Stability of ferrous-iron-rich bridgmanite under reducing midmantle conditions

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Our current understanding of the electronic state of iron in lower-mantle minerals leads to a considerable disagreement in bulk sound speed with seismic measurements if the lower mantle has the same composition as the upper mantle (pyrolite). In the modeling studies, the content and oxidation state of Fe in the minerals have been assumed to be constant throughout the lower mantle. Here, we report high-pressure experimental results in which Fe becomes dominantly Fe2+ in bridgmanite synthesized at 40–70 GPa and 2,000 K, while it is in mixed oxidation state (Fe3+/∑Fe = 60%) in the samples synthesized below and above the pressure range. Little Fe3+ in bridgmanite combined with the strong partitioning of Fe2+ into ferropericlase will alter the Fe content for these minerals at 1,100 to 1,700-km depths. Our calculations show that the change in iron content harmonizes the bulk sound speed of pyrolite with the seismic values in this region. Our experiments support no significant changes in bulk composition for most of the mantle, but possible changes in physical properties and processes (such as viscosity and mantle flow patterns) in the midmantle.

bridgmanite | lower mantle | oxidation state | spin transition | bulk sound speed

The variable oxidation state of iron has a profound impact on a range of mantle properties, including the redox conditions and iron partitioning (1, 2). The strong partitioning of trivalent Al into bridgmanite in the lower mantle affects the stability of Fe3+ in the phase because the substitution requires defects or charge coupling (3). McCammon (4) reported a large amount of Fe3+ (Fe3+/∑Fe = 60%; fraction of Fe3+ with respect to total Fe in a phase) in Al-bearing bridgmanite synthesized in a multianvil press, which was subsequently confirmed under reducing conditions (1, 5). Stabilization of Fe3+-Al charge-coupled substitution and charge disproportionation where 3Fe2+ (bridgmanite) → 2Fe3+ (bridgmanite) + Fe0 (metal) both help explain the large amount of Fe3+ under reducing conditions. However, the multianvil studies are limited to ~800-km depth (26 GPa and 2,300 K). High Fe3+/∑Fe has been reported in bridgmanite samples synthesized at higher pressures (2, 6–9). However, the existing data are sparse, and bridgmanite has the capacity for large amounts of Fe3+ under oxidizing conditions (5, 6, 10). Despite these issues, bridgmanite has been assumed to contain a large amount of Fe3+ throughout the lower mantle (1).

The energetics of Fe2+ and Fe3+ incorporation in bridgmanite, however, can change at higher pressures. Whereas oxygen-defect substitution is energetically competitive for the incorporation of trivalent cations at lower pressures, charge-coupled substitution may be increasingly stabilized at higher pressures (11). Also, the spin configuration of valence electrons in Fe in minerals undergoes changes in the lower mantle (12). Because in bridgmanite the spin behavior of Fe is different depending on the oxidation state and the coordination environment, site preferences of Fe2+ and Fe3+ change with pressure (13, 14). These factors affect the stable oxidation state and substitution mechanism at different pressures.

We examined the Fe3+/∑Fe of bridgmanite at a wide range of pressure–temperature conditions related to the lower mantle under reducing conditions. In our experiments, we mixed Fe2+-rich starting materials with approximately bridgmanite stoichiometry with 2–5 wt% Fe metal powder following the method used in multianvil syntheses (1). We enriched all starting materials with 67–95% 57Fe. We loaded the sample mixture into diamond-anvil cells (DACs) together with a pressure medium (SI Appendix, Fig. S1). We heated 14 different samples to 2,000–2,300 K at different pressures with the synthesis monitored by using synchrotron X-ray diffraction (XRD) during and after heating (SI Appendix, Fig. S2). Energy-dispersive X-ray spectroscopy (EDS) in an aberration-corrected electron microscope (ACEM) showed that the bridgmanite samples synthesized at 47 and 56 GPa contain 0.19 ± 0.02 of Fe3+ and 0.10 ± 0.03 of Al4+ on the basis 3 oxygens, which agrees well with the composition of the starting materials within 10% uncertainties from the EDS measurements. Both XRD and ACEM (EDS and imaging) showed that our samples contain bridgmanite and metallic iron (with a small amount of silica only at P < 40 GPa), but found no other phases (see Materials and Methods and SI Appendix for details).

We conducted synchrotron Mössbauer spectroscopy (SMS) on both the temperature-quenched samples at high pressure (hereafter “quench” SMS) and the de novo pressurized samples at 40–70 GPa and 300 K (hereafter “sinch” SMS) (Fig. 1 and SI Appendix, Fig. S3). We used quench SMS for Fe3+/∑Fe, because the...
quench SMS allows for unambiguous determination of the oxidation state of Fe. The spin effect on isomer shift (IS) and quadrupole splitting (QS) generally overlaps with the oxidation effect at high pressures (SI Appendix, section S2 and Fig. S4). The interpretation of the parameters is still controversial at high pressure (13, 14) (SI Appendix, section S3). In contrast, from quench SMS, we can relate IS and QS to the oxidation states of Fe, because near 0 GPa, both Fe$^{2+}$ and Fe$^{3+}$ should be high spin in bridgmanite, and the effects from Fe in different crystallographic sites on the Mössbauer parameters are much less significant than the oxidation states (15) (SI Appendix, section S3). The IS and QS of bridgmanite are also well known at 1 bar with good agreement among existing studies (2, 4, 5) (SI Appendix, section S3 and Fig. S4). Because bridgmanite is metastable at ambient conditions, iron in the phase could be easily oxidized by air or moisture. Therefore, quench SMS were performed for the samples in an inert medium (Ar or Ne) in the DAC at 0–3 GPa.

We found that the quench SMS spectra of bridgmanite synthesized at 47–63 GPa are distinct from the spectra at lower and higher pressures (Fig. 1A and SI Appendix, Fig. S3). The spectra in this pressure range have much more well-defined quantum beats compared with those in other pressure ranges. The synthetic SMS spectrum of Fe$^{2+}$-rich bridgmanite agrees well with the measured SMS spectra of bridgmanite synthesized at the pressure range (Fig. 1A). Our spectral fitting showed that Fe$^{3+}/\Sigma$Fe drops to 13–22% at 47–63 GPa, whereas it is ~60% at lower and higher pressures (Fig. 2 and SI Appendix, Fig. S4 and Table S1). Our glass-starting material contains 10% of Fe$^{3+}/\Sigma$Fe, similar to the Fe$^{3+}/\Sigma$Fe observed at 51–63 GPa. This similarity means that the system does not produce Fe$^{3+}$ over this pressure range. The other Mössbauer parameters, QS and IS, are in agreement with the previous studies (SI Appendix, Fig. S4B), indicating that the changes found in the spectra originated from Fe$^{3+}$ content.

Among the recovered samples for SMS, one synthesized at 47 GPa (Figs. 1 and 2) was sufficiently thinned for electron energy loss spectroscopy (EELS) (Fig. 3). EELS can measure Fe$^{3+}/\Sigma$Fe through energy changes during electronic transitions, which is a completely different physical process compared with SMS. Therefore, EELS provides an independent determination of Fe$^{3+}/\Sigma$Fe in bridgmanite, complementing the SMS data analysis which can be sensitive to starting models. However, the intense electron beam is known to alter Fe$^{3+}/\Sigma$Fe during EELS measurements, even for minerals stable at ambient conditions (16). Therefore, we optimized EELS parameters until we found no changes in Fe$^{3+}/\Sigma$Fe of the standard mineral specimens: olivine, andradite, and crosnstedite (Fig. 3). All of the EELS spectra measured for the sample showed negligible spectral signatures from Fe$^{3+}$ in both L$_2$ and L$_3$, indicating that iron in the sample is predominantly Fe$^{2+}$ (Fig. 3). Spectral fitting indicated that Fe$^{3+}/\Sigma$Fe should be <10%, which agrees with our quench SMS for the same sample.

Our Fe$^{3+}/\Sigma$Fe at the lowest pressure (35 GPa) agrees well with the multianvil results (1, 5) on aluminous bridgmanite under reducing conditions at 26 GPa (Fig. 2). There are three other datasets from laser-heated DAC (LHDAC) experiments (7–9), which have a wide enough pressure range for comparison with our dataset, although these datasets have fewer data points, with larger gaps between the points (Fig. 2). None of these three datasets show a clear drop in Fe$^{3+}/\Sigma$Fe at 47–63 GPa. However, there are a few important differences in the experiments. The chemical compositions of these three datasets are all different from each other and also from our study (see SI Appendix for details). The three data points in Sinnmo et al. (7) all have different chemical compositions. A data point at 93 GPa in Piet et al. (9) was obtained from a different starting material with much more Al. Prescher et al. (8) used Fe$^{3+}$-rich bridgmanite synthesized at 25 GPa as a starting material, which is different from our study and the other two (7, 9), where starting materials were amorphous. Unlike amorphous starting materials, which are highly metastable at high pressure and therefore affected less by kinetic effects during high-temperature synthesis of bridgmanite, conversion from Fe$^{3+}$-rich to Fe$^{2+}$-rich bridgmanite would
have a higher kinetic barrier to overcome. We loaded metallic Fe to ensure the reducing conditions during synthesis. None of the three studies loaded metallic Fe. However, Simno et al. (7) observed metallic iron after synthesis. Therefore, the redox conditions for the dataset from the study might be comparable to our dataset. Despite these differences and fewer data points, it is interesting that all three datasets suggest a possible decrease in Fe$^{3+}$/∑Fe (by 20–30%) in the midmantle (Fig. 2). The different experimental methods and composition may contribute to the different pressures in the Fe$^{3+}$/∑Fe decrease and its magnitude observed in the datasets (7–9).

The drop of Fe$^{3+}$/∑Fe found here (Fig. 2) requires changes in substitution mechanisms in bridgmanite with pressure (Fig. 4B). Existing data (1, 5) suggest that the dominant factors for high Fe$^{3+}$/∑Fe in bridgmanite at 25–30 GPa are the VIII$\text{Al}^{3+}$—VI$\text{Al}^{3+}$ charge-coupled substitution where VIII and VI represents the eight (or A) and six (or B) coordinated sites in a perovskite-type structure, respectively [charge disproportionation (SI Appendix, Reaction S2)]. Previous studies also indicate smaller but important contributions from the VIII$\text{Al}^{3+}$—VI$\text{Al}^{3+}$ charge-coupled substitution (SI Appendix, Reaction S5) and oxygen vacancy substitution (SI Appendix, Reaction S6) at 25–26 GPa, even when bridgmanite contains equal amounts of Al and Fe (SI Appendix, section S4). With an increase in pressure between 25 and 51 GPa, oxygen vacancies are expected to disappear (11) (SI Appendix, Reaction S10), and the VIII$\text{Al}^{3+}$—VI$\text{Al}^{3+}$ configuration (SI Appendix,Reaction S11) may become energetically more favorable than the VIII$\text{Fe}^{3+}$—VI$\text{Al}^{3+}$ configuration, leading to minimum Fe$^{3+}$/∑Fe at 53–63 GPa. The proposed change may be driven by smaller volume of the VIII$\text{Al}^{3+}$—VI$\text{Al}^{3+}$ configuration. Such a configuration will increase the content of Al in the A site, which decreases the volume of the A site where larger-sized Mg and Fe existed. It will also decrease the content of Al in the B site, which reduces the volume of the B site by increasing in the content of smaller-sized Si. However, conversion of Fe$^{3+}$ to Fe$^{2+}$ would increase the volume of the A site. Our in situ SMS indicates the appearance of a new Fe site with QS as high as 4 mm/s at the pressure where Fe$^{3+}$/∑Fe rapidly decreases (42 GPa; Fig. 1B and SI Appendix, Fig. S5), suggesting either changes in spin state or local structure for Fe$^{2+}$ in the A site (SI Appendix, section S4.5). If such changes can decrease the ionic radius of Fe$^{2+}$, it will further stabilize the VIII$\text{Al}^{3+}$—VI$\text{Al}^{3+}$ configuration and therefore decrease Fe$^{3+}$/∑Fe. At 25–50 GPa, Fe$^{3+}$ would remain in the A site (SI Appendix, section S4.5).

Ferric iron in the B site undergoes a high- to low-spin transition at 50–70 GPa (10, 14). If this spin transition results in a smaller ionic radius of Fe$^{3+}$, likely comparable with that of Al$^{3+}$, the charge disproportionation would become more stable, and Fe$^{3+}$/∑Fe would increase by stabilization of the VIII$\text{Fe}^{3+}$—VI$\text{Al}^{3+}$ configuration (Fig. 4A and SI Appendix, section S4.7). We calculated the volume change in charge disproportionation of Fe to such a configuration (SI Appendix, Fig. S8C and section S4.7) and found that the volume of the VIII$\text{Fe}^{3+}$—VI$\text{Al}^{3+}$ configuration is significantly smaller, supporting the proposed change in the substitution mechanism at pressures >70 GPa.

Our results indicate that almost all of the iron in bridgmanite is ferrous (Fe$^{2+}$), with little ferric (Fe$^{3+}$) iron at 1,100- to 1,700-km depths (hereafter low ferric iron bridgmanite zone; LIBZ), whereas bridgmanite in the lower mantle regions above and below LIBZ contains >50% of iron in the ferric oxidation state (hereafter high ferric iron bridgmanite zone; HIBZ).

Because Fe$^{2+}$ enters bridgmanite (2), bridgmanite will be depleted in Fe in LIBZ (also can be referred to as low-iron bridgmanite zone) compared with HIBZs (also can be referred to as high-iron bridgmanite zone), and ferropericlase will have an increased amount of Fe in LIBZ compared with HIBZs (Fig. 4B). A number of studies have been conducted to compare the density and velocity profiles of compositional models (pyrolite) with seismic observations. However, these models have assumed that the compositions of individual minerals, in particular Fe content and oxidation state, do not change throughout the lower mantle (18–20). Both experiments and computations have found that the bulk modulus (and therefore bulk speed) of ferropericlase decreases considerably within the pressure range where the phase is in a transitional state from high spin to low spin (therefore, a mixed-spin state), although the bulk modulus of ferropericlase with high-spin Fe is essentially the same as that with low spin (18–21). In contrast, the spin transition has no significant impact on density and shear velocity profiles (18–21).

The bulk sound speed profile of pyrolite along the mantle geotherm shows significant discrepancy with seismic values if it is calculated by assuming constant Fe$^{3+}$/∑Fe in bridgmanite (therefore constant mineral compositions) throughout the lower mantle. As shown in Fig. 4A, such discrepancies are clear at 1,300- to 1,800-km and 2,100- to 2,400-km depths, if bridgmanite is rich in Fe$^{3+}$ and Fe$^{2+}$ (and therefore ferropericlase has low and high Fe contents), respectively, throughout the lower mantle (see Materials and Methods for details). Although the bulk sound speed depression should be detectable, such large-scale structures have not been found in the lower mantle (22). Decreasing the content of ferropericlase provides a substantially better fit. However, the required decrease increases the bulk sound speed of mineralogical models above the seismic values throughout the lower mantle and results in a much lower Mg/Si ratio for the lower mantle than the upper mantle. The change in Mg/Si ratio would make the lower mantle nonpyrolitic as a result, making the lower mantle richer in Si.

We include the observed Fe$^{3+}$/∑Fe change in the calculation (the red curve in Fig. 4A). From the iron partition coefficients for Fe$^{2+}$- and Fe$^{3+}$-rich bridgmanite (2, 23), we obtained 0.27 and 0.15 Fe# of ferropericlase (for 1 oxygen base chemical formula) in LIBZ and HIBZs for pyrolite composition in response to the Fe oxidation state change in bridgmanite, respectively (see Materials and Methods for details). The higher Fe content in ferropericlase in LIBZ (0.27 Fe#) will significantly increase the spin transition pressure for the Fe (18, 20). As shown in Fig. 4D (blue curves), because the spin transition does not occur until much greater depths, ferropericlase with higher Fe content in LIBZ will have only high-spin Fe$^{2+}$. Ferropericlase (with lower Fe content) in HIBZs would not decrease bulk sound speed significantly because the mixed-spin state, which causes the severe bulk modulus decrease for 0.15 Fe#, occurs at the depths of LIBZ. Instead, ferropericlase has almost all Fe$^{2+}$ in high spin in shallow
Shim et al. PNAS

HIBZ at 660- to 1,100-km depths and low spin in the deep HIBZ at 1,700- to 2,900-km depths.

Unlike the models without the bridgmanite Fe\(^{3+}/\sum\)Fe change, we found no significant reduction in the bulk sound speed profile of pyroilite when we incorporate the observed Fe\(^{3+}/\sum\)Fe change in the calculation (Fig. 4A). The bulk sound profile of pyroilite with the bridgmanite Fe\(^{3+}/\sum\)Fe change agrees well with average [preliminary reference Earth model (PREM)] seismic values for the lower mantle (17). We also found that the density profile of pyroilite agrees well with seismic values (SI Appendix, Fig. S10). Fe\(^{3+}/\sum\)Fe in bridgmanite decreases and increases above and below LFB at over a pressure interval of 10–20 GPa. Such a gradual change will not result in any sharp changes in the lower mantle seismic profiles, consistent with the absence of global seismic discontinuities in the 1,000- to 2,000-km depth interval.

We showed that the reduction of Fe\(^{3+}\) in bridgmanite at 1,100- to 1,700-km depths reconciles the discrepancy in bulk sound speed profile between pyroilite lower-mantle composition and seismic observations. Therefore, there is no need for differences in major element chemistry between the upper and lower mantle, consistent with seismic observations of slabs penetrating to the lowermost mantle and therefore whole mantle convection (24).

An important unknown in the model above is possible compositional sensitivity of the depth interval for the Fe\(^{3+}/\sum\)Fe drop in bridgmanite. A recent Brillouin spectroscopy study (25) found good agreement in velocities between Fe\(^{3+}\)-rich bridgmanite in Mg\(_9\)Fe\(_{10}\)Al\(_{5}\)Si\(_{2}\)O\(_{22}\) and seismic 1D model (PREM) at pressures expected for the shallower lower mantle. However, the velocities of Fe\(^{3+}\)-rich bridgmanite showed significant mismatch with the seismic model at depths >1,300 km, while Fe\(^{2+}\)-rich bridgmanite agrees better with the seismic model in the region. The observations led to a proposal that Fe\(^{3+}/\sum\)Fe in bridgmanite decreases at the depth range. The proposed depth is remarkably similar to the depth expected for the Fe\(^{3+}/\sum\)Fe drop in bridgmanite found in our study (1,100 km), despite the difference in the total Fe content.

Recently, elevated viscosity has been reported (26) near the depth of low-Fe\(^{3+}\)-rich bridgmanite (LIBZ) (Fig. 4C). Most P-wave tomographic models (27) also show a transition from minimum radial correlation of seismic structures at 700–1,000 km to enhanced correlation at depths greater than ~1,500 km (Fig. 4D). Recent tomographic models have found stagnation or broadening of some subducting slabs (28) and horizontal deflections of some mantle plumes (29) near this depth range. Numerical simulations demonstrated that the viscosity elevation at 1,000–1,500 km can produce such seismic observations (26).

Being the dominant phase in the region (70 vol%), bridgmanite controls the viscosity of the lower mantle (30). According to our study, bridgmanite in LIBZ at 1,100–1,700 km contains little or no Fe\(^{3+}\) and therefore a lower amount of Fe because of strong partitioning of Fe\(^{2+}\) to ferropericlase. Although the effect of Fe is still unknown for the viscosity of bridgmanite due to technical difficulties, iron can decrease viscosity as shown in other minerals (31). Because iron reduces the melting temperature of bridgmanite and viscosity can be scaled to homologous temperature (temperature normalized to material’s melting temperature) (32), low-Fe content bridgmanite at 1,100–1,700 km would have a high viscosity, providing a plausible explanation for
the viscosity increase (26) without invoking any major changes in chemical composition over this depth range.

**Materials and Methods**

**Starting Materials.** We used two different starting materials with the same composition: 28.8 wt% MgO, 53.6 wt% SiO₂, 12.8 wt% FeO, and 4.8 wt% Al₂O₃. We synthesized 15 bridgmanite samples ([SI Appendix, Table S1](#)). For the 3-oxide formula unit of bridgmanite, the synthesized bridgmanite contained 0.19Fe and 0.10Al, which are both elevated from the samples studied previously, including pyroxene and glass-starting materials, respectively. The SMS data of these materials indicate that the pyroxene contains no detectable amount of Fe²⁺ and the glass-starting material contains Fe³⁺/ΣFe ≈ 10% ([SI Appendix, Fig. S3 and section S3](#)).

**Sample Preparation.** To ensure reducing conditions, we mixed our starting materials with reduced Fe metal powder (2-5 wt%) following the method used in multianvil syntheses by Frost et al. ([1](#), SI Appendix, Figs. S1 and S9). A potential disadvantage of mixing metallic Fe with the starting materials is the complexity of measured SMS due to Mössbauer signal from Fe in both metal and bridgmanite. To reduce the problem, we used metallic Fe with a natural level of Fe²⁺ (2%) and starting materials with Fe³⁺ enrichment (67-95%). We also limited the amount of metallic iron to <5 wt%. The powder mixture was compressed between diamond anvils to make a rigid foil. The foil was loaded into the hole in a preindented Re gasket. The foil was probed by three to four grains of the starting materials to allow Ar or Ne to flow in to separate the foil from the diamond anvils during cryogenic or gas loading ([SI Appendix, Table S1](#)). The separation of the sample foil from the diamond anvils is particularly important to prevent direct contact between the diamond anvils and the sample foil and therefore to ensure lower thermal gradient during laser heating. One sample was loaded with a KCl medium. The KCl was dried at 1,073 K for 24 h before loading. Some ruby chips were loaded on the gasket or the edge of the sample chamber as pressure sensors, to avoid direct contact between the ruby chips and our sample foils. Pressures were measured by using both ruby (34) and diamond pressure scales (35) after temperature quench.

**High-Pressure Synthesis.** At a target pressure, double-sided laser heating was conducted to 2,000–2,300 K at sectors 13 and 16, Advanced Photon Source (APS). By scanning the infrared laser beams (1,065 nm), we transformed the entire foil of the starting material + Fe metal powder mixture into bridgmanite + Fe metal powder. The size of hot spot was 20-25 µm, and the laser fluence was calculated by 2-5 µm during scanning. In the first scan, each spot was heated for 5–10 min until the starting material transformed to bridgmanite. From the second scan, each spot was heated for 1–5 min. The scan was repeated for multiples of time. Each spot was heated for a total of ~10–30 min. Thermal radiation spectra from both sides of the sample were measured by using an imaging spectrometer and fitted to the Planck black-body radiation function to obtain temperatures. To avoid memory effects from preexisting electronic configuration of Fe and the crystal structure, once bridgmanite was formed at a target pressure, the samples were never heated again at different pressures. The pressure before and after heating was measured. We found pressure changes <5 GPa. However, pressure in the DAC during laser heating should be higher due to thermal pressure (36, 37). Previous studies have shown a ~5 GPa increase for heating to 2,000–2,300 K (38), which is included in the estimated error bars presented in Fig. 2.

**Synchronous XRD.** Diffraction patterns were measured during laser heating and after temperature quench for nine different samples at different pressures, ranging between 31 and 105 GPa, to ensure the synthesis of bridgmanite ([SI Appendix, Fig. S2](#)). The measurements were conducted at beamlines 13IDD (39) and 16IDB (40) of the APS. At GECARS, monochromatic X-ray beams with a wavelength of 0.3344 Å were focused to an area of 3 × 4 µm² on the sample in LHDAC. At the High-Pressure Collaborative Access Team (HPCAT), monochromatic X-ray beams with a wavelength of 0.3515 Å were focused to an area of 5 × 6 µm² on the sample in LHDAC. Powder diffraction images were collected by using MarCCD detectors. The laser beams were aligned coaxially with the X-ray beam.

**SMS.** Nuclear forward scattering was conducted at sector 3 of APS (Fig. 1 and [SI Appendix, Fig S3](#)). A 14.4-keV X-ray beam was focused on an area of 6 × 6 µm² in the sample. The storage ring was operated in top-up mode with 24 bunches separated by 153 ns. Nuclear resonant scattering was measured in a time window of 15–130 ns with a typical data collection time of 8–12 h. We conducted SMS on both the temperature-quenched samples at high pressure (in situ SMS) and decompressed samples at 0–3 GPa in DAC (quench SMS). A total of 14 samples were successfully measured in situ high pressure in DAC after laser heating. Ten samples were successfully quenched to 0–3 GPa, where SMS was conducted. The spectral fitting was performed by using the CONUSS package (41) ([SI Appendix, section S3](#) for details).

**EELS.** We expanded the beam size at the sample to 100–200 nm in a transmission electron microscope (TEM) mode with sufficiently low accelerating voltage at 120 kV to reduce the electron dosage of the sample, while allowing enough total intensity to provide good signal-to-noise ratios for the spectra. The measurements were performed in a JEOL ARM200 ACEM with a Gatan Enfinium spectrometer. The energy resolution was 0.7–0.9 eV. We avoided the area with metallic iron grains to obtain EELS spectra from pure bridgmanite. We also measured the EELS spectra of minerals with known oxidation states of Fe (olivine, pyroxene, andradite, and cronstedite) using the same instrumental conditions and used them for spectral fitting to extract Fe²⁺/ΣFe. The fraction of ferric iron (Fe³⁺/ΣFe) was determined by the EELS analysis methods in ref. 42.

**Lower-Mantle 1D Profile Calculations.** The bulk sound speed and density profiles were calculated for pyrolite by using the Burman toolkit (44) combined with the parameters listed in [SI Appendix, Table S2](#) (14, 45, 45-47) along the mantle geotherm (48). We corrected volume and elasticity for compositional differences using a linear assumption. We assumed that thermal parameters were not sensitive to compositional differences.

We conducted calculations for a CaO–MgO–Al₂O₃–SiO₂–FeO system with oxide compositions from the pyrolite composition in Ringwood (69). The bulk composition was fixed throughout the lower mantle for all of the pyrolite profiles we calculated. Iron partition coefficients were 0.58 (2) and 0.12 (23) for Fe¹⁺/Fe²⁺ (HIBZs) and Fe²⁺/Fe³⁺ (LIBZ) bridgmanite systems, respectively. From the partition coefficients and the pyrolite composition, we obtained: 0.045Fe²⁺/Fe³⁺ and 0.045Fe²⁺/Fe³⁺ in bridgmanite and 0.15Fe²⁺/Fe³⁺ in ferropericlase for Irid-fuine (2) and 0.04Fe²⁺/Fe³⁺ in bridgmanite and 0.27Fe²⁺/Fe³⁺ in ferropericlase for LIBZ. All Al₂O₃ entered bridgmanite, and all CaO was incorporated into CaSiO₂ perovskite in our models.

Our Fe# values for bridgmanite and ferropericlase in HIBZ was consistent with the Fe# reported for pyrolite with Fe³⁺-rich bridgmanite in Iri-fune et al. (2), 0.09–0.10 and 0.12–0.14, respectively. Ferropericlase in the study had slightly lower Fe# than ours because it contained other cations, such as Si, Al, Ni, Cr, and Na, the total content of which was 0.02–0.06 cation#. In our calculation, we assumed that Si and Al did not enter ferropericlase and did not consider minor oxide components with weight percent less than 1%.

The bulk sound speed and density of ferropericlase were calculated for their corresponding iron contents (0.15 and 0.27 Fe# in Fig. 4A and [SI Appendix, Fig. S3](#)). We calculated the softening of bul sound speed in ferropericlase in mixed spin using the methods and parameters presented in previous studies (18, 20). Both theory and experiments have shown that spin transition pressure increases with Fe content in ferropericlase (50–53). Temperature also increases the spin transition pressure and the interval of the spin transition zone (54, 55). Therefore, we consider data obtained at high pressure-temperature (18, 20). Because there are no data of the experimental data for our two compositions, we adapted the spin transition pressures reported for 0.1875 and 0.25 Fe# ferropericlase at mantle-related high temperatures (18, 20) for 0.15 HIBZ and 0.27 LIBZ Fe# respectively. Density profiles of all three presented pyrolite models are in agreement, consistent with previous results (18, 20), in that ferropericlase
spin transition does not have significant impact on density (SI Appendix, Fig. S10).

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Supporting Information: Stability of Ferrous-Iron-Rich Bridgmanite under Reducing Mid-Mantle Conditions

S1 Synthesis of starting materials

The glass starting material was synthesized from an oxide mixture of (Mg,Fe)SiO$_3$ pyroxene + Al$_2$O$_3$ using laser levitation method under CO+CO$_2$ mixture gas atmosphere to ensure reducing conditions(1). The pyroxene starting materials were synthesized from a stoichiometric mixture in an iron capsule at 2 GPa and 1,673 K in a piston-cylinder device for 24 hours.

Figure S1: High-pressure sample synthesis method in this study. (A) A schematic diagram of the laser-heated diamond-anvil cell (LHDAC), (B) A microphotograph of the bridgmanite + Fe metal mixture at 63 GPa after laser heating. The size of the sample chamber is 100 $\mu$m in diameter. A $^{57}$Fe enriched (95%) starting material is mixed with metallic Fe with a natural level of $^{57}$Fe (2%) in this setup for reducing conditions during the high pressure synthesis.
Figure S2: Synchrotron X-ray diffraction patterns (black dots) of the bridgmanite + Fe metal mixtures measured in the diamond-anvil cell at in situ high pressure after laser heating to 2,000–2,300 K. The red and blue curves are the calculated diffraction patterns from Rietveld refinement and their differences from observed diffraction intensities, respectively. The calculated peak positions of the phases in the sample are shown in black vertical bars. (A) 31(2) GPa with unit-cell parameters of bridgmanite: \(a = 4.6462(6) \text{ Å}, b = 4.8125(17) \text{ Å}, \text{ and } c = 6.7106(12) \text{ Å}, \) and \(V = 150.05(4) \text{ Å}^3\) for \(R_{wp} = 0.0064\) where \(R_{wp}\) is the fit residual factor. (B) 56(3) GPa with unit-cell parameters of bridgmanite: \(a = 4.5491(5) \text{ Å}, b = 4.7392(8) \text{ Å}, \text{ and } c = 6.5806(7) \text{ Å}, \) and \(V = 141.87(2) \text{ Å}^3\) for \(R_{wp} = 0.0029\). (C) 72(4) GPa with unit-cell parameters of bridgmanite: \(a = 4.4627(3) \text{ Å}, b = 4.6740(4) \text{ Å}, c = 6.4741(5) \text{ Å}, \) and \(V = 135.04(1) \text{ Å}^3\) for \(R_{wp} = 0.0025\). The 2D diffraction images were integrated to 1D diffraction patterns using the DIOPTAS software. The tilt and sample-to-detector distance were measured using CeO\(_2\) or LaB\(_6\) diffraction standards. We fit the diffraction patterns using the GSAS package (2). The Rietveld refinements of the measured patterns confirm the synthesis of bridgmanite. The observed diffraction patterns are well fit with bridgmanite, metallic Fe, and pressure medium (Ne, Ar, or KCl) except for the synthesis at pressures below 40 GPa where a small amount of stishovite was observed (Fig. S2a). Small amounts of stishovite have also been documented in previous multi-anvil synthesis of Fe,Al-bearing bridgmanite (3–5). The unit cell parameters of bridgmanite (provided in the caption of Fig. S2) are consistent with those reported for Fe-rich and Al-rich bridgmanite(6, 7).
Mössbauer spectroscopy (Fig. S3) for the recovered samples has some important advantages for the accurate determination of Fe$^{3+}/\Sigma$Fe. First, the quench SMS allows for unambiguous determination of the oxidation state of Fe. The spin effect on isomer shift ($IS$) and quadrupole splitting ($QS$) generally overlaps with the oxidation effect. For example, the $QS$ of Fe$^{2+}$ decreases by the high-spin (HS) to low-spin (LS) change, becoming similar to that of HS Fe$^{3+}$, and the $QS$ of Fe$^{3+}$ increases by the spin transition, becoming similar to that of HS Fe$^{2+}$ (Fig. S4b; (5, 9)). Near 0 GPa, both Fe$^{2+}$ and Fe$^{3+}$ should be in HS in bridgmanite and therefore $IS$ and $QS$ can be directly related to oxidation states of Fe, whereas at high pressure the spin transition of iron makes the assignment ambiguous. Second, the $IS$ and $QS$ of bridgmanite are well known at 1 bar and existing studies are all in good agreement (Fig. S4b; (4, 5, 8, 10–13)). However, they are still controversial at high pressure (5, 13, 14). Third, at lower pressure in the stability field of bcc-Fe, the Mössbauer signal from metallic Fe is much easier to distinguish due to magnetic ordering in bcc-Fe. An example can be found in the 70 GPa spectrum in Fig S3c.
Figure S3: Synchrotron Mössbauer spectra (circles: measured intensities; curves: fitted spectra). (A) The starting materials at 1 bar. (B) Synthetic spectra of bridgmanite at 1 bar with different amount of Fe$^{3+}$ using $IS$ and $QS$ values from McCammon et al. (8). (C) Bridgmanite recovered to 0–3 GPa after synthesis at different pressures and 2,000–2,300 K. (D) Bridgmanite at in situ high pressure after laser heating. The high frequency features in the spectrum at 70 GPa in c are from metallic Fe in the sample. In the other quench spectra, natural level of $^{57}$Fe (2%) and low content (2–5 wt%) of metallic Fe produce no significant spectral signatures.
S3 Synchrotron Mössbauer Spectroscopy

S3.1 Comparison with synthetic spectra

Using the Mössbauer parameters reported in McCammon et al. (8), we calculate two synchrotron Mössbauer spectra, one with 100% and the other with 0% Fe$^{3+}$. The shape of the spectra measured on the samples from pressures between 47–63 GPa compares better with the synthetic spectrum for 0% Fe$^{3+}$, while the spectra at other pressures compare better with the synthetic spectrum for 100% Fe$^{3+}$ (Fig. 1).

S3.2 Spectral fitting

The spectral fitting was performed for both binned and unbinned spectra using the CONUSS package (15). Results from fitting binned spectra are presented in Tab. S1. In order to avoid non-uniqueness of the fit results, we conducted Monte-Carlo search in CONUSS in the beginning of all the fittings we performed. We also attempted various different starting models, including high Fe$^{3+}$/∑Fe models for the spectra measured in the bridgmanite samples synthesized at 50–70 GPa and low Fe$^{3+}$/∑Fe models for the spectra measured in the bridgmanite samples synthesized at pressures lower than 50 GPa and higher than 70 GPa. We found that the results presented in Tab. S1 fit the observed spectra significantly better than other models we attempted through Monte-Carlo searches and manual tests. Also, the $QS$ and $IS$ of bridgmanite in our results based on time-domain Mössbauer spectroscopy show excellent agreement with those reported by energy-domain Mössbauer spectroscopy studies (Fig. S4b).

S3.3 Sites Q0, Q1, and Q2 in quench SMS

Fitting for our quench SMS requires a three site model, a low $QS$ site (Fe$^{3+}$), a high $QS$ site (Fe$^{2+}$), and a site with $QS = 0$ mm/s (sites Q1, Q2, and Q0, respectively, in Tab. S1). The two former sites have $QS$ values agreeing well with those reported for Fe$^{3+}$ and Fe$^{2+}$. Most Mössbauer studies
performed at 1 bar have identified a site with $QS \approx 1.5–2.2 \text{ mm/s}$ in bridgmanite, which can be assigned to HS Fe$^{2+}$ (3, 10–12). In previous Mössbauer studies which identified Fe$^{3+}$ in bridgmanite at 1 bar, a site with $QS \approx 0.8–1.1 \text{ mm/s}$ was reported and assigned to HS Fe$^{3+}$ (3, 11, 12) (Fig. S4b).

Although a slightly elevated $QS$ value was found for the Fe$^{2+}$ site at the pressure where we observed the lowest Fe$^{3+}/\Sigma$Fe, the magnitude is small compared with the range of values reported in previous studies for the same site. For the Fe$^{3+}$ site, the $QS$ remains essentially the same. The isomer shift ($IS$) of the Fe$^{3+}$ site is 0.3–0.5 mm/s and the $IS$ difference ($\Delta IS$) between the Fe$^{2+}$ and Fe$^{3+}$ sites is 0.6–1.0 mm/s (Tab. S1), which are also in good agreement with previous studies (4, 8). The data scatter found in our dataset for $\Delta IS$ is similar to that reported in (4), considering the fact that SMS yields relative $IS$ (i.e., $\Delta IS$) and therefore data scatter of $\Delta IS$ affected by both sites themselves and reference site.

We fit un-binned data and found that site Q0 (a site with $QS = 0$, mostly ~6% in “quench” SMS) is not required. The fitting results without site Q0 are still in agreement with binned data fit results with site Q0, but with larger estimated uncertainties. This observation suggests that Q0 originates from binning. From the low $QS$ values, site Q0 could be assigned to another Fe$^{3+}$ site in bridgmanite. However, even if we include the sites as Fe$^{3+}$, the trend we found in Fe$^{3+}/\Sigma$Fe does not change and the increase is insignificant considering the experimental uncertainties as shown in Fig. S4.

**S3.4 Sites P1 and P2 in in-situ SMS**

For the in-situ SMS, the most satisfying fit was obtained if a three-site model was considered for the spectra up to 35 GPa and a four-site model was considered for the spectra at higher pressures. An exception is a spectrum measured at 75 GPa where a three-site model provided a sufficiently good fit. All of our sites found in in-situ SMS have been documented in previous Mössbauer studies on bridgmanite (5, 12, 13). We did not observe a site at $QS \approx 1 \text{ mm/s}$, which was documented in some high-pressure studies (Fig. S5).

Unlike the case for the Mössbauer parameters of quenched bridgmanite, the assignments for the Fe sites at in situ high pressure are highly controversial. The pressure dependent changes
Figure S4: Mössbauer parameters of Fe in Al-free and Al-bearing bridgmanite. (A) Fe$^{3+}$/∑Fe and (B) quadrupole splitting ($QS$) of Fe in bridgmanite. The parameters were measured for the samples quenched to 0–3 GPa. Case 1 excludes site Q0 ($Q = 0$ mm/s) in the estimation of Fe$^{3+}$/∑Fe, $[Q1]/([Q0]+[Q1]+[Q2])$, and case 2 assumes site Q0 is from Fe$^{3+}$, $([Q0]+[Q1])/([Q0]+[Q1]+[Q2])$. We also plot data from previous studies (4, 5, 8, 10–12, 16–18, 18–24). The error bars are estimated uncertainties. The gray scale for the symbols of the previous data points represents Al# for 3O basis bridgmanite formula (black: Al# ≥ 0.1 and white: Al# 0). In b, the vertical bars on the right side indicate the ranges of $QS$ suggested for Fe$^{2+}$ and Fe$^{3+}$ with different spin states (9, 25).
Figure S5: Mössbauer parameters of Fe in bridgmanite at in situ high pressures. (A) Percentage of Fe$^{3+}$-like sites (low-\(QS\) sites), \([P1]/([P1]+[P2]+[P3])\) for case 1 and \(([P0]+[P1])/([P0]+[P1]+[P2]+[P3])\) for case 2. (B) Quadrupole splitting (\(QS\)) of Fe in bridgmanite. The error bars are estimated uncertainties. For comparison, we plot Mössbauer parameters from other in situ high pressure measurements (5, 13, 14, 19).
in Mössbauer parameters are not in agreement. More importantly, the effects of electron spin configuration on the Mössbauer parameters of Fe makes the assignments of particular Mössbauer parameters to the oxidation state of Fe much more uncertain at high pressure. For example, theoretical calculations (9) have suggested that the high-spin to low-spin change in Fe$^{2+}$ decreases the $QS$ value similar to that of high-spin Fe$^{3+}$ and vise versa (Fig. S4b). Furthermore, although it has been documented by many researchers, the assignment of a particular spin state and valence state for the site with $QS \geq 4$ mm/s (site P3 in our study) remains controversial (9, 14, 25, 26) (see S3.5). Therefore, the quench measurements provide much more robust data for the estimation of Fe$^{3+}/\Sigma$Fe.

Our $QS$ values obtained from in situ spectra show the best agreement with a recent Mössbauer study on cold compressed Al-free bridgmanite (5) (Fig. S5b), although pressures where changes occur are different, which might be due to the Al effects. Site P1 has the $QS$ value formerly assigned to Fe$^{3+}$ at high pressure. However, it is difficult to attribute the entire amount to HS Fe$^{3+}$ because LS Fe$^{2+}$ has a very similar $QS$. Nevertheless, the trend in the percentage of site P1 of in situ SMS (Fig. S5a) is very similar to that of Fe$^{3+}/\Sigma$Fe obtained from the quench spectra (Fig. 2), suggesting that much of site P1 in Fig. S5a may be from HS Fe$^{3+}$.

For site P2, although pressures where the value changes occur are different, likely because of differences in composition, our $QS$ values are in excellent agreement with ones reported in (5) (Fig. 2b), despite the differences in synthesis pressure and composition (our samples are synthesized at much higher pressures). Our $QS$ values and the values from ref.5 are in general slightly greater than those reported in (12), while pressure dependent changes are comparable in all three studies.

S3.5 Site P3 in in-situ SMS

The in-situ spectra show similar changes as quench spectra: progressive change from flat to more developed quantum beats with an increase in pressure. However, unlike the case for the quench spectra, more quantum beats are observed and they do not disappear above 70 GPa. Instead, they remain in the spectra up to the maximum pressure of the experiments. Spectral fitting reveals the
difference is related to the appearance of a high $QS$ ($\approx 4.0 \text{ mm/s}$) site at 42 GPa, site P3 (Fig. S5b). The appearance of the high $QS$ site has been documented in recent experiments but at different pressures (5, 13, 14, 19, 21). The assignments of the sites to particular spin state or valence state remain controversial: intermediate spin (14, 27) versus high/low spin (5, 26, 28). It is notable that the pressure at which site P3 coincides with the pressure at which Fe$^{3+}/\Sigma$Fe of bridgmanite begins to drop.

**S3.6 Site P0**

Although it is minor (3–27%), our fitting for the binned data requires a site with $QS = 0 \text{ mm/s}$ for in situ (site P0) SMS (Fig. S6 and Tab. S1). Unlike Q0, P0 is required in un-binned fitting. This site should be from either bridgmanite or metallic iron because our XRD (both in situ and quench) and TEM show that our synthesis products contain only bridgmanite and metallic iron (Figs S2 and S9).

The low $QS$ value without a magnetic hyperfine field may indicate that the site is from non-magnetic high-pressure polymorphs of metallic iron (such as hcp- and fcc-Fe). High-pressure studies have reported a very low $QS$, $0\sim0.1 \text{ mm/s}$, in hcp-Fe (29, 30), which is in good agreement with site P0. We have in situ SMS with a stainless steel foil for isomer shift measurements at four different pressures, e.g., 31, 51, 56, and 63 GPa. However, the fraction of P0 at 51–63 GPa is extremely small and therefore fitting result for $IS$ is not much reliable as other values for other sites. At 31 GPa, where the fraction of P0 is the highest, we obtained $IS = 0.8 \text{ mm/s}$ which is higher than $IS$ reported for cold-compressed hcp-Fe at high pressure, $-0.2\sim-0.3 \text{ mm/s}$ (29, 30). However, it is difficult to compare our measured $IS$ values with existing data. Because low $QS$ sites produce long-wavelength flat feature in SMS similar to Fig. S3b and $IS$ shifts the spectral component along time axis, reliable determination of $IS$ is particularly difficult. The problem becomes even more difficult when $QS = 0 \text{ mm/s}$ which is the case for P0. Fcc-Fe is stable at a lower pressure range ($\leq$50 GPa) as also indicated by our XRD, but the $IS$ of high-pressure fcc-Fe is not known. Although all the reported $IS$ values of metallic Fe are for cold-compressed samples, our metallic Fe phases were heated and therefore thermally annealed.
Figure S6: Percentage of the site (P0) with $QS = 0$ mm/s. The gray shaded area is the range of the percentage of metallic iron formed through the charge disproportionation of Fe$^{2+}$ in bridgmanite estimated from our Fe$^{3+}/\sum$Fe data from quench SMS.

There are two possible sources for detection of Mössbauer spectra of metallic iron in our study: metallic iron initially mixed with the starting material for redox control and metallic iron produced by charge disproportionation. The charge-disproportionated metallic iron is more likely the source for site P0 because it is formed from the starting materials with 67–95% $^{57}$Fe-enrichment, whereas the pre-loaded metallic iron has only natural level $^{57}$Fe (2%). The percentage of charge-disproportionated metallic iron should be related with Fe$^{3+}/\sum$Fe in bridgmanite by the ratio predicted by charge disproportionation: $3\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + \text{Fe}^{0}$.

Because site assignments are more straightforward, we used the Fe$^{3+}/\sum$Fe values obtained from quenched bridgmanite. Because the glass starting material contains 10% Fe$^{3+}/\sum$Fe, we subtract the amount for calculating lower bounds for the amount of metallic iron. The percentage of site P0 measured from in situ SMS shows a reasonable agreement with the predicted percentage of charge-disproportionated metallic iron, except for two data points (Fig. S6). For “quench” SMS, we avoided spots with strong signal from metallic iron (easily distinguishable from magnetic signal in bcc-Fe).
To our knowledge, none of the previous Mössbauer studies have detected metallic iron produced by the charge disproportionation of Fe$^{2+}$ in bridgmanite. The elevated amount of total Fe in our experiments may allow us to detect the metallic iron. Frost and McCammon(31) attributed the difficulty in observing the metallic iron in multi-anvil experiments to the fact that multi-anvil does not provide a closed system and therefore oxidation by other agents are possible.

Some studies (5, 13, 14) have reported a site with $QS=0.1\sim1.4\text{ mm/s}$ in bridgmanite at high pressure. While the low $QS$ reported in (5) is similar to that of site P0, it is difficult to directly related these two sites, because $I_S$ was not provided in the study. Although sites with $I_S=0\sim0.5\text{ mm/s}$ have been reported(13, 14), their $QS$ are different from our values.
Table S1: Fitting results for the Mössbauer spectra of our samples. Med: pressure medium; SM: starting materials (py: pyroxene; gl: glass); \( P_{syn} \): synthesis pressure; Chisq: \( \chi^2 \) of the fitting; Wt: percentage of the site (%); IS and \( \Delta IS \): isomer shift (mm/s); QS: quadrupole splitting (mm/s); Wd: width of electrical field gradient distribution (mm/s); \( \sigma \): 1\( \sigma \) estimated uncertainty. IS is the isomer shift of sites SM1 (starting material), Q1 (quench SMS), and P1 (in situ SMS) measured with respect to stainless steel. \( \Delta IS \)'s are the isomer shifts relative to those of sites SM1, Q1, and P1, assuming that these sites have \( IS = 0.4 \text{ mm/s} \). Wd of sites Q0 and P0 was fixed to 0.5 mm/s during fitting. \( \text{Fe}^{3+} = \frac{[\text{site Q1}]}{([\text{site Q1}] + [\text{site Q2}])} \).
S4 Substitution of Fe and Al in Bridgmanite

The observed variation in Fe\(^{3+}/\Sigma\)Fe should be related to changes in substitution mechanism of Fe and Al in bridgmanite at high pressures. Substitution of Fe and Al is sensitive to multiples of factors, including energetics of vacancies in the crystal structure of bridgmanite, spin transition of Fe\(^{3+}\) and Fe\(^{2+}\), and entropy of mixing between the A and B sites (8 and 6 coordinated sites, respectively) for Fe\(^{3+}\) and Al\(^{3+}\). The spin transition of Fe in bridgmanite is sensitive to the symmetry of the sites which Fe enters, such as the A and B sites(25).

Because of the uncertainties in assigning the site identified from in situ SMS (section S3.4) to particular spin and oxidation states of Fe and the existence of metallic iron, we combine our data with the existing datasets on the bridgmanite (Figs S7 and S8) to infer the crystal chemistry of bridgmanite at different pressures. The analysis below also examines the relevance of our composition to the mantle compositions. In Fig. S7, we highlighted the data points from redox controlled experiments by larger symbols. The data points with hexagonal symbols were measured under reducing conditions (4, 16). The data points with left pointing triangle symbols were measured at an oxygen fugacity 2–3 orders of magnitude more oxidizing than the IW buffer (22).

S4.1 Al\# versus Fe\(^{3+}/\Sigma\)Fe

Earlier multi-anvil studies(4, 16) found a strong positive correlation between the amount of Al and Fe\(^{3+}/\Sigma\)Fe (Fig. S7a), supporting the Fe\(^{3+}\)–Al charge coupled substitution:

\[
\text{VIII} \text{Mg}^{2+} + \text{VI} \text{Si}^{4+} \rightarrow \text{VIII} \text{Fe}^{3+} + \text{VI} \text{Al}^{3+},
\]  

(S1)

where superscripts VIII and VI represent the 8 and 6 fold coordinated sites (or the A and B sites), respectively. Because the starting materials of the controlled experiments, including our study, contain predominantly ferrous iron (Fe\(^{2+}\)), the substitution of Fe\(^{3+}\) requires a process to produce
Figure S7: The crystal chemistry of Al,Fe-bearing bridgmanite from this study (circles) and previous studies (4, 16, 18, 20, 22, 23, 32). Larger symbols highlight the data from bridgmanite samples synthesized under controlled redox conditions (4, 16, 22): (A) Al# versus Fe\(^{3+}/\sum\)Fe with data points color-coded with total amounts of Fe (\(\sum \text{Fe} = \text{Fe}^{2+} + \text{Fe}^{3+}\)), (B) Al# versus Fe\(^{3+}\)# with data points color-coded with Al/Fe ratio, (C) Al/Fe versus Fe\(^{3+}/\sum\)Fe with data points color-coded with Al#, and (D) total amount of Fe (\(\sum \text{Fe}\)) versus Fe\(^{3+}/\sum\)Fe with data points color-coded with Al#. For our study, we plotted only the data point collected at our lowest pressure (35 GPa) because it is the closest pressure condition to the controlled experiments in multi-anvil press. We plot two data points: one directly from fitting, and the other after subtracting the amount of Fe\(^{3+}\) from the starting materials. The amounts of ions (Al# and Fe\(^{3+}\)#) are in atomic number for a 3O formula unit of bridgmanite. The grey and black bars at the top of the figures indicate corresponding values for the bridgmanite samples synthesized from pyrolitic starting materials (18, 20, 23, 33) and the bridgmanite samples in this study, respectively.
Fe$^{3+}$, i.e., charge disproportionation of Fe:

$$4 \text{VIII} \left( \text{Fe}_{3/4} \text{Al}_{1/4} \right)^{3+} \left( \text{Al}_{1/4} \text{Si}_{3/4} \right)^{4+} \text{O}_3 \rightarrow 2 \text{VIII} \text{Fe}^{3+} \text{VI} \text{Al}^{3+} \text{O}_3 + \text{Fe}^0 + 3 \text{SiO}_2.$$  \hspace{1cm} (S2)

As predicted by this reaction, stishovite (SiO$_2$) has been often found in the syntheses of Fe,Al-bearing bridgmanite, including our study at $P < 40$ GPa (Fig. S2).

In Fig. S7a, the colors of the data points indicate the amount of total Fe ($\Sigma$Fe) in bridgmanite. Despite the fact that our $\Sigma$Fe is higher (0.19), our data points at 35 GPa agree well with the trend observed from bridgmanite with lower $\Sigma$Fe. In our case, starting materials contain $\sim$10% Fe$^{3+}/\Sigma$Fe. Even if we subtract the pre-existing Fe$^{3+}$, our data point still remains in the linear trend formed by majority of the controlled data points. Lauterbach et al. (4) studied the bridgmanite samples with high $\Sigma$Fe comparable to ours (black hexagons in Fig. S7a). The data points by Lauterbach et al. also follow the trend and form a similar linear trend together with our data points. Therefore, the data points for elevated $\Sigma$Fe up to at least 0.2 still follow the linear trend between Al# and Fe$^{3+}/\Sigma$Fe. The figure also shows that the Al# of our bridgmanite overlaps with Al#'s reported in the bridgmanite samples in pyrolitic compositions, although our Al# is on the higher side. The left-pointing triangle data point at Al# $\simeq$ 0.7 was reported for bridgmanite synthesized under oxidizing conditions(22). The data point is clearly deviated from the trend by majority of the data, suggesting that oxidizing conditions can further increase Fe$^{3+}/\Sigma$Fe by $\sim$30%.

**S4.2 Al# versus Fe$^{3+}$#**

Fig. S7b shows Al# versus Fe$^{3+}$# in bridgmanite. The colors of the data points represent Al/Fe in bridgmanite. In Al-free bridgmanite (white-colored data points in Fig. S7b), the $^{\text{VIII}}$Fe$^{3+} - ^{\text{VI}}$Fe$^{3+}$ charge coupled substitution should be dominant and the data points are located at the Al# $<$ Fe$^{3+}$# side of the figure.

$$^{\text{VIII}} \text{Mg}^{2+} + ^{\text{VI}} \text{Si}^{4+} \rightarrow ^{\text{VIII}} \text{Fe}^{3+} + ^{\text{VI}} \text{Fe}^{3+}. $$  \hspace{1cm} (S3)
Again, the existence of Fe$^{3+}$ in bridgmanite synthesized from Fe$^{2+}$-dominant starting materials requires charge disproportionation of Fe:

$$3 \text{VIII} \text{Fe}^{2+} \text{SiO}_3 \rightarrow \text{VIII} \text{Fe}^{3+} \text{VI} \text{Fe}^{3+} \text{O}_3 + \text{Fe}^0 + \text{SiO}_2.$$ (S4)

Except for the two data points from (4), all aluminous bridgmanite points with Al/Fe ≥ 0.2 (yellow to black) are located either on the Al#:Fe$^{3+}$# = 1:1 line or in the Al# > Fe$^{3+}$# field in Fig. S7b. If the Fe$^{3+}$–Al charge coupled substitution is dominant in Al-bearing bridgmanite, the ratio between Al and Fe$^{3+}$ should be close to 1:1 (reaction (S1)). Our data points at 35 GPa is located on or slightly below the Al#:Fe$^{3+}$# = 1:1 line, suggesting that the Fe$^{3+}$–Al charge coupled substitution is dominant, similar to the majority of the existing data. In fact, our data point follows the trend formed by similar colored data points (Al/Fe = 0.5–0.7).

For the case of Al/Fe ≫ 1 (purple to black), even if all \text{VIII} \text{Fe}^{3+} in the A site are charge balanced by \text{VI} \text{Al}^{3+} in the B site, the data points will remain the Al# ≥ Fe$^{3+}$# field. In this case, the excess Al$^{3+}$ after charge balanced by Fe$^{3+}$ (reaction (S1)) should be charge balanced through the following two substitutions:

$$\text{VIII} \text{Mg}^{2+} + \text{VI} \text{Si}^{4+} \rightarrow \text{VIII} \text{Al}^{3+} + \text{VI} \text{Al}^{3+},$$ (S5)

i.e., the Al–Al charge coupled substitution. Or if all Al exists in the B site (VI) due to its smaller ionic radius, some oxygen vacancies should exist:

$$\text{VI} \text{Si}^{4+} + \frac{1}{2} \text{O}^{2-} \rightarrow \text{VI} \text{Al}^{3+} + \frac{1}{2} \text{V}^0_O,$$ (S6)

where $V^0_O$ is the oxygen vacancy. These two substitution mechanisms do not involve with Fe$^{3+}$ and therefore do not require the charge disproportionation of Fe.

It is interesting that the data points with Al/Fe ≈ 1 do not lie on the Al#:Fe$^{3+}$# = 1:1 line. Instead, they all exist in the Al# > Fe$^{3+}$# field. Even when Al is somewhat lower than total Fe (Al/Fe = 0.5–0.7; the data points with orange colors), bridgmanite contains more Al than Fe$^{3+}$. This
indicates that although the effect might be smaller than the Fe$^{3+}$–Al charge coupled substitution (reaction (S1)), some other substitution mechanisms, such as reactions (S5) and (S6), are needed to explain the excess Al which are not charge balanced by Fe$^{3+}$ in these data points. In this study, the amount of Fe$^{3+}$ in bridgmanite decreases with an increase in pressure between 35 and 51 GPa, suggesting the contribution from other substitution mechanism, such as the Al–Al charge coupled substitution (reaction (S5)), should increase with pressure.

### S4.3 Al/Fe ratio versus Fe$^{3+}$/\(\sum\)Fe

Al/Fe ratio is an important parameter in different substitution mechanisms (reactions (S3), (S1), (S5), and (S6)). Fig. S7c shows that Fe$^{3+}$/\(\sum\)Fe is not sensitive to Al/Fe ratio at least between 0.3 and 2.0. For example, red-colored data points were measured for Al# ≃ 0.1, which is the case for our study, and they show no statistically significant correlation between Fe$^{3+}$/\(\sum\)Fe and Al/Fe. The orange colored symbols (Al# ≃ 0.06), also indicate no strong correlation between the parameters. It is clear from the figure that Al# is much more dominant factor for Fe$^{3+}$/\(\sum\)Fe.

As indicated by the bars above Fig. S7c, our Al/Fe ratio overlaps with the Al/Fe ratio of the bridgmanite samples in pyrolitic composition, although our value is near the lower end of the range, because Fe# is more elevated that Al# compared with other studies. The large range of the reported Al/Fe value is partly due to the fact that pyrolitic composition varies among different studies. In addition, due possibly to the Soret diffusion, some laser-heated diamond-anvil cell studies with a local heating method, instead of scanning heating (which is the case for this study), may suffer Fe loss relative to Al, leading to elevated Al/Fe ratios.

### S4.4 Total amount of Fe (\(\sum\)Fe) versus Fe$^{3+}$/\(\sum\)Fe

Our samples have an elevated amount of total Fe (\(\sum\)Fe = Fe$^{2+}$ + Fe$^{3+}$) than bridgmanite in pyrolitic compositions (Fig. S7d). Although the data is sparse at \(\sum\)Fe > 0.16, at least the existing data show no clear correlation between \(\sum\)Fe and Fe$^{3+}$/\(\sum\)Fe. For example, the orange-colored data points (Al# ≃ 0.07; slightly lower than our sample) show no statistically significant increase or decrease in
Fe$^{3+}/\Sigma$Fe with a change in $\Sigma$Fe. In fact, the orange-colored data points extend to $\Sigma$Fe much higher (0.32) than our sample (0.19), showing no significant change in Fe$^{3+}/\Sigma$Fe within ±10%. Our Al# (0.1) corresponds to the red color. Although the range is much more limited, it still does not show any statistically significant trend up to 0.14, and our Fe$^{3+}/\Sigma$Fe is similar to the data points with similar Al# at lower $\Sigma$Fe. This plot also confirms that Al# is most influential to Fe$^{3+}/\Sigma$Fe.

**S4.5 Possible changes in substitution mechanism between 30 and 50 GPa**

Our bridgmanite samples synthesized at $P < 40$ GPa show $35\% \leq$ Fe$^{3+}/\Sigma$Fe $\leq 55\%$. At our lowest pressure (35 GPa), bridgmanite shows a high Fe$^{3+}/\Sigma$Fe value consistent with those reported in previous multi-anvil studies with controlled redox conditions (4, 16). Therefore, the high Fe$^{3+}/\Sigma$Fe at the lower pressure range is likely from the charge disproportionation of Fe combined with the Fe$^{3+}$–Al$^{3+}$ charge coupled substitution as proposed previously (reaction (S2)). Our starting materials have a composition of (Mg$_{0.76}$Fe$_{0.19}$Al$_{0.05}$)(Al$_{0.05}$Si$_{0.95}$)O$_3$, where iron is dominantly Fe$^{2+}$ and Al is charge balanced by itself. Therefore, a transformation of our starting materials to bridgmanite with high Fe$^{3+}/\Sigma$Fe will result in formation of silica, as shown in reaction (S2). We indeed observed X-ray diffraction lines of stishovite which is a high-pressure polymorph of SiO$_2$ stable at this pressure range.

Between 35 and 51 GPa, Fe$^{3+}$# decreases with respect to Al# with pressure, suggesting an increase of the amount of excess Al which are not charge balanced by Fe$^{3+}$ (Fig. S7b). As discussed in section S4.2, the excess Al requires either the Al$^{3+}$–Al$^{3+}$ charge coupled substitution (the left side of the following reaction) or oxygen vacancy substitution (the right side of the following reaction):

$$3\ \text{VIII} (\text{Mg}_{2/3}\text{Al}_{1/3}) \text{VI} (\text{Al}_{1/3}\text{Si}_{2/3})\text{O}_3 \leftrightarrow 2\ \text{VIII} \text{Mg} \text{VI} \text{AlO}_3 - \frac{1}{2} + 2\text{SiO}_2. \quad (S7)$$

Although the Al$^{3+}$–Al$^{3+}$ charge coupled substitution is energetically more favorable than the oxygen vacancy substitution at elevated pressures, the oxygen vacancy substitution remains competitive at least at lower pressures (34). Indeed, the amount of oxygen reported in (4) supports the existence of
oxygen vacancies in bridgmanite synthesized at 26 GPa.

We observed a gradual decrease in Fe$^{3+}/\Sigma$Fe between 30 and 50 GPa, reaching to a minimum of 10%. Because the starting material contains similar amount of Fe$^{3+}$, the system does not produce Fe$^{3+}$ anymore between 50 and 65 GPa. Because we observed pure bridgmanite without any other phases at 40–70 GPa, it is most likely that the crystal chemistry of bridgmanite without Fe$^{3+}$ in our study would be:

$$^{\text{VIII}} \left( \text{Mg}_{0.76} \text{Fe}_{0.19} \text{Al}_{0.05} \right)^{\text{VI}} \left( \text{Al}_{0.05} \text{Si}_{0.95} \right) \text{O}_3,$$

(S8)

where Al$^{3+}$ in the A site is charge balanced by Al$^{3+}$ in the B site.

Alternatively, all Al$^{3+}$ may enter the B site of bridgmanite at 50–70 GPa. However, the configuration requires high concentration of oxygen vacancies which may become increasingly unfavorable at $P>30$ GPa(35). Furthermore, oxygen vacancy substitution requires significant amount of free SiO$_2$ exsolving out of bridgmanite (the right side of reaction (S7)), which is not consistent with our XRD observation at 50–70 GPa.

From these configurations in bridgmanite at different pressures, the decrease in Fe$^{3+}/\Sigma$Fe between 35 and 50 GPa can be explained by:

$$4^{\text{VIII}} \left( \text{Mg}_{2/4} \text{Fe}_{2/4}^{3+} \right)^{\text{VI}} \text{Al}^{2+} \text{O}_{3-\frac{1}{4}} + \text{Fe}^0 + 5\text{SiO}_2 \rightarrow 7^{\text{VIII}} \left( \text{Mg}_{2/7} \text{Fe}_{3/7}^{2+} \text{Al}_{1/7}^{3+} \right)^{\text{VI}} \left( \text{Al}_{3/7}^{3+} \text{Si}_{5/7} \right) \text{O}_3,$$

(S9)

where the left and right sides represents bridgmanite at ~30 and ~50 GPa, respectively. The reaction can be broken into two steps. First, oxygen vacancy substitution (reaction (S6)) becomes energetically less favorable than the Al–Al charge coupled substitution (reaction (S5)) with an increase in pressure:

$$4^{\text{VIII}} \left( \text{Mg}_{2/4} \text{Fe}_{2/4}^{3+} \right)^{\text{VI}} \text{Al}^{2+} \text{O}_{3-\frac{1}{4}} + 2\text{SiO}_2 \rightarrow 5^{\text{VIII}} \left( \text{Mg}_{2/5} \text{Fe}_{2/5}^{3+} \text{Al}_{1/5}^{3+} \right)^{\text{VI}} \left( \text{Al}_{3/5}^{3+} \text{Si}_{2/5} \right) \text{O}_3,$$

(S10)

where excess Al in the B site moves to the A site. In this reaction, no Fe$^{3+}$ is required to transform to Fe$^{2+}$ while silica will disappear. Second, the $^{\text{VIII}} \text{Al}^{3+} - ^{\text{VI}} \text{Al}^{3+}$ charge coupled substitution (reac-
tion (S5)) becomes more favorable than the charge disproportionation of Fe combined with Fe$^{3+}$–Al charge coupled substitution (reaction (S2)):

$$S^{VIII}(Mg_{2/5}Fe_{2/5}Al_{3/5})^{VI}(Al_{3/5}Si_{2/5})O_3 + Fe^0 + 3SiO_2 \rightarrow 7^{VIII}(Mg_{2/7}Fe_{2/7}Al_{3/7})^{VI}(Al_{3/7}Si_{5/7})O_3.$$  

(S11)

Both steps involve consumption of silica. This is consistent with our observation that diffraction peaks of stishovite were found only at lower pressures.

The stabilization of the $^{VIII}[Al^{3+}]^{VI}[Al^{3+}]$ configuration can be explained by smaller-sized Al entering the A site where larger-sized Mg$^{2+}$, Fe$^{2+}$, and Fe$^{3+}$ exist, and by larger-sized Al leaving the B site which can be occupied more by Si which is smaller in size. Catalli et al. (21) reported that the unit-cell volume of Al-bearing MgSiO$_3$ bridgmanite is greater than that of Mg-endmember bridgmanite at 1 bar but becomes essentially the same as that of Mg-endmember at 70 GPa, suggesting that the $^{VIII}[Al^{3+}]^{VI}[Al^{3+}]$ configuration becomes increasingly favorable with pressure.

However, in reaction (S9) smaller-sized Fe$^{3+}$ transforms to larger-sized Fe$^{2+}$ in the A site. Therefore, it is important to know whether the volume advantage of the $^{VIII}[Al^{3+}]^{VI}[Al^{3+}]$ configuration can overcome the disadvantages. It is interesting to note that a new Fe site with a very high $QS$ value (site P3 in Tab. S1) appears at 42 GPa in our high-pressure SMS spectra. The pressure where the P3 site appears (Fig. S5b) coincides with the pressure where Fe$^{3+}$/∑Fe reaches the minimum (Fig. 2). Because both Mössbauer and EELS indicate very low Fe$^{3+}$ in the bridgmanite quenched from the pressure range, the P3 site should be Fe$^{2+}$. Appearance of the P3 site in bridgmanite has been documented previously and interpreted as intermediate spin Fe$^{2+}$ (14, 27). Alternatively, the high $QS$ value of P3 can be also related to changes in local environment for Fe in the crystal structure of bridgmanite (26, 28). If such changes can result in a decrease in ionic radius of Fe$^{2+}$ at 40–70 GPa, it may drive reaction (S9) to the right side (low Fe$^{3+}$/∑Fe). We note that Fe$^{3+}$ remains in the A site throughout the pressure range.
S4.6 Possible changes in substitution mechanism between 50 and 100 GPa

In Al-free bridgmanite, Fe$^{3+}$ enters the B site of bridgmanite for the Fe$^{3+}$–Fe$^{3+}$ charge coupled substitution (reaction (S3)), and undergoes a transition from high spin to low spin at high pressure\((36, 37)\). Such transition may stabilize Fe$^{3+}$ and increase the amount in bridgmanite. Although Fe$^{3+}$ may not enter the B site in Al-bearing bridgmanite at lower pressures, as we assumed in section S4.5, low-spin Fe$^{3+}$ may be competitively small in size to enter the B site with respect to Al\((21)\). Assuming such effects, the Fe$^{3+}/\Sigma$Fe increase at 70 GPa found in this study can be explained by:

\[
4 \text{VIII}(\text{Fe}^{2+}_{3/4}\text{Al}^{3+}_{1/4}) \text{VI}(\text{Al}^{3+}_{1/4}\text{Si}^{3+}_{3/4})\text{O}_3 \rightarrow 2 \text{VIII}(\text{HS}\text{Fe}^{2+}_{1-x}\text{Al}^{3+}_x) \text{VI}(\text{LS}\text{Fe}^{2+}_{1-x}\text{Al}^{3+}_x)\text{O}_3 + \text{Fe}^{0} + 3\text{SiO}_2, \quad (S12)
\]

where Fe$^{3+}/\Sigma$Fe increases in bridgmanite because of the stabilization of low-spin Fe$^{3+}$ in the B site and Fe$^{3+}$–Al$^{3+}$ mixing between the A and B sites of bridgmanite. Such process was proposed previously in bridgmanite synthesized from Fe$^{3+}$,Al-bearing starting materials\((21)\) with iron predominantly Fe$^{3+}$ based on changes in SMS and unit-cell volume.

We found that the configuration on the right side of reaction (S12) has a smaller volume than the left side as shown in section S4.7, if low-spin Fe$^{3+}$ enters the B site. Although the P3 site appears when Fe$^{3+}/\Sigma$Fe reaches the minimum at ~40 GPa (Fig. 2), at 70 GPa where Fe$^{3+}/\Sigma$Fe increases from the minimum, spectral fitting indicates a sudden drop to 5–8% in the site fraction of P3. At the same pressure, the fraction of the P1 site (Fe$^{2+}$-like site) increases. Above the pressure, the fraction of the P3 site increases again to 33–49%. The IS and QS of the P3 site do not show significant changes across the drop of its fraction at 70 GPa. However, due to the limited resolution in SMS, this does not rule out the possibility that P3 at \(P < 70\) GPa is different from P3 at \(P > 70\) GPa: at the lower pressure the site is due to either intermediate spin or local structural environment change for Fe$^{2+}$ and at the higher pressure the site is due to low-spin Fe$^{3+}$ in the B site.

Reaction (S12) requires the system to produce silica. However, we did not observe any diffraction lines which can be assigned to silica at pressures between 40 and 105 GPa. Detection limit for synchrotron diffraction in LHDAC is 5–10%. It is important to note that charge disproportionation
of 3Fe$^{2+}$ to 2Fe$^{3+}$ + Fe$^{0}$ in reaction (S12) produces 3 moles of silica. However, charge disproportionation of the same amount of Fe$^{2+}$ at ∼30 GPa requires 5 moles of silica (reaction (S9)), if bridgmanite at 30 GPa contains oxygen vacancies. Therefore, the observation of silica at lower pressure, despite the detection limit, is likely because of the existence of oxygen vacancies in bridgmanite at lower pressure (reaction (S6)).

S4.7 Effect of spin transition on the charge disproportionation of iron

Frost et al. (16) hypothesized that the smaller ionic radius of Fe$^{3+}$ relative to Fe$^{2+}$ in bridgmanite and the higher density of Fe metal may drive the charge disproportionation of iron at high pressure (reaction (S2)), not the low oxygen fugacity of the lower mantle. More recently Xu et al. (37) proposed that the spin transition makes the ionic radius of Fe$^{3+}$ smaller and therefore causes an increase in Fe$^{3+}$/∑Fe through charge disproportionation in Al-free bridgmanite. The Gibbs free energy change, $\Delta G$, of charge disproportionation can be expressed as:

$$\Delta G = \Delta U + P\Delta V - T\Delta S,$$

where $U$, $S$, $P$, $V$, and $T$ are internal energy, entropy, pressure, volume, and temperature, respectively. If volume plays a key role as suggested, the charge disproportionation can be examined from the effects of Fe$^{2+}$ and Fe$^{3+}$ on the molar volume of bridgmanite.

Previous studies reported the unit-cell volumes of bridgmanite with different amounts of Fe$^{3+}$, Fe$^{2+}$, and Al in LHDAC (6, 21, 36) (Tab. S2). The studies measured the equations of state using the same experimental setup: they all are measured under an Ar pressure medium, annealed by laser heating, and constrained by the same Au pressure scale (38). Therefore, the dataset enables us to conduct internally consistent comparisons of the molar volume of bridgmanite at different pressures.

The lower mantle is a multi-phase system and therefore other phases may affect the charge
Table S2: Equation of state (EOS) parameters for bridgmanite, ferropericlase, and CaSiO$_3$ perovskite. $V_0$, $K_0$, $K'_0$, $\gamma_0$, $q$, and $\theta_0$ are the molar volume, bulk modulus, the pressure derivative of $K_0$, Grüneisen parameter, logarithmic volume derivative of $\gamma$, and Debye temperature, respectively. † This composition shows a sharp decrease in volume between 50 and 60 GPa according to (21). However, we fit the whole data to one equation for the simplicity. The refit does not create significant artifacts in the calculation results within the $2\sigma$ uncertainty shown in Fig. S8c.

<table>
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<tr>
<th>Bridgmanite</th>
<th>$V_0$ (cm$^3$/mol)</th>
<th>$K_0$ (GPa)</th>
<th>$K'_0$</th>
<th>Refs.</th>
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</thead>
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<tr>
<td>Fe$^{2+}$(15 mol%)</td>
<td>24.585</td>
<td>259(1)</td>
<td>4</td>
<td>(6)</td>
</tr>
<tr>
<td>Fe$^{3+}$(17 mol%) †</td>
<td>24.959</td>
<td>228(5)</td>
<td>4.5(3)</td>
<td>(36)</td>
</tr>
<tr>
<td>Fe$^{3+}$(10 mol%)Al(10 mol%) †</td>
<td>24.813</td>
<td>265(5)</td>
<td>3.0(3)</td>
<td>(21)</td>
</tr>
<tr>
<td>Fe$^{3+}$(10 mol%)Al(10 mol%), high spin</td>
<td>24.813</td>
<td>262(5)</td>
<td>3.0(3)</td>
<td>(21)</td>
</tr>
<tr>
<td>Fe$^{3+}$(10 mol%)Al(10 mol%), low spin</td>
<td>24.390</td>
<td>268(10)</td>
<td>4.0(3)</td>
<td>(21)</td>
</tr>
<tr>
<td>Al$^{3+}$(20 mol%)</td>
<td>24.665</td>
<td>244(1)</td>
<td>4</td>
<td>(21)</td>
</tr>
<tr>
<td>Mg end member</td>
<td>24.435</td>
<td>261(1)</td>
<td>4</td>
<td>(6)</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>1.4</td>
<td>$q$</td>
<td>$\theta_0$ (K)</td>
<td>Refs.</td>
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<td>$q$</td>
<td>1.4</td>
<td>1100</td>
<td>(39)</td>
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<th>Ferropericlase</th>
<th>$V_0$ (Å$^3$)</th>
<th>$K_0$ (GPa)</th>
<th>$K'_0$</th>
<th>Refs.</th>
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<td>Fe(21 mol%), High spin</td>
<td>11.412</td>
<td>159.1</td>
<td>4.11</td>
<td>(40)</td>
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<tr>
<td>Fe(21 mol%), Low spin</td>
<td>11.171</td>
<td>170.0</td>
<td>4.00</td>
<td>(40)</td>
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<td>$\gamma_0$</td>
<td>1.45</td>
<td>$q$</td>
<td>$\theta_0$ (K)</td>
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<tr>
<td>$q$</td>
<td>1.5</td>
<td>706</td>
<td>(40)</td>
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<table>
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<tr>
<th>CaSiO$_3$ Perovskite</th>
<th>$V_0$ (Å$^3$)</th>
<th>$K_0$ (GPa)</th>
<th>$K'_0$</th>
<th>Refs.</th>
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</thead>
<tbody>
<tr>
<td>Ca end member</td>
<td>27.45</td>
<td>236</td>
<td>3.9</td>
<td>(39)</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>1.89</td>
<td>$q$</td>
<td>$\theta_0$ (K)</td>
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<td>$q$</td>
<td>0.898</td>
<td>796</td>
<td>(39)</td>
<td></td>
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disproportionation. In an Al-free system, the charge disproportionation can be expressed as:

\[(Mg_{1-x}Fe^{2+}_x)SiO_3 + xMgO \rightarrow \frac{x + 3}{3}(Mg_{1-y}Fe^{3+}_y)(Fe^{3+}_ySi_{1-y})O_3 + \frac{1}{3}xFe^0,\]  
(S14)

for a ferropericlase bearing system. \(x\) is the amount of iron undergoing the charge disproportionation and \(y = x/(x + 3)\). There is only one free parameter, which is \(x\). In a system without ferropericlase:

\[(Mg_{1-x}Fe^{2+}_x)SiO_3 \rightarrow \frac{3 - 2x}{3}(Mg_{1-y}Fe^{3+}_y)(Fe^{3+}_ySi_{1-y})O_3 + xSiO_2 + \frac{1}{3}xFe^0,\]  
(S15)

where \(z = x/(3 - 2x)\).

For an Al-bearing system with ferropericlase, the charge disproportionation is:

\[(Mg_{1-\frac{x'}{4}}Fe^{2+}_{\frac{x'}{4}}Al^{3+}_{\frac{x'}{4}})(Al^{3+}_{\frac{x'}{4}}Si_{1-\frac{x'}{4}})O_3 + x'MgO \rightarrow \frac{x' + 3}{3}(Mg_{1-y'}Fe^{3+}_{y'})O_3 + \frac{1}{3}x'Fe,\]  
(S16)

where \(x'\) is the amount of Fe undergoing the charge disproportionation and \(y' = 2x'/(x' + 3)\). In a ferropericlase-absent system, it is:

\[(Mg_{1-\frac{x'}{4}}Fe^{2+}_{\frac{x'}{4}}Al^{3+}_{\frac{x'}{4}})(Al^{3+}_{\frac{x'}{4}}Si_{1-\frac{x'}{4}})O_3 \rightarrow \frac{3 - 2x'}{3}(Mg_{1-z'}Fe^{3+}_{z'})O_3 + x'SiO_2 + \frac{1}{3}x'Fe^0,\]  
(S17)

where \(z' = 2x'/(3 - 2x')\).

We computed changes in molar volume (\(\Delta V\)) in these reactions using the bridgmanite dataset(6, 21, 36) and literature data on ferropericlase(41), silica(42), and iron (43) for \(x = 0.1\) and \(x' = 0.1\) (Fig. S8c). We assumed that: (1) the unit-cell volume linearly increases with the iron contents, which is valid when iron content is low, and (2) Fe\(^{3+}/\sum\)Fe is small in Al-free bridgmanite (6). The unit-cell volume of bridgmanite with both Fe\(^{2+}\) and Al (hereafter Fe\(^{2+}\),Al-bridgmanite) is not known mainly because Al stabilizes Fe\(^{3+}\) instead of Fe\(^{2+}\) at lower pressures. The individual effects of Fe\(^{2+}\) and Al on the unit-cell volume of bridgmanite are known separately from (6, 21), respectively, and
Figure S8: Energetics of the charge disproportionation (CD) of iron in bridgmanite. (A) The fraction of HS Fe$^{3+}$ (black) and Fe$^{3+}/\sum$Fe (%) (red), and (B) Free energies of the charge disproportionation in Al-free bridgmanite at high pressure and 2000 K from first-principles calculations(37). (C) $P\Delta V$ of charge disproportionation calculated from experimental data at 300 K (6, 21, 36). In (B) and (C), the values greater than zero favor Fe$^{2+}$, while the values smaller than zero favor Fe$^{3+}$. The values presented in (C) are for transforming 0.1 mol Fe$^{2+}$ to 0.067 mol Fe$^{3+}$ + 0.033 mol Fe$^{0}$ in bridgmanite (reactions (S14)–(S17)). The shaded area indicates 2σ uncertainty of the calculations. The light and dark colored lines in (C) are for ferropericlase-free (reaction (S17)) and ferropericlase-bearing (reaction (S16)) systems, respectively.

Therefore used combinedly in this calculation.

For Al-free systems (blue curves in Fig. S8c), the “2Fe$^{3+}$ (in bridgmanite) + Fe$^{0}$ (metal)” assemblage has slightly smaller volume (negative $P\Delta V$) throughout the lower mantle, although the magnitude is within the 2σ uncertainty of the calculation and the datasets. The $P\Delta V$ reaches minimum at 50–60 GPa where Fe$^{3+}$ in the B site undergoes a high-spin to low-spin change(36). Although the $P\Delta V$ calculated from experimental data have slightly different trend from that computed from ab initio calculation(37) (Fig. S8b), they are in qualitative agreement in that they both remain negative above 40 GPa. In the computation(37), a high-spin to low-spin change in Fe$^{3+}$ in the B site is responsible for the negative $P\Delta V$, stabilizing the charge disproportionation at high pressure. Although $P\Delta V$ has negative values at high pressure, the magnitude may still remain comparable to
other terms in Eq. (S13). \( \Delta U \) is not well known for bridgmanite at high pressure. According to a calorimetry study at ambient pressure, enthalpy differences among bridgmanite samples in different compositions up to 10 mol\% Al ranges between 5 and 10 kJ/mol (34).

As shown in Fig. S8c, Al decreases \( P\Delta V \) substantially at pressures above 60 GPa, due to the appearance of low-spin Fe\(^{3+} \) in the B site in Fe\(^{3+},\)Al-bridgmanite(21): \( \text{VIII} [\text{HS Fe}^{3+}\text{Al}^{3+}] \text{ VI [LS Fe}^{3+}\text{Al}^{3+}] \). Catalli et al. (21) found that the unit-cell volume of Fe\(^{3+},\)Al-bridgmanite becomes essentially the same as that of Mg-endmember bridgmanite at pressures higher than the spin transition. The larger decrease in \( P\Delta V \), therefore, may explain the increase in Fe\(^{3+}/\sum\)Fe at 70 GPa in our study. We note, however, this calculation ignores the effects from the Al–Al charge coupled substitution and oxygen vacancy substitution which are important factors for the Fe\(^{3+}/\sum\)Fe decrease at pressures between 30 and 40 GPa, as discussed above. Therefore, the application of our calculation presented in this section is limited to the crystal chemistry of bridgmanite at pressures higher than 50 GPa.

It is also important to note that our calculations in this section are based on compressibility measurements at 300 K, whereas the configurations observed in our experiments are preserved from temperatures higher than 2,000 K by fast temperature quenching. The slight difference in pressure between where \( P\Delta V \) becomes significantly negative and where Fe\(^{3+}/\sum\)Fe increases can be because of the thermal effects.
Figure S9: Scanning Transmission Electron Microscopy (STEM) of the bridgmanite sample recovered from 47 GPa and 2000 K: Bright Field (BF) image and Energy Dispersive X-ray Spectroscopy (EDS) elemental maps. The bright yellow spots in the Fe map are the metallic iron grains. The metallic iron grains are likely the pre-loaded iron for redox control, rather than charge disproportionated metalli iron, because this particular sample has a very low Fe$^{3+}/\Sigma$Fe.
References


Figure S10: Density profiles of pyrolite with (A) constant Fe contents in bridgmanite ($0.04\text{Fe}^{2+}\#$) and ferropericlase ($0.27\text{Fe}#$), (B) constant Fe content in bridgmanite ($0.045\text{Fe}^{2+}\#$ and $0.045\text{Fe}^{3+}\#$) and ferropericlase ($0.15\text{Fe}#$), and (C) depth-dependent changes in $\text{Fe}^{3+}/\sum\text{Fe}$ of bridgmanite (red curve). The light red shaded area in (A) represents estimated uncertainty. The open circles are from seismic measurement (PREM(44)).