Formation of large low shear velocity provinces through the decomposition of oxidized mantle

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Large Low Shear Velocity Provinces (LLSVPs) in the lowermost mantle are key to understanding the chemical composition and thermal structure of the deep Earth, but their origins have long been debated. Bridgmanite, the most abundant lower-mantle mineral, can incorporate extensive amounts of iron (Fe) with effects on various geophysical properties. Here our high-pressure experiments and ab initio calculations reveal that a ferric-iron-rich bridgmanite coexists with an Fe-poor bridgmanite in the 90 mol% MgSiO3–10 mol% Fe2O3 system, rather than forming a homogeneous single phase. The Fe3+-rich bridgmanite has substantially lower velocities and a higher $V_p/V_s$ ratio than MgSiO3 bridgmanite under lowermost-mantle conditions. Our modeling shows that the enrichment of Fe3+-rich bridgmanite in a pyrolitic composition can explain the observed features of the LLSVPs. The presence of Fe3+-rich materials within LLSVPs may have profound effects on the deep reservoirs of redox-sensitive elements and their isotopes.
The large low shear velocity provinces (LLSVPs) are two massive and mysterious regions sitting beneath Africa and the Pacific and occupy ~3–9% of the volume of the Earth. They are characterized by their lower-than-average seismic wave velocities and extend by thousands of kilometers laterally and up to >1000 km vertically above the core–mantle boundary (CMB). As the largest seismic heterogeneities in the lower mantle, they may hold the key to understanding the thermal, chemical, and dynamical evolution of the Earth. Different shear-wave tomography models have reached agreement that the shear-wave velocity anomaly (dlnVs) ranges from −0.5 to −1.0% in the shallow part of LLSVPs, while it could be up to −3.0% in the bottom parts. The compressional-wave tomography models also reveal negative anomalies of compressional-wave velocities (Vp) (refs. 8,9), although the amplitude, shape, and geographical location of Vp anomaly vary widely among different models. The Vp anomaly generally has a smaller amplitude than the Vs anomaly, causing a high dlnVs/dlnVp ratio. In particular, waveform and travel-time seismic studies reveal that the LLSVPs have sharp edges along their margins, which is also supported by the large lateral dVp/dVs gradients at the boundary of LLSVPs.

The systematic and discontinuous contrasts in seismic properties indicate that the LLSVPs are likely composed of distinct chemical materials from the surrounding mantle. A chemically distinct origin of the LLSVPs may be implicated by their density anomalies as well; however, large discrepancies for the density anomaly associated with the LLSVPs exist in the literature. Recent tidal tomography based on body tide displacements found that the mean density of the lower two-thirds of the two LLSVPs is ~0.5% higher than that of the surrounding mantle. On the contrary, a study using Stonelley modes suggested an overall negative density anomaly within LLSVPs, without excluding the possibility of a high-density anomaly within the lowermost LLSVPs. It is still unknown whether the regional differences in density anomaly are caused by the choice of observations used to constrain density models or reflect the nature of LLSVPs associated with their origins.

Hypotheses for the origin of chemically distinct LLSVPs include processes associated with the accumulation of subducted oceanic crust over Earth history and the differentiation and solidification of an ancient basal magma ocean. Sunken piles of subducted oceanic crust, which is compositionally different from and significantly denser than the pyrolitic lower mantle, was proposed to explain LLSVPs because of the low velocity of calcium silicate perovskite (CaSiO3, CaPv) (ref. 18). However, there are significant discrepancies in the velocity of CaPv between two experimental studies and between experiments and theoretical results. Elastic properties from ab initio simulations for the entire MORB assemblage indicate that subducted oceanic crust has relatively higher velocities than the ambient mantle. Moreover, geodynamic simulations suggested that the present-day subducted oceanic crust is too thin to provide enough negative buoyancy to survive viscous stirring and it hence is difficult to amass coherent thermochemical structures and shapes at the CMB similar to LLSVPs. Alternatively, LLSVPs may be composed of primordial residues from basal magma ocean crystallization or core–mantle differentiation that have not yet been fully homogenized by the mantle convection. These primordial materials would need to be intrinsically more dense than the surrounding mantle to overcome mantle stirring. Dense Fe-Ni-S liquid, for instance, was proposed to explain the LLSVPs, but the amount of this liquid remaining in the deep mantle, which depends on the drainage of melt to the core, is under debate.

Consistent with both efficient drainage of metallic melt and a primordial origin of the LLSVPs is chemical heterogeneity produced by redox reactions in the magma ocean. Ferrous iron (Fe2+) in silicate melts has been observed to disproportionate to ferric iron (Fe3+) plus metallic iron (Fe0) at high pressures. Segregation of precipitated Fe0 from the magma ocean into the core would enrich Fe3+ in the mantle. Bridgmanite (Bdg), the dominant Fe3+-bearing mantle mineral, hosts Fe3+ through the Fe3+–Fe2+ or Fe3+–Al2+ charge-coupled substitution in the deep mantle. In particular, a Fe3+-rich Bdg with the chemical composition of (Mg0.9Fe0.1)(Si0.9Fe0.1)O3 was recently synthesized by Liu et al. Oxidized domains enriched with such Fe3+-rich Bdg would be distinct from a pyrolic lower mantle in sound velocity and density and may be responsible for the origins of lower-mantle seismic and geochemical heterogeneities, such as the LLSVPs. The conditions of formation of such Fe3+-rich Bdg in a mantle phase assemblage and its elastic properties at lower-mantle-relevant temperatures are vital to test this hypothesis, but these questions remain unclear.

In this work, we combine high pressure-temperature (P-T) experiments, ab initio calculations, and geodynamic simulations to study the formation of Fe3+-rich Bdg, its thermoelastic properties, and its dynamics in the mantle, to evaluate whether enrichment in Fe3+-rich Bdg can explain the seismic signatures of LLSVPs.

Results

The coexistence of Fe3+-rich and Fe-poor bridgmanite phases. We conducted a series of multi-anvil experiments with the bulk composition of 90 mol% MgSiO3–10 mol% Fe3O4 from 10-24 GPa along a mantle geotherm (Supplementary Table 1). At 10 GPa and 1573 K (Fig. 1d), the run products consist of separate MgSiO3 and Fe3O4 phases, demonstrating low solubility of Fe3O4 in clinopyroxenes at upper-mantle conditions due to the incompatibility between large Fe3+ and small tetrahedral site. At 15 GPa, an iron-rich akimotoite (Aki) forms with 33 mol% of MgSiO3 and 67 mol% of Fe3O4, coexisting with (Mg0.17Fe0.83)SiO3 wadsleyite and SiO2 stishovite (Fig. 1c). This indicates that the iron-rich Aki coexisting with iron-depleted oxides/silicates are energetically more stable than a single-phase MgSiO3–Fe3O4 solid solution with intermediate iron content. At 24 GPa and 1873 K, which corresponds to the P–T conditions around the uppermost lower mantle, the products consist of Fe-poor Bdg and Fe-rich Aki with 44–49 mol% Fe in both Mg and Si sites (Fig. 1a and Supplementary Table 1), instead of forming a single phase of (Mg0.9Fe0.1)(Si0.9Fe0.1)O3 Bdg. The Fe-rich Aki is evenly distributed in the matrix of the Fe-poor Bdg (Fig. 1a). The run products of experiments running at the same P–T conditions for 8 and 24 h have the same compositions within analytical uncertainty (Supplementary Table 1), confirming that the experiments reached equilibrium. In situ XRD measurements coupled with a diamond anvil cell (DAC) show that this Fe-rich Aki phase transforms to Bdg phase at 23.5 ± 1.0 GPa and 300 K (Supplementary Fig. 1). Moreover, this Fe3+-rich Bdg phase completely transforms back to Aki with the same lattice parameters as the starting Aki phase after the decompression of the DAC (Supplementary Fig. 1). The reversible phase transition of this Fe-rich phase means that for our multi-anvil experiments at the P–T conditions of the uppermost lower mantle, Fe3+-rich Bdg coexists with Fe-pool Bdg.

A previous multi-anvil study synthesized Fe3+-only bridgmanite with 2–4 mol% Fe3+ in the cation sites but did not observe the Fe3+-rich Bdg phase, possibly because the bulk Fe content of their experiments is not high enough to enable the formation of such Fe3+-rich Bdg. Moreover, the presence of unreacted MgO and SiO2 in their run products (Fig. 1 in ref. 39) suggests that their starting materials may not be homogenous or
their experiments did not reach chemical equilibrium. Another study\(^{40}\) synthesized Fe\(^{3+}\)-only Bdg with the starting material of 90 mol% MgSiO\(_3\)–10 mol% Fe\(_2\)O\(_3\) using laser-heated diamond anvil cell (LH-DAC)\(^{40}\). However, the chemical composition of Fe\(^{3+}\)-only Bdg was not reported, possibly because there was a significant loss of Fe and Mg during melting\(^{40}\), and some Fe\(^{3+}\) was reduced through reaction with diamond during laser heating\(^{41}\). In addition, the proportion of the Fe-rich Bdg phase is much smaller than the Fe-poor Bdg (Fig. 1), and therefore it is difficult to detect without a detailed analysis of the run products in ref. \(^{40}\).

We also performed ab initio calculations (see methods and supplementary materials) to investigate the stability of (Mg\(_{0.5}\)Fe\(_{0.5}\))(Si\(_{0.5}\)Fe\(_{0.5}\))O\(_3\) Bdg under lower-mantle conditions. Our results show that the assemblage of (Mg\(_{0.5}\)Fe\(_{0.5}\))(Si\(_{0.5}\)Fe\(_{0.5}\))O\(_3\) and MgSiO\(_3\) Bdg has a lower Gibbs free energy than a single-phase Bdg with the chemical composition of their experiments did not reach chemical equilibrium. Another study\(^{40}\) synthesized Fe\(^{3+}\)-only Bdg with the starting material of 90 mol% MgSiO\(_3\)–10 mol% Fe\(_2\)O\(_3\) using laser-heated diamond anvil cell (LH-DAC)\(^{40}\). However, the chemical composition of Fe\(^{3+}\)-only Bdg was not reported, possibly because there was a significant loss of Fe and Mg during melting\(^{40}\), and some Fe\(^{3+}\) was reduced through reaction with diamond during laser heating\(^{41}\). In addition, the proportion of the Fe-rich Bdg phase is much smaller than the Fe-poor Bdg (Fig. 1), and therefore it is difficult to detect without a detailed analysis of the run products in ref. \(^{40}\).

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**Elastic properties and sound velocities of (Mg\(_{0.5}\)Fe\(_{0.5}\))(Si\(_{0.5}\)Fe\(_{0.5}\))O\(_3\) bridgmanite.** Determining the seismic signature of a separate Fe\(^{3+}\)-rich phase in equilibrium with the mantle phase assemblage requires elastic properties of this phase as a function of pressure and temperature conditions in the mantle. The elastic properties of (Mg\(_{0.5}\)Fe\(_{0.5}\))(Si\(_{0.5}\)Fe\(_{0.5}\))O\(_3\) Bdg up to 130 GPa and 3000 K were theoretically obtained from ab initio calculations.

Because Bdg may also accommodate Al in the octahedral site\(^{31,38,42}\), we also conducted calculations on an end-member composition (Mg\(_{0.5}\)Fe\(_{0.5}\))(Si\(_{0.5}\)Al\(_{0.5}\))O\(_3\) to quantify the effect of Al on the elasticity of Bdg. In these calculations, the octahedral site (B-site) Fe\(^{3+}\) in (Mg\(_{0.5}\)Fe\(_{0.5}\))(Si\(_{0.5}\)Fe\(_{0.5}\))O\(_3\) Bdg undergoes a high-spin (HS) state to a low-spin (LS) state transition with increasing pressure (Fig. 2a), while the dodecahedral-site (A-site) Fe\(^{3+}\) in both compositions remain in the HS state throughout the lower-mantle conditions\(^{43}\).

Our calculated volumes of HS- and LS-(Mg\(_{0.5}\)Fe\(_{0.5}\))(Si\(_{0.5}\)Fe\(_{0.5}\))O\(_3\) Bdg agree well with experimental measurements at 300 K (ref. \(^{36}\)) (Fig. 2a). The calculated spin transition of the B-site Fe\(^{3+}\) occurs between 49 and 55 GPa at 300 K\(^{36}\), which is slightly higher and narrower than experimental results\(^{36}\). The predicted volume collapse (\(\Delta V^{HS-LS}\)) caused by the spin transition of B-site Fe\(^{3+}\) is ~4.3% at 300 K, higher than experimental measurements (2.7%)\(^{36}\) but consistent with previous theoretical calculations\(^{44}\) on (Mg\(_{0.5}\)Fe\(_{0.5}\))(Si\(_{0.5}\)Fe\(_{0.5}\))O\(_3\) Bdg assuming that \(\Delta V^{HS-LS}\) is linearly dependent on Fe\(^{3+}\) content. The \(\Delta V^{HS-LS}\) discrepancy between experimental and theoretical studies is probably caused by the difference in the pressure range for the mixed-spin (MS) state. The predicted volumes of (Mg\(_{0.5}\)Fe\(_{0.5}\))(Si\(_{0.5}\)Al\(_{0.5}\))O\(_3\) Bdg also show excellent agreement with experimental results at 300 K\(^{42}\). These comparisons demonstrate the high reliability of our DFT + U calculations in predicting elastic properties, as suggested by previous studies\(^{43–45}\).

The spin transition of B-site Fe\(^{3+}\) in (Mg\(_{0.5}\)Fe\(_{0.5}\))(Si\(_{0.5}\)Fe\(_{0.5}\))O\(_3\) Bdg generates a strong effect on bulk modulus (\(K_S\)) and \(V_p\), which both show deep valleys that broaden and decrease in magnitude with increasing temperature (Supplementary Fig. 3). The magnitude and width of the \(K_S\) and \(V_p\) anomalies are controlled by the fraction of LS B-site Fe\(^{3+}\) (\(n_{LS}\)) and the pressure and temperature dependences of \(n_{LS}\) (see Supplementary Materials). Compared to MgSiO\(_3\) Bdg\(^{46}\), both (Mg\(_{0.5}\)Fe\(_{0.5}\))(Si\(_{0.5}\)Fe\(_{0.5}\))O\(_3\) and

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**Fig. 1** Back-scattered scanning electron microscope images of recovered experimental phase assemblages forming from 90% MgSiO\(_3\) + 10% Fe\(_2\)O\(_3\) starting mixture after equilibrium at mantle pressure-temperature conditions for 6–10 h. Bridgmanite/akimotoite with ~50 mol% Fe\(_2\)O\(_3\) substitution in both Mg and Si sites (bright phases in (a–c)) coexists with normal mantle minerals such as Fe-poor bridgmanite (dark phases in (a) and (b)) at ~20 GPa, or with wadsleyite (gray phase in (d)) + stishovite (dark phase in (c)) at 15 GPa, while Fe\(_2\)O\(_3\) (bright phase in (d)) was stabilized as a separate phase with Fe-depleted clinopyroxene (dark phase in (d)) at 10 GPa.
(Mg$0.5$Fe$0.5$)(Si$0.5$Fe$0.5$)O$_3$ Bdg have much lower elastic moduli ($K_S$ and $G$) and velocities ($V_P$ and $V_S$) (Supplementary Fig. 4). At lowermost-mantle conditions, the differences in $K_S$, $G$, $V_P$, and $V_S$ between (Mg$_{0.3}$Fe$_{0.5}$)(Si$_{0.5}$Fe$_{0.5}$)O$_3$ and MgSiO$_3$ Bdg are about $\sim$5%, $\sim$37%, $\sim$17%, and $\sim$28%, respectively, which in turn causes a higher $V_P$/$V_S$ ratio of 2.1 in (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.5}$Fe$_{0.5}$)O$_3$ Bdg (Supplementary Fig. 4). By comparison, the differences in $K_S$, $G$, $V_P$, and $V_S$ between (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.5}$Al$_{0.5}$)O$_3$ and MgSiO$_3$ Bdg are about $\sim$4%, $\sim$18%, $\sim$9%, and $\sim$14%, respectively.

**Discussion**

Combining elastic data from previous studies$^{20,45-47}$ with our results, we modeled the density and velocity anomalies caused by the presence of Fe$^{2+}$-rich Bdg relative to the pyrolitic composition, which can effectively reproduce the reference seismic velocities and density of PREM$^{37,38}$. The chemical assemblage has pyrolytic mineral fractions (15% ferropericlase ($F_p$) + 78% Bdg + 7% CaPv) in which a portion of Fe$^{2+}$-bearing Bdg was substituted by (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.5}$Fe$_{0.5}$)O$_3$. We find that the enrichment of (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.5}$Fe$_{0.5}$)O$_3$ Bdg in the assemblage can explain the seismic features of the LLSPVs$^{4,8,9}$. The $V_S$ anomalies of $\sim$1.5% to $\sim$3.0% and the large $\Delta V_P/\Delta V_P > 2.0$ observed in LLSPVs$^{4,8,9}$ can be reproduced by the enrichment of 10–15% (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.5}$Fe$_{0.5}$)O$_3$ Bdg in pyrolite at 110 GPa (Fig. 3). If LLSPVs are hotter ($\Delta T_{LLSPVs} > 0$), the required proportion of (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.5}$Fe$_{0.5}$)O$_3$ Bdg would accordingly decrease; for example, it will decrease by $\sim$2% if $\Delta T_{LLSPVs}$ is $\sim$400 K. For a pyrolitic composition, Bdg also contains $\sim$5 mol% Al$_2$O$_3$, which does not significantly change its velocities and density$^{48}$. When 5 mol% Al$_2$O$_3$ is incorporated into Bdg, the $V_P$ and $V_S$ anomalies caused by the presence of 15% (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.3}$Fe$_{0.5}$Al$_{0.3}$)O$_3$ Bdg at $\Delta T_{LLSPVs}$ equal to $\sim$400 K will be $\sim$1.5% and $\sim$3.1% (Fig. 3), respectively, which can also reproduce the $\Delta V_P/\Delta V_P > 2.0$.

In addition, we find that the required proportion of (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.5}$Fe$_{0.5}$)O$_3$ Bdg increases with the decreasing of Fe$^{2+}$ content in the modeled assemblage (noted by the FeO content in Fp, Fe$^{2+}$/Fe$^{3+}$) to explain the same $V_P$ and $V_S$ anomalies (Fig. 4). If there is no Fe$^{2+}$, the (Mg$_{0.3}$Fe$_{0.5}$)(Si$_{0.5}$Fe$_{0.5}$)O$_3$ fraction that can reproduce the $V_S$ anomaly of $\sim$3.0% would be raised to $\sim$17% at $\Delta T_{LLSPVs}$ equal to $\sim$400 K (Fig. 4 and Supplementary Fig. 5), which corresponds to a $V_P$ anomaly of $\sim$1.0% and a $\Delta V_P/\Delta V_P$ of $\sim$3.0. The $\Delta V_P/\Delta V_P > 2.0$ tends to be reproduced at relatively low Fe$^{2+}$ contents (Fig. 4). If Fe$^{2+}$/Fe$^{3+} > 0.9$ (Fe$^{2+}$/Fe$^{3+}$ is the FeO content of Fp in a normal pyrolytic lower mantle, 18 mol%), the $\Delta V_P/\Delta V_P$ ratio is less than 2.0. In contrast, when Fe$^{2+}$/Fe$^{3+}$ < 0.25, the $\Delta V_P/\Delta V_P$ ratio $\geq$ 2.0 can be reproduced for different $V_S$ anomalies (Fig. 4). Our modeling implies that the enrichment of (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.5}$Al$_{0.5}$)O$_3$ Bdg in the pyrolite assemblage with relatively lower Fe$^{2+}$ content can explain the velocity anomalies and the $\Delta V_P/\Delta V_P$ ratio observed in LLSPVs$^{4,8,9}$.

In contrast to velocity anomalies, the modeled density anomaly (dln$\rho$) could be positive, zero, or negative, depending on the (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.5}$Fe$_{0.5}$)O$_3$ abundance, temperature anomaly, and the fraction of Fe$^{2+}$ in Fp. To produce a $V_S$ anomaly of $\sim$3.0% for the assemblage enriched in (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.5}$Fe$_{0.5}$)O$_3$ Bdg, the dln$\rho$ decreases from $+1.2\%$ at $\Delta T_{LLSPVs}$ of 0 K and Fe$^{2+}$/Fe$^{3+}$ of 0.5 to $-0.5\%$ at $\Delta T_{LLSPVs}$ of $\sim$400 K and Fe$^{2+}$/Fe$^{3+}$ of 0.0 (Figs. 3, 4, and Supplementary Fig. 5). In general, the density anomaly is correlated with the magnitude of $V_S$ anomalies. For $\Delta V_P < 1.0\%$, the dln$\rho$ could be positive if $\Delta T_{LLSPVs}$ is 0 K; however, if $\Delta T_{LLSPVs}$ equals to $\sim$400 K, the dln$\rho$ could be positive only when $\Delta V_P < 2.5\%$ (Fig. 4). Our modeling suggests that the lowermost parts of LLSPVs with large negative velocity anomalies (<$\sim$3.0%) could be denser than the ambient mantle, while the relatively shallow part of LLSPVs with $\sim$0.5% to $\sim$1.0% $V_S$ anomalies on average likely have slightly lighter density than the ambient mantle. Recent work proposed that the bottom two-thirds of the two LLSPVs are $\sim$0.5% denser than the surrounding mantle$^{14}$, while Koelemeijer et al.$^{15}$ argued that the overall density of the LLSPVs is lower than the surrounding mantle. Such different conclusions may be related to different depth sensitivities of the datasets considered$^{49}$, regardless of the input observations. Also, geodynamic modeling studies$^{30,51}$ suggested that the density anomalies of the LLSPVs relative to the surrounding mantle could be positive near the top and bottom of the LLSPVs but neutral or slightly negative in the middle of the LLSPVs. The density of LLSPVs could also be laterally inhomogeneous due to their
internal convection and the entrainment of multiple compositional components into the LLSVPs.

The present model for chemical heterogeneities within the LLSVPs is consistent with Fe-rich remnants of a basal magma ocean created early in Earth’s history. Ferrous Fe in dense silicate melts associated with the basal magma ocean would partially disproportionate to Fe$^{3+}$ plus Fe$^0$ at high pressures and segregation of precipitated Fe$^0$ from the magma ocean into core would enrich silicate melt in Fe$_2$O$_3$ component. A thermodynamic model of magma ocean crystallization suggests that the silicate melt fraction would be gradually enriched in iron with Fe/(Fe$^{3+}$ + Mg) > 0.3 in the lower mantle after 60 wt% of the melt has solidified. The Fe/(Fe$^{3+}$ + Mg) ratio in the residual melt remaining in the lowermost mantle could be up to 0.5 near the end of the crystallization. The amount of Fe$^{3+}$ in this melt depends on the amount of Fe$^{2+}$ that would disproportionate into Fe$^{3+}$ plus Fe$^0$ and the efficiency of Fe$^0$ droplet segregation. The required bulk composition with MgSiO$_3$:Fe$_2$O$_3$ equal to 9:1 could be produced when 40–80% Fe$^{2+}$ undergoes the disproportionation reaction and all Fe$^0$ migrates into the core. Fe$^{3+}$ would be incorporated into bridgmanite with further crystallization, and our experiments and ab initio calculations indicate that in these Fe$^{3+}$-rich regions, a portion of (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.5}$Fe$_{0.5}$)O$_3$ silicate would form as a separate phase, coexisting with Fe$^{3+}$-poor silicate. Due to the large excess density, (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.5}$Fe$_{0.5}$)O$_3$ bridgmanite could descend to the base of the lower mantle through mantle convection and result in Fe$^{3+}$-rich bridgmanite piles. Our geodynamic modeling demonstrates that such Fe$^{3+}$-rich piles with ~18% (Mg$_{0.5}$Fe$_{0.5}$)(Si$_{0.5}$Fe$_{0.5}$)O$_3$ Bdg, which is ~1.5% intrinsically denser than the ambient mantle (Fig. 5), could form large-scale thermochemical structures in the lowermost mantle without being mixed into the background mantle throughout Earth’s history (Fig. 5), which may accumulate to form LLSVPs.

Our findings imply that the segregation of Fe$^{3+}$-rich domains may cause heterogeneity in the redox states of the Earth’s mantle, that is, the oxygen fugacity of the lowermost mantle may not be as low as inferred in previous studies. We also expect these Fe$^{3+}$-rich domains to be enriched in heavy iron isotopes because Fe$^{3+}$ has a larger Fe force constant than Fe$^{2+}$ (ref. 56), which may affect the iron isotopic features of the deep Earth. The presence of lower-mantle oxidizing heterogeneities would have profound effects on the cycles of volatiles and the deep reservoirs of redox-sensitive elements. For instance, the dense reduced Fe-C/H/S melts formed at the mantle transition zone and shallow
lower mantle by slab/mantle interaction, if they reach the lowermost mantle, could be converted back to an oxidized state instead of sinking into the core. Dynamic cycling with respect to mantle redox heterogeneity could provide new insights into the thermochemical evolution of the bulk silicate Earth and possibly the oxidation of the atmosphere.

**Methods**

**High pressure-temperature experiments.** The experiments were conducted using the 1000-ton multi-anvil apparatus at the University of Michigan. The COMPRES 8/3 and 10/5 cell assemblies were employed in the experiments. The starting material was a mixture of high purity (>99.99%) MgO, SiO₂, and Fe₂O₃ at a molar ratio of 9:9:1, which corresponds to a bulk composition of (Mg₉.₉Fe₀.₁)O₃. The mixture was heated at 1073 K overnight to remove the moisture and structural water before loading into a platinum capsule. The sample was compressed to target pressure and equilibrated at high temperature for 6–10 h to allow sufficient equilibrium. It was then quenched to room temperature and decompressed to 1 bar.

The recovered sample was polished, coated with carbon, and examined for texture and composition using the JOEL-7800FLV Scanning Electron Microscope (SEM) and SX-100 Electron Microprobe Analysis (EPMA) at the Electron Microbeam Analysis Laboratory (EMAL) of the University of Michigan. An accelerating voltage of 15 kV and a beam current of 10 nA were employed for imaging and analysis. Forsterite and magnetite were used as standards for Mg, Si, and Fe quantification using EPMA.

**First-principles calculations.** Isothermal elastic tensors ($C^\text{ijkl}_{\text{q,m}}$) of crystals in a Cartesian coordinate system usually can be calculated from Eq. (1) (ref. 96):

$$C^\text{ijkl}_{\text{q,m}} = \frac{1}{V} \left[ \frac{\partial^2 F}{\partial \delta_{ij} \partial \delta_{kl}} + \frac{1}{2} P \delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} \right]$$

where $c_{ijkl}$ are infinitesimal strains, $P$ is the isotropic pressure, and $F$ is the Helmholtz free energy, which can be expressed in the quasi-harmonic approximation (QHA) as:

$$F(c_{ij},V,T) = U(c_{ij},V) + \frac{1}{2} \sum q,m \omega_{q,m}^2 (c_{ij},V) + k_B T \sum q,m \ln (1 - \exp (-\frac{\hbar \omega_{q,m}}{k_B T}))$$

where $V$ is the equilibrium volume of the crystal and $T$ is temperature. Subscripts $q$ and $m$ refer to the phonon wave vector and the normal mode index, respectively. $\hbar$ and $k_B$ are Planck and Boltzmann constants, and $\omega_{q,m}$ is the vibrational frequency of the $m$th mode along with the wave vector $q$. $U$ is the static energy at the equilibrium volume $V$. The second and third terms are the zero-point and vibrational energy contributions, respectively. Adiabatic elastic constants ($C^\text{ijkl}_{\text{q,m}}$) can be derived from:

$$C^\text{ijkl}_{\text{q,m}} = \frac{\partial^2 U}{\partial \delta_{ij} \partial \delta_{kl}} + \frac{T}{V} \sum q,m \frac{\partial \omega_{q,m}}{\partial c_{ij}} \frac{\partial \omega_{q,m}}{\partial c_{kl}}$$

where $S$ is the entropy and $C^\text{T}_{ij}$ is the constant volume heat capacity. Therefore, calculations of elastic tensors at high pressure and temperature using this usual method require a vibrational density of states (VDoS) of many strained configurations, which demand a tremendous amount of computational power to calculate based on the DFT. Wu and Wentzcovitch proposed an analytical approach to calculate the thermal contribution to the elastic tensor, only requiring VDoS for unstrained configurations at different equilibrium volumes. This approach greatly reduces the computation cost to the level of <10% of the usual method without loss of accuracy.

To obtain elastic tensors at static conditions and VDoS for unstrained configurations at different equilibrium volumes, we performed first-principles calculations using Quantum Espresso package based on the DFT, plane wave, and pseudopotential. Local density approximation (LDA) was adopted for the exchange-correlation function. The energy cutoff for electronic wave functions was...
set as 70 Ry. The Mg pseudopotential was generated using the von Barth and Car method for all channels using a 2.5 Bohr cutoff radius and five configurations, 3s23p0, 3s13p1, 3s13p0.53d0.5, 3s3p0.5, 3s13d1, with weights of 1.5, 0.6, 0.3, 0.3, 0.2, respectively. The pseudopotentials for Si and O were generated using the Troullier-Martins method with the cutoff radius of 1.77 Bohr for Si and 1.54 Bohr for O. Valence configurations for Si and O are 3s3p43d2 and 2s2p4, respectively. The pseudopotentials for Al and Fe were generated using the Vanderbilt method with a valence configuration of 3s23p1 and a cutoff radius of 1.77 Bohr for Al, and a valence configuration of 3s3p43d24s4p2 and a cutoff radius of 1.8 Bohr for Fe. To address the large on-site Coulomb interactions among the localized electrons (Fe 3d electrons)\textsuperscript{43}, we introduced a Hubbard U correction to the LDA (LDA+U) for all DFT calculations. U values for Fe\textsuperscript{3+} on a and b sites in bridgmanite were non-empirically determined using linear response methods in previous work\textsuperscript{43} and adopted in this study. The initial structure was constructed by replacing one nearest-neighbor Mg\textsuperscript{2+}–Si\textsuperscript{4+} pair with one Fe\textsuperscript{3+}–[Si\textsuperscript{4+}] pair\textsuperscript{43}. Crystal structures at variable pressures were well optimized on a 6 × 6 × 4 k-point mesh, and VDoS were calculated using the finite displacement method as implemented in the code PHONOPY\textsuperscript{97}. The elastic tensors at static conditions were calculated from the linear dependence of stress on the small strain. Owing to the enormous computational cost of calculating the vibrational density of state based on LDA+U, we used the 20-atom unit cell for (Mg\textsubscript{0.5}Fe\textsubscript{0.5})(Si\textsubscript{0.5}Al\textsubscript{0.5})O\textsubscript{3} bridgmanite\textsuperscript{45,46}. Similar to previous studies on the elastic properties of Fe-bearing bridgmanite\textsuperscript{45,46}, we only report results for aggregate elastic moduli, not individual elastic configurations and therefore to supercell size, which can accommodate different configurations for the same composition. The aggregate elastic moduli, K\textsubscript{s} and G, are quite insensitive to the atomic configuration\textsuperscript{48–50}. The Helmholtz free energy calculated from Eq. (2) within the QHA versus volume was fitted by the isothermal third-order finite strain equation of state, and then we can obtain all thermodynamic properties, such as pressures at different temperatures and volumes. Our results show that (Mg\textsubscript{0.5}Fe\textsubscript{0.5})(Si\textsubscript{0.5}Al\textsubscript{0.5})O\textsubscript{3} bridgmanite has a larger volume than (Mg\textsubscript{2}Fe\textsubscript{2})(Si\textsubscript{2}Al\textsubscript{2})O\textsubscript{3} bridgmanite (Fig. 2). The substitution of Al\textsuperscript{3+} for LS Fe\textsuperscript{3+} in the octahedral site causes a slight decrease of ~1.0% in volume at >80 GPa. Compared to pristine Bdg (MgSiO\textsubscript{3}), these two Fe\textsuperscript{3+}– and Al\textsuperscript{3+}-rich species have larger volumes; for example, at 90 GPa and 2000 K, the volumes of (Mg\textsubscript{0.5}Fe\textsubscript{0.5})(Si\textsubscript{0.5}Al\textsubscript{0.5})O\textsubscript{3} and (Mg\textsubscript{0.5}Fe\textsubscript{0.5})(Si\textsubscript{0.5}Fe\textsubscript{0.5})O\textsubscript{3} are 3.5% and 4.4% larger than that of MgSiO\textsubscript{3}, respectively.

Using the equation of states, we transferred volume- and temperature-dependent elasticity into pressure- and temperature-dependent elasticity. The adiabatic bulk modulus K\textsubscript{S} and shear modulus G can be obtained by computing the Voigt-Reuss-Hill averages\textsuperscript{71} from elastic tensors. Thus, compressional and shear velocities can be calculated from the equations $V_p = \sqrt{(K_S + \frac{4}{3}G)/\rho}$ and $V_s = \sqrt{G/\rho}$ (ρ is density). Bulk moduli (K\textsubscript{s}), shear moduli (G), compressional-wave velocity ($V_p$), and shear-wave velocity ($V_s$) are also derived from LDA+U calculations as shown in Supplementary Fig. 3. Compared to (Mg\textsubscript{0.5}Fe\textsubscript{0.5})(Si\textsubscript{0.5}Fe\textsubscript{0.5})O\textsubscript{3} Bdg, (Mg\textsubscript{0.5}Fe\textsubscript{0.5})(Si\textsubscript{0.5}Al\textsubscript{0.5})O\textsubscript{3} Bdg has a lower density, similar K\textsubscript{s} but much larger G at >90 GPa, which results in much higher velocities in (Mg\textsubscript{0.5}Fe\textsubscript{0.5})(Si\textsubscript{0.5}Al\textsubscript{0.5})O\textsubscript{3} Bdg. At 100 GPa and 2000 K, the differences in density, K\textsubscript{s}, G, $V_p$, and $V_s$ between (Mg\textsubscript{0.5}Fe\textsubscript{0.5})(Si\textsubscript{0.5}Al\textsubscript{0.5})O\textsubscript{3} and (Mg\textsubscript{0.5}Fe\textsubscript{0.5})(Si\textsubscript{0.5}Fe\textsubscript{0.5})O\textsubscript{3} are −10.4%, −0.9%, 19.2%, 8.1%, and 14.8%, respectively. Elastic moduli and velocities almost linearly depend on pressure and temperature after B-site Fe\textsuperscript{3+} spin transition and their first pressure and temperature derivatives are comparable to those of MgSiO\textsubscript{3} Bdg (Supplementary Table 3).

\textbf{Ab initio investigation on the stability of (Mg\textsubscript{0.5}Fe\textsubscript{0.5})(Si\textsubscript{0.5}Fe\textsubscript{0.5})O\textsubscript{3} bridgmanite.} Through high-pressure and high-temperature experiments, we find the formation of iron- rich bridgmanite (Mg\textsubscript{0.5}Fe\textsubscript{0.5})(Si\textsubscript{0.5}Fe\textsubscript{0.5})O\textsubscript{3} coexisting with Fe- poor bridgmanite, instead of forming a single phase of (Mg\textsubscript{0.9}Fe\textsubscript{0.1})(Si\textsubscript{0.9}Fe\textsubscript{0.1})O\textsubscript{3}. Through high-pressure and high-temperature experiments, we find the formation of iron-rich bridgmanite (Mg\textsubscript{0.5}Fe\textsubscript{0.5})(Si\textsubscript{0.5}Fe\textsubscript{0.5})O\textsubscript{3} coexisting with Fe-poor bridgmanite, instead of forming a single phase of (Mg\textsubscript{0.9}Fe\textsubscript{0.1})(Si\textsubscript{0.9}Fe\textsubscript{0.1})O\textsubscript{3}.

\begin{align*}
G_{\text{Hill}}(P, T) &= \frac{c_{\text{mag}}^{\text{Hill}}(P, T) + c_{\text{stat}}^{\text{Hill}}(P, T)}{2} - T S_{\text{conf}}
\end{align*}

where $S_{\text{conf}}$ is the configurational entropy ($S_{\text{conf}} = k_B \ln M$, M is the configuration degeneracy). $G_{\text{Hill}}^{\text{mag}}(P, T)$ and $G_{\text{Hill}}^{\text{stat}}(P, T)$ can be derived from

\begin{align*}
G_{\text{Hill}}^{\text{mag}}(P, T) &= \frac{c_{\text{mag}}^{\text{Hill}}(P, T)}{2} - T S_{\text{mag}}
\end{align*}

Fig. 5 Formation of thermochemical piles in the lowermost mantle from iron-rich materials. The temperature (left column) and composition (right column) fields from the surface to the core-mantle boundary are shown at 4.5 Gyr for case 1 (a, b), case 2 (c, d), case 3 (e, f), and case 4 (g, h). In cases 1, 2, 3, and 4, the Rayleigh number is $R_a = 1 \times 10^4$, $1 \times 10^5$, $1 \times 10^6$, and $1 \times 10^7$, respectively, and the iron-rich materials (shown by golden colors in the right panels) are 1.2%, 1.2%, 1.2%, and 1.5% intrinsically denser than the background mantle materials (shown by black colors in the right panels), respectively. Large thermochemical piles form after 4.5 Gyr for all cases.
Eqs. (3–6) in Supplementary Materials. Thus, the Gibbs formation free energy of the decomposition reaction for pure HS/LS state can be expressed as:

\[
\Delta G = \frac{1}{2} \left( G_{\text{stat}}^{\text{Fe}^3+} - G_{\text{stat}}^{\text{Fe}^{2+}} \right) - \frac{1}{2} \left( G_{\text{vib}}^{\text{Fe}^3+} - G_{\text{vib}}^{\text{Fe}^{2+}} \right) - \sum_f \left( \Delta f_i \right)
\]

where \(\Delta f_i\) is the contribution to the Gibbs free energy linearly depends on Fe³⁺ content. G is negative at lower-mantle conditions and \(\sum f_i\) is the internal energy or the Gibbs free energy without the vibrational contribution.

As shown in Supplementary Fig. 2, \(\Delta G\) is negative at lower-mantle conditions regardless of the spin state of B-site Fe³⁺ in [(Mg₁₋ₓFeₓ)₃(Si₁₋ₓFeₓ)O₃] bridgmanite. This implies that the assemblage of (Mg₆Fe₃O₁₄) and SiO₂ is more stable than the single-phase [(Mg₁₋ₓFeₓ)₃(Si₁₋ₓFeₓ)O₃] bridgmanite, consistent with our experimental results (Fig. 1). In addition, our LDA-U calculations extend the occurrence of this decomposition reaction to the lowest-mantle conditions, where (Mg₆Fe₃O₁₄) bridgmanite is still more stable than [(Mg₁₋ₓFeₓ)₃(Si₁₋ₓFeₓ)O₃] bridgmanite. In order to check the effect of the exchange-correlation function on the results, we also repeated the entropy change of this reaction using the generalized gradient approximation with Hubbard U correction (GGA+U). U values for Fe³⁺ on A and B sites in bridgmanite are 3.3 and 4.5 eV, respectively. The ÅH predicted by the GGA+U calculations is similar to that from the LDA+U calculations (Supplementary Fig. 2), both of which favor the mixed phases over the single phase.

Thermoelastic models for the estimations of velocity and density heterogeneities. Previous studies \(^{20,64}\) suggested that the pyrolitic lower mantle that consists of 15% Mg₂Fe₂Si₃O₁₀ ferropericlase (Fp), 78% Mg₂Fe₂Si₂O₆ bridgmanite (Fe³⁺-Bdg), and 7% CaSiO₃ Ca-perovskite (CaPv) can admirably reproduce the velocity and density profiles of PREM model \(^{22}\) for the lower mantle. Combining the thermoelastic properties \(^{20,64,67}\) of these three major minerals with our elastic data for LS-(Mg₁₋ₓFeₓ)₃(Si₁₋ₓFeₓ)O₃ and (Mg₁₋ₓFeₓ)₃(Si₁₋ₓAlₓ)O₃ bridgmanite, consistent with our experimental results (Fig. 1), in addition, our LDA-U calculations extend the occurrence of this decomposition reaction to the lowest-mantle conditions, where (Mg₆Fe₃O₁₄) bridgmanite is still more stable than [(Mg₁₋ₓFeₓ)₃(Si₁₋ₓFeₓ)O₃] bridgmanite. In order to check the effect of the exchange-correlation function on the results, we also repeated the entropy change of this reaction using the generalized gradient approximation with Hubbard U correction (GGA+U). U values for Fe³⁺ on A and B sites in bridgmanite are 3.3 and 4.5 eV, respectively. The ÅH predicted by the GGA+U calculations is similar to that from the LDA+U calculations (Supplementary Fig. 2), both of which favor the mixed phases over the single phase.

The whole-mantle dynamics is simulated in a 2D Cartesian box with an aspect ratio of 2:1. The model domain contains 1536 and 512 elements in the horizontal and vertical directions, respectively. Models are basally heated, with the top and bottom having a fixed temperature at \(T = 0\) and \(T = 1\), respectively. The top and bottom boundaries are both free-flip and the side boundaries are reflective. The viscosity is determined by \(\eta = \eta_0 \exp(0.5 - T)\), where \(\eta_0\) is a viscosity pre-factor, and \(A\) is the activation energy. Here, \(\eta_0\) is 1.0 and 30.0 for the upper mantle and the lower mantle, respectively, and \(A = 9.21\) which leads to the viscosity changing four orders of magnitude as temperature increases from 0 to 1. Initially, the whole mantle was assumed to be hot with a temperature of \(T = 0.72\) (or 1800 K) everywhere, and we introduced a global layer of iron-rich materials in the lowermost 300 km of the mantle.

We performed four cases. Case 1 is the reference case in which the iron-rich materials are 1.2% intrinsically denser (with a buoyancy number of \(B = 0.48\)) than the background mantle materials and the Rayleigh number, which controls the vigor of mantle convection, is \(Ra = 1 \times 10^5\). Cases 2 and 3 have a Rayleigh number of \(Ra = 1 \times 10^4\) and \(Ra = 1 \times 10^5\), respectively, while other parameters are the same as case 1. In case 4, the iron-rich materials are 1.5% intrinsically denser (with a buoyancy number of \(B = 0.6\)) than the background mantle materials, and other parameters are the same as case 1.

Data availability

The data are available in the main text, the supplementary materials, and from the corresponding authors.

Code availability

The open-source Quantum Espresso package used in this study is available at https://www.quantum-espresso.org/.

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Author contributions
W.Z.W. and J.C.L. conceived and designed this project. W.Z.W. performed the theoretical calculations. J.C.L., F.Z., S.M.D., and J.L. performed the experiments. M.M.L. conducted the geodynamic simulations. W.Z.W., J.C.L., and Z.F. wrote the paper, and all authors contributed to the discussion of the results and revision of the paper.

Competing interests
The authors declare no competing interests.

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