± 3 and 76 ± 17 GPa). The different single crystal XRD patterns were tentatively attributed to metastable structures described by Finkelstein et al. (2015) such as compressed enstatite and β-post-orthopyroxene (see section S4).
Between 80 ± 13 and 128 ± 18 GPa, pyroxenoid structures persist and coexist with two diffuse rings at 2θ ~ 35° and 2θ ~ 44°, respectively, denoted P1 and P2, whose intensities increase with pressure. For all shocks above 129 ± 20 GPa, only the diffuse rings come from the shocked enstatite (see shocks at 159 ± 35 and 337 ± 55 GPa in Figure 1).

Azimuthal integration of the diffuse signal was done as a function of pressure and density along the Hugoniot (Figure 2). We first investigate the possibility that the diffuse pattern is produced by Bd or post-perovskite (Ppv), the thermodynamically stable phases between 80 ± 13 GPa and the equilibrium melting line (i.e., above 170 GPa). The comparison of our spectra with simulated diffraction patterns (Figure S5) of both polycrystalline Bd and Ppv with 3 nm large crystals (twice smaller than first stishovite crystals observed in laser-shocked silica glass; Gleason et al., 2015) excludes the formation of these high-pressure polymorphs at nanosecond scale. Then, the spectra and the positions of P1 and P2 were compared and found to be similar to the ones obtained in both static and dynamic compression experiments performed on MgSiO3 glass (Kono et al., 2018; Morard et al., 2020). Fourier transform analyses of these compressed glasses have shown that both the appearance of P2 and the shift toward higher q values of P1 are attributed to the continuous change from fourfold to sixfold Si-O coordination (Ghosh et al., 2014; Kono et al., 2018). By analogy, we suggest that enstatite transforms into a disordered phase under shock compression at nanosecond scale between 80 ± 13 and 179 ± 37 GPa, which changes continuously toward a sixfold Si-O structure. Complete refinement at the atomic scale would require larger q range. Based on our previous measurements on MgSiO3 glass (Morard et al., 2020), we find a striking agreement for peak positions of diffuse signal from...
cold compressed glass and shocked disordered enstatite at similar densities (Figure 2), suggesting the transformation of crystalline enstatite into a sixfold Si-O disordered structure under shock compression.

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; De Koker & Stixrude, 2009; Mosenfelder et al., 2009; Stixrude & Karki, 2005).

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 shock experiment (Fratanduono et al., 2018). In addition, VISAR images show that at 128 ± 18 and 159 ± 35 GPa, shocked MgSiO3 presents a large absorption length of ~20 μm at 532 nm, in good agreement with Fratanduono et al. (2018) at submelting conditions (see Figure S6). On the contrary, the VISAR data for the experiment above 300 ± 46 GPa (Figure S6) only show only ghost fringes due to an interfering reflection on the rear side of the silicate (no antireflection coating), indicating that MgSiO3 is opaque or weakly reflecting. This is consistent with the properties predicted for the equilibrium liquid in Soubiran and Militzer (2018).

Figure 3a shows the pressures and densities of shocked enstatite deduced from our velocity measurements with the corresponding lattice structure probed by XRD at nanosecond timescales. Figure 3b shows existing pressure-density measurements obtained in gas gun experiments at the microsecond scale and the interpreted phases from velocimetry. The pressure range in which we observe crystalline XRD patterns corresponds to three different regimes on the microsecond scale Hugoniot: compressed enstatite up to 15 GPa, a mixed phase region that is expected to contain multiple phases (Akins et al., 2004) and extend up to 70 GPa, and akimotoite (70–90 GPa). The disordering of enstatite observed in our experiment occurs at
conditions where Bd and Ppv are considered to form at microsecond scale and leads us to consider disordered MgSiO$_3$ as a reaction intermediate in the formation of Bd and Ppv from shocked enstatite.

4. Discussion

In order to understand transformation kinetics in shocked enstatite and to overcome the limitations inherent to the pressure-density diagram, we investigate possible temperature differences between MgSiO$_3$ enstatite shocked state formed in gas gun (microsecond equilibration at peak pressure) and in laser experiments (nanosecond equilibration at peak pressure). The following interpretation is based on an analogy with recent results on shocked SiO$_2$ (Gleason et al., 2015, 2017; Shen et al., 2016; Shen & Reed, 2016) and assumes that Bd or Ppv actually form in gas gun experiments as interpreted in Akins (2003), Luo et al. (2004), and Mosenfelder et al. (2009).

In shocked SiO$_2$, polycrystalline stishovite nucleates and grows within few nanoseconds from a sixfold Si-O coordinated amorphous phase that has the same structure as the melt obtained at higher pressures (Gleason et al., 2015; Shen et al., 2016; Shen & Reed, 2016). Hundred picoseconds behind the shock front, the thermodynamic conditions in the high-pressure amorphous state lay on the extension of the liquid state Hugoniot below the equilibrium melting line (Figure S7). During crystallization, temperature increases by ~1000 K up to the Hugoniot of stishovite (Shen et al., 2016; Shen & Reed, 2016) although pressure and density do not change significantly compared to the reachable experimental accuracy. We propose that such mechanism occurs in shocked MgSiO$_3$ but at longer timescales.

Since optical emission of shocked enstatite was not recorded in our experiment, we estimated the temperature of our shots—in which disordered MgSiO$_3$ has formed—based on existing Hugoniot measurements of liquid MgSiO$_3$ (Fratanduono et al., 2018) and Hugoniot predictions for both liquid and glassy MgSiO$_3$ from atomistic simulations (De Koker & Stixrude, 2009; Militzer, 2013; Millot et al., 2020), which all use an initial density of 3.22–3.26 g·cm$^{-3}$ (Figure 4). The resulting temperatures at 80 ± 13 and at 159 ± 35 GPa differ by 500–1500 K with existing gas gun measurements (Luo et al., 2004) and, a contrario, are in an excellent agreement with the Hugoniot of Ppv deduced from equilibrium atomistic simulations (Militzer, 2013). This difference between the shock temperature estimated in our nanosecond-scale experiment (with in situ observation of disordered MgSiO$_3$) and the shock temperature measured in microsecond-scale experiments (which compressed state is interpreted as Bd or Ppv based on compression curves) suggests that shocked orthoenstatite first amorphizes and recrystallizes into Bd or Ppv within few microseconds. Therefore, the crystallization kinetics of high-pressure polymorphs in shocked MgSiO$_3$ would be 2–3 orders of magnitude slower than the one occurring in SiO$_2$. This reveals that the degree of polymerization of shocked silicates may be a key parameter to understand recrystallization kinetics in natural environment, for example, shock veins in meteorites.

We mention that the crystalline state of the unshocked sample does not influence the kinetics of crystallization since we observed the same behavior when starting from MgSiO$_3$ glass (Morard et al., 2020).
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5. Conclusions

We studied the structure of shocked [100] orthoenstatite using ultrafast XRD. We found that orthoenstatite densifies while keeping crystalline pyroxene-like structures up to 76 ± 17 GPa. At 80 ± 13 GPa and above, it amorphizes into a dense disordered phase with the same structure as observed in statically compressed MgSiO3 glass. Between 80 ± 13 and 128 ± 18 GPa, the signal of the disordered phase coexists with diffraction spots from pyroxene-like structures, indicating that disordering is incomplete or occurs after first crystalline transformations. Between 128 ± 18 GPa and the melting conditions, only the disordered phase is observed. The liquid, sampled between 300 ± 46 and 337 ± 55 GPa, presents a similar structure. We propose that the disordered state is a reaction intermediate on the transition pathway toward dense MgSiO3 polymorphs, such as akimotoite, Bd, and Ppv, that would crystallize from it at peak pressure. As these high-pressure polymorphs have been indirectly shown to form in microsecond-scale shock experiments (Akins et al., 2004; Luo et al., 2004; Mosenfelder et al., 2009) and are absent from our nanosecond-scale measurements, we expect their crystallization to occur within 0.01–1 μs. This differs significantly from the crystallization kinetics of stishovite in shocked SiO2 which occurs at (sub)nanosecond scale (Gleason et al., 2015; Shen et al., 2016).

Future XRD measurements should investigate the formation of Bd and Ppv at microsecond scale in shock-compressed enstatite, that is, using a gas gun facility.

Data Availability Statement

Data can be found online (osf.io/jz9wt).

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