



# Effects of iron on the lattice thermal conductivity of Earth's deep mantle and implications for mantle dynamics

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Edited by Ho-kwang Mao, Carnegie Institution for Science, Washington, DC, and approved March 7, 2018 (received for review October 23, 2017)

**Iron may critically influence the physical properties and thermochemical structures of Earth's lower mantle. Its effects on thermal conductivity, with possible consequences on heat transfer and mantle dynamics, however, remain largely unknown. We measured the lattice thermal conductivity of lower-mantle ferropericlase to 120 GPa using the ultrafast optical pump-probe technique in a diamond anvil cell. The thermal conductivity of ferropericlase with 56% iron significantly drops by a factor of 1.8 across the spin transition around 53 GPa, while that with 8–10% iron increases monotonically with pressure, causing an enhanced iron substitution effect in the low-spin state. Combined with bridgmanite data, modeling of our results provides a self-consistent radial profile of lower-mantle thermal conductivity, which is dominated by pressure, temperature, and iron effects, and shows a twofold increase from top to bottom of the lower mantle. Such increase in thermal conductivity may delay the cooling of the core, while its decrease with iron content may enhance the dynamics of large low shear-wave velocity provinces. Our findings further show that, if hot and strongly enriched in iron, the seismic ultralow velocity zones have exceptionally low conductivity, thus delaying their cooling.**

ferropericlase | thermal conductivity | geodynamics | large low shear-wave velocity provinces | ultralow velocity zones

The large low shear-wave velocity provinces (LLSVPs) mapped at the bottom of the Earth's mantle are most likely hot, chemically differentiated regions (1), and their chemical component is best explained by an enrichment in iron (2, 3). It has further been suggested that the seismic ultralow velocity zones (ULVZs) observed on the core–mantle boundary (CMB) (4, 5) consist of thin pockets of strongly iron-rich materials (6, 7). The presence of iron in host minerals in the deep lower mantle can significantly influence the physical and chemical properties of these regions (8, 9), including their density, sound velocity, and transport and rheological properties. Iron further affects lower-mantle thermal conductivity, which in turn, may alter mantle dynamics and heat transfer. The influence of iron on the lower-mantle thermal conductivity operates at several different levels. Of particular interest are variations in global iron fraction (i.e., the total amount of iron oxide in mantle aggregate), the pressure-induced spin transition (10, 11), and changes in iron partitioning between bridgmanite (Bm) and ferropericlase (Fp), the two dominant minerals in the lower mantle (11, 12). Specifically, lateral variations in iron fraction at the lowermost mantle could change the lattice thermal conductivity of the region, as iron content in candidate lower-mantle minerals has been shown to influence their thermal conductivities. Moreover, the softening of bulk sound velocity ( $V_{\phi}$ ) across the spin transition of iron (8, 13, 14) at the middle part of the lower mantle may influence the thermal conductivity as well, since the lattice thermal conductivity scales approximately with  $V^2$ , where  $V$  is the sound velocity including longitudinal and transverse velocities, based on a simplified classic model for the thermal transport (15). Precise determination of the effects of iron substitution and spin transition

on the thermal conductivity of candidate lower-mantle materials would, therefore, provide critical insights into the thermal state and dynamics of the lower mantle (16), and into the heat transfer across the CMB (17).

The lattice and radiative thermal conductivities of constituent lower-mantle materials transfer heat by different mechanisms and thus, could play distinct roles in controlling the heat flux and thermal gradient in the deep lower mantle. Typically, the lattice thermal conductivity increases with pressure but decreases with temperature; however, the radiative thermal conductivity shows an opposite trend and is often assumed to be more important than the lattice component at high pressure–temperature ( $P$ - $T$ ) conditions in the lowermost mantle. The radiative thermal conductivity is largely influenced by the electronic structure of a material, but optical absorption spectroscopic measurements (18, 19) showed that the spin transition has little effect on the Fp radiative conductivity at lower-mantle conditions. On the contrary, as precise and reliable measurements remain a great challenge, little is known about the lattice thermal conductivity of lower-mantle materials under relevant  $P$ - $T$  conditions, especially the effects of iron substitution and spin transition. Therefore, current understanding of the lower-mantle–lattice thermal conductivity has been largely based on theoretical calculations (20–24) or simplified model extrapolations using results at

## Significance

Presence of iron in Earth's lower mantle may critically affect its physical properties and thermochemical structures. However, its effects on thermal conductivity and dynamics of deep mantle remain unknown. We studied lattice thermal conductivity of lower-mantle ferropericlase to 120 GPa using ultrafast optics. We observed an enhanced iron substitution effect in the low-spin iron-rich ferropericlase, with thermal conductivity that significantly drops across spin transition. Combined with bridgmanite data, we provided a self-consistent radial profile of lower-mantle thermal conductivity, which is dominated by pressure, temperature, and iron effects and shows a twofold increase throughout the lower mantle. If ultralow velocity zones are hot and strongly enriched in iron, their exceptionally low thermal conductivity will delay their cooling, influencing lowermost mantle dynamics.

Author contributions: W.-P.H. and J.-F.L. designed research; W.-P.H. and F.D. performed research; T.O. and J.-F.L. synthesized the samples; W.-P.H. and T.O. contributed new reagents/analytic tools; W.-P.H. analyzed data; and W.-P.H., F.D., and J.-F.L. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

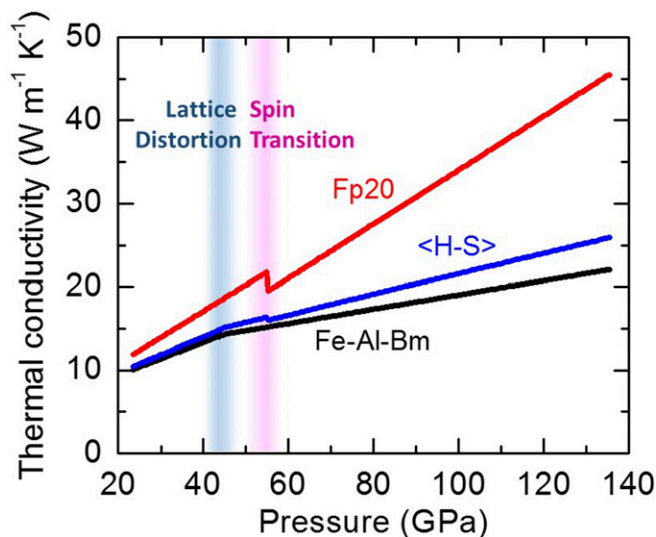
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This article contains supporting information online at [www.pnas.org/lookup/suppl/doi:10.1073/pnas.1718557115/-DCSupplemental](http://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1718557115/-DCSupplemental).

Published online April 2, 2018.





**Fig. 2.** Modeled lattice thermal conductivity of lower-mantle Fp and Bm at high pressures and room temperature. Thermal conductivity for Fp with an iron content of 20% (Fp20; red curve) is obtained by linear interpolation of our data shown in Fig. 1A. The data for Fe-Al-Bm (black curve) are a polynomial fit to the results by Hsieh et al. (29). We calculate the Hashin-Shtrikman average  $\langle H-S \rangle$  (blue curve), defined as the geometric average of the lower and upper Hashin-Shtrikman bounds (SI Text), of the thermal conductivity for a lower-mantle aggregate made of 80% volume of Fe-Al-Bm and 20% volume of Fp20 in a simplified pyrolite mineralogical model. The blue and red shaded areas represent the pressure ranges where the pressure-induced lattice distortion occurs in Fe-Al-Bm and the spin transition occurs in Fp20, respectively.

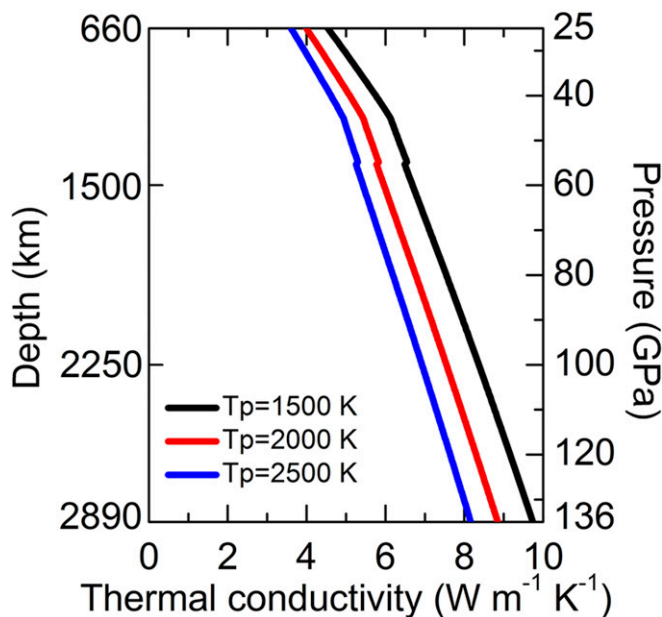
and it increases with pressure until  $P \sim 50$  GPa. Further compression results in a significant drop of the thermal conductivity by a factor of  $\sim 1.8$  between 53 and 62 GPa, which can be associated with the spin transition. The spin transition zone is theoretically and experimentally known to result in softening of the bulk sound velocity (8), and it is shown here to play a key role in reducing the thermal conductivity (Fig. 1B). After the transition, the thermal conductivity of the low-spin Fp increases monotonically to  $29 \text{ W m}^{-1} \text{ K}^{-1}$  at 115 GPa,  $\sim 40\%$  smaller than Fp8 at similar pressure. In contrast to the iron substitution effect in the high-spin Fp, the iron substitution effect is drastically enhanced in the low-spin state due to the stronger phonon-defect scattering and larger magnitude of the softening of bulk sound velocity across the spin transition. The enhanced iron substitution effect in the low-spin Fp that we observe here may result in an exceptionally low thermal conductivity in iron-rich regions at the lowermost mantle that was proposed to be a source of the ULVZs (31) (modeling and discussions are given below).

### Modeling Lower-Mantle Thermal Conductivity

In Fig. 2, we summarize our high-pressure, room temperature lattice thermal conductivities of major candidate lower-mantle minerals with relevant Fe and Al contents in the lower mantle [i.e., (Fe,Al)-bearing bridgmanite (Fe-Al-Bm) (black curve in Fig. 2) taken from ref. 29 and Fp20 (red curve in Fig. 2)]. The thermal conductivity of Fp20 is linearly interpolated from our data shown in Fig. 1A for an iron content of 20% and shows a small discontinuity of  $\sim 10\%$ , smaller than our measurement uncertainty, around 50–60 GPa due to the spin transition in Fp (SI Text has details). Our results on the Fp20 and Fe-Al-Bm enable us to further calculate the lattice thermal conductivity of the lower-mantle mineral aggregate at high pressure and room temperature. For simplicity, we assume that the lower mantle is composed of a simplified pyrolite compositional model containing Fe-Al-Bm with a proportion of 80% in volume and Fp20

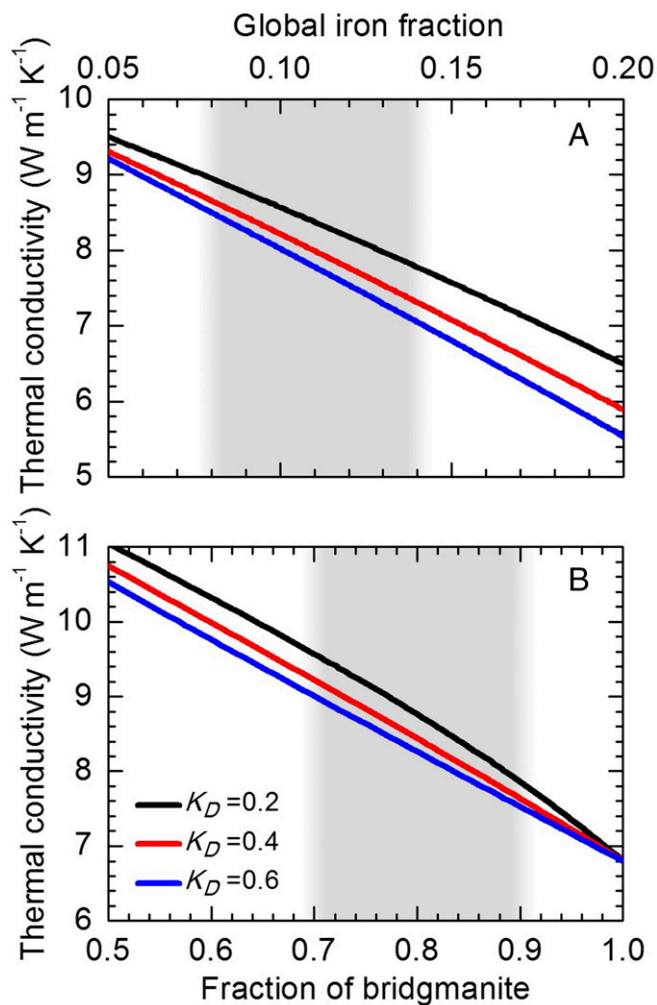
with 20% in volume (8). We then calculate Hashin-Shtrikman bounds of aggregate thermal conductivity, which are the narrowest bounds for a multiphase system, and take the geometric average of these bounds as an estimator of lower-mantle thermal conductivity (blue curve in Fig. 2; SI Text has details). The pressure derivative is slightly reduced around 45 GPa due to the smaller increasing rate of Fe-Al-Bm thermal conductivity with pressure, which results itself from the pressure-induced lattice distortion on the iron sites (29). Again, a small discontinuity around 50–60 GPa is caused by the spin transition in Fp20. Note that the aggregate thermal conductivity is dominated by the Bm thermal conductivity due to its dominant volume fraction in the lower mantle. Changes in the Fp thermal conductivity triggered by the spin transition and the potential variation of the onset pressure and range of the spin transition with different iron content play a relatively minor role in affecting the lower-mantle aggregate thermal conductivity.

To model the lattice thermal conductivity at relevant lower-mantle compositional and  $P$ - $T$  conditions, we further consider integrated effects of pressure, temperature, and iron partitioning ( $K_D$ ) between Bm and Fp as well as the pressure-induced spin transition in Fp and pressure-induced lattice distortion in Bm due to the Fe and Al substitutions (SI Text has details). Note that our modeling here does not account for potential iron saturation effects, where the thermal conductivity saturates when the iron content is larger than a threshold value, for which no experimental data are available to indicate its existence to date. For applications to the typical lower mantle and LLSVPs, where global iron content should be in the range of 8–12%, the iron saturation effects may be very limited (SI Text), if occurring at all, and therefore, should not alter our conclusions. By contrast, in regions strongly enriched in iron, as is possibly the case for ULVZs, saturation effects should be accounted for (see below). In Fig. 3, we plot lower-mantle thermal conductivity at three



**Fig. 3.** Lattice thermal conductivity of a representative lower-mantle mineral aggregate at high pressures and temperatures. We use Hashin-Shtrikman average for the thermal conductivity by considering integrated effects of pressure, temperature, iron partitioning, iron spin transition, and lattice distortion. Bm volume fraction of 0.8, global iron fraction of 0.09, a depth-dependent iron partitioning coefficient by Irifune et al. (12), and the temperature effect of  $T^{-1/2}$  dependence are used to model the mantle thermal conductivity. Data for Bm are from Fe-Al-Bm (29). The small discontinuity around 50–60 GPa is caused by the spin transition of iron in Fp.





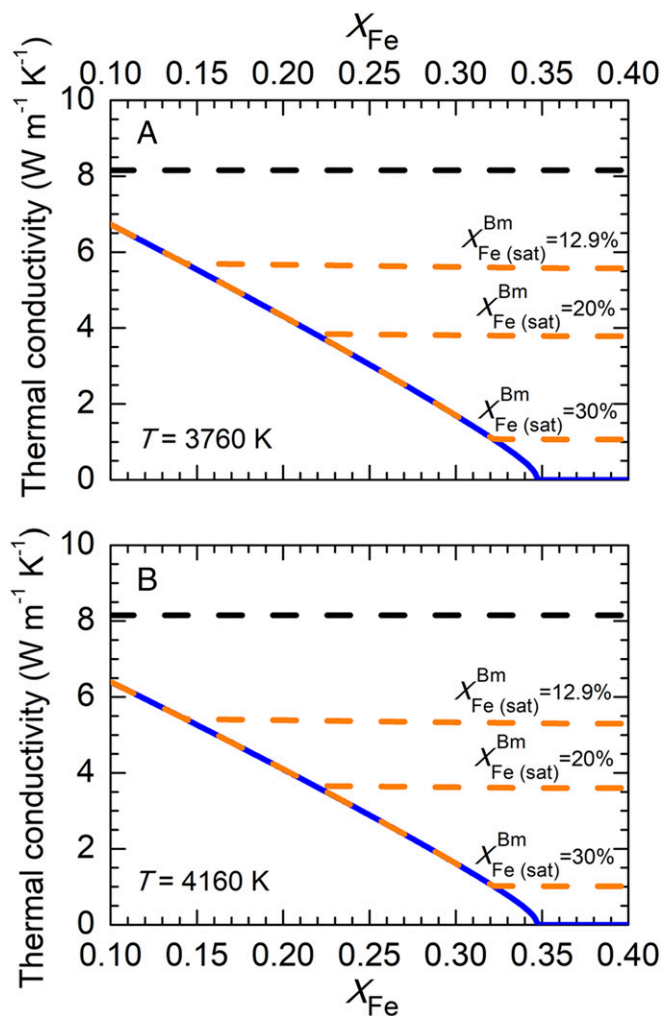
**Fig. 4.** Thermal conductivity of a representative lower-mantle mineral aggregate as a function of (A) global iron fraction and (B) fraction of Bm, with different iron partitioning coefficient at the lowermost mantle conditions. Calculations are made for a representative temperature  $T = 3,000$  K at a depth of 2,800 km ( $P = 130.2$  GPa). In A, the fraction of Bm is set to  $X_{\text{Bm}} = 0.8$ , and in B, the global iron fraction is set to  $X_{\text{Fe}} = 0.09$ . Data for Bm are from Fe-Al-Bm (29). The effect of the spin transition in Fp, which results in a small discontinuity in the thermal conductivity around 50–60 GPa, is included. Gray shaded areas represent expected variations in the fractions of global iron and Bm in the lowermost mantle.

different potential temperatures assuming that the temperature dependences of the Bm and Fp both follow the typical  $T^{-1/2}$  dependence (25, 32, 33). Changes in  $K_D$  with depth were taken from the work by Irifune et al. (12). Our modeling shows that thermal conductivity increases by about a factor of two from top to bottom of the lower mantle. A variation of temperature by 500 K, typical of the lateral anomalies expected in the lowermost mantle (3), induces a change in thermal conductivity of  $\sim 1$  W m<sup>-1</sup> K<sup>-1</sup> (i.e.,  $\sim 12\%$  of the estimated aggregate conductivity). Fig. 4 further quantifies the influences of the global iron content ( $X_{\text{Fe}}$ ) and fraction of Bm ( $X_{\text{Bm}}$ ) on lower-mantle thermal conductivity. Varying either  $X_{\text{Fe}}$  by 4% or  $X_{\text{Bm}}$  by 10%, as is expected in the lowermost mantle (3), again leads to a change in thermal conductivity of  $\sim 1$  W m<sup>-1</sup> K<sup>-1</sup>. By contrast, as shown in Figs. S5 and S6, spin transition in Fp and variations of  $K_D$  with depth play relatively minor roles in affecting lower-mantle thermal conductivity. Although our calculations are based on extrapolations of room temperature data, variations of the lower-mantle thermal conductivity profiles shown in Fig. 3 due to changes in the

onset pressure and range of spin transition at high temperatures are small. Finally, we note that the lattice thermal conductivity in the lowermost mantle is constrained to  $\sim 8$  W m<sup>-1</sup> K<sup>-1</sup> (Fig. 3), larger than the available experimental data for the lower-mantle radiative thermal conductivity (34, 35),  $\sim 0.5$ – $3$  W m<sup>-1</sup> K<sup>-1</sup>, at similar  $P$ - $T$  conditions, indicating the lattice conductivity mainly contributes to the heat transfer in Earth's deep lower mantle.

#### Consequences on Deep-Mantle Dynamics and Evolution

The combination of our data for Fp and previous measurements for Fe-Al-Bm (29) allows us to build self-consistent radial profiles of lower-mantle thermal conductivity that account for pressure, thermal, and compositional effects. While it may not drastically alter mantle convection, a twofold increase of thermal conductivity with depth throughout the lower mantle may, according to purely thermal simulations of mantle convection



**Fig. 5.** Thermal conductivity for hot, iron-rich aggregate at the bottom of the mantle, representing seismic ULVZs. Calculations are made at a depth of  $z = 2,880$  km ( $P = 134.7$  GPa), iron partitioning  $K_D = 0.4$ , fraction of Bm  $X_{\text{Bm}} = 0.9$ , and real temperatures of (A)  $T = 3,760$  K and (B)  $T = 4,160$  K. Results are plotted as a function of the global fraction of iron,  $X_{\text{Fe}}$ . In each plot, the thick horizontal dashed line shows the thermal conductivity at the bottom of the mantle along a geotherm  $T_p = 2,500$  K ( $T = 3,360$  K) and for an aggregate with  $X_{\text{Bm}} = 0.8$  and  $X_{\text{Fe}} = 0.09$ , representative of the average lower mantle (blue curve in Fig. 3). Blue curves do not account for possible iron saturation effects and would unphysically go to zero for  $X_{\text{Fe}} \sim 0.35$ . Orange dashed curves account for iron saturation in Bm with different threshold values (labels on curves) and iron saturation in Fp with a threshold value  $x_{\text{Fe(sat)}}^{\text{Fp}} = 56\%$ .

(36), delay the cooling of the core. In thermochemical simulations, a twofold increase helps stabilize reservoirs of chemically differentiated materials at the bottom of the system (37) and may affect the distribution of plumes in the deep mantle (38). In particular, the number of plumes generated outside the thermochemical reservoirs is reduced, and their spacing is increased, in agreement with seismic observations (38). By contrast, the consequences of thermal conductivity changes due to compositional variations on mantle convection have, so far, not been investigated. If, as suggested by probabilistic tomography (3), LLSVPs are hotter than average by about 400–500 K and enriched in iron by ~3%, their thermal conductivity might be lower than that of surrounding mantle by ~20%, affecting, in turn, their dynamics. Finally, it has been suggested that, because it triggers a change in density, the spin transition in Fp, which is responsible for the reduction of thermal conductivity that we observed in Fp56, may affect mantle dynamics (39–42). Potential effects include enhanced flow velocities (39–41), allowing cold downwelling to spread more easily around the CMB, and the destabilization of reservoirs of dense material (42). The exact amplitude of these effects is, however, still debated. Although the decrease in lower-mantle thermal conductivity induced by the spin transition has not yet been included in numerical simulations of convection, the amplitude of this decrease is small (Fig. S5), and its impact on lower-mantle dynamics may thus be limited (41).

Because thermal conductivity is partially controlling the heat flux at the CMB, lateral variations in thermal conductivity related to variations in temperature and iron fraction may further influence core dynamics and geodynamo. Previous calculations using recent data for thermal conductivity of Bm (29) indicate that, while heat flux is mostly controlled by thermal pattern at the CMB, the lateral variations in thermal conductivity still play a significant role. Our data for Fp would increase this effect.

Our findings may further have strong implications for the evolution of the ULVZs observed at the bottom of the mantle (4, 5). Several explanations have been proposed for their structures, including pockets of partial melting (43) and patches of materials enriched in iron oxides, in particular iron-rich Fp (31), subducted banded iron formation (44), and postperovskite (45). The detailed geographical distribution of ULVZs may provide hints about their nature: recent geodynamic modeling (7) suggests that ULVZs would be preferentially located well within LLSVPs if they are related to partial melt, while they would be concentrated along the edges of LLSVPs if they consist of chemically denser (e.g., iron-rich) materials. While a full seismic coverage of the CMB region has not yet been completed, available seismic observations indicate that ULVZs are preferentially located within or at the edges of LLSVPs (46) (i.e., in regions likely hotter than average mantle). Compared with average lower mantle, ULVZs may thus be simultaneously hotter and strongly enriched in iron. Following this hypothesis, their thermal conductivity would be strongly reduced. This low conductivity would be further reduced by a possible enrichment in Bm, as LLSVPs may be enriched in Bm (3). For instance, taking  $K_D = 0.4$ ,  $X_{Bm} = 0.9$ , and a temperature of 3,760 K (i.e., ~400 K higher than the bottom temperature for a potential geotherm  $T_p = 2,500$  K), modeling of our measurements predicts a thermal conductivity of  $\sim 6.3 \text{ W m}^{-1} \text{ K}^{-1}$  for an enrichment in iron of 3% compared with pyrolytic composition (i.e.,  $X_{Fe} = 12\%$ ; corresponding to iron fractions in Bm and Fp of  $x_{Fe}^{Bm} = 10.8\%$  and  $x_{Fe}^{Fp} = 23.2\%$ , respectively) and  $\sim 1.7 \text{ W m}^{-1} \text{ K}^{-1}$  for an enrichment in iron of 21% ( $X_{Fe} = 30\%$ ; corresponding to  $x_{Fe}^{Bm} = 27.9\%$  and  $x_{Fe}^{Fp} = 49.1\%$ ) (Fig. 5A and *SI Text*). These values are lower than the estimated thermal conductivity for the average lower mantle (blue curve in Fig. 3) by ~23 and 80%, respectively. Therefore, if ULVZs started hotter and were strongly enriched in iron at the early stage of the Earth's interior, they may have had (and still have) a very low thermal

conductivity compared with the surrounding mantle. This, in turn, may have delayed their cooling, allowing the persistence of small pockets of hot materials up to now. ULVZs may thus be substantially hotter than LLSVPs, further decreasing their thermal conductivity. Assuming that ULVZs are hotter than LLSVPs by 400 K (i.e., 800 K higher than a potential geotherm  $T_p = 2,500$  K) and for  $K_D = 0.4$  and  $X_{Bm} = 0.9$ , thermal conductivity for  $X_{Fe} = 30\%$  is around  $1.6 \text{ W m}^{-1} \text{ K}^{-1}$  (Fig. 5B). By contrast, a low thermal conductivity would enhance convection within ULVZs and thus, may accelerate their cooling, provided that these structures can be animated by convection. However, because ULVZs observed so far are thin elongated structures, it is not clear whether convection is able to operate within them. The hypothesis that ULVZs are strongly enriched in iron oxide implies that the fractions of iron in Bm and Fp reach high values: 20% or higher. Because our data for Bm (29) are limited to  $x_{Fe}^{Bm} = 12.9\%$ , extrapolation to higher values of  $x_{Fe}^{Bm}$  may be biased. This appears clearly in blue curves in Fig. 5, showing that thermal conductivity of the aggregate would unphysically go to zero for values of  $X_{Fe} \sim 35\%$ , corresponding to  $x_{Fe}^{Bm} \sim 33\%$  for  $K_D = 0.4$  and  $X_{Bm} = 0.9$ . Instead, the iron saturation effects may occur for values of  $x_{Fe}^{Bm}$  larger than a threshold value,  $x_{Fe(sat)}^{Bm}$ , limiting the decrease in thermal conductivity with increasing  $x_{Fe}^{Bm}$ . To date, however, there are no indications or experimental data constraining  $x_{Fe(sat)}^{Bm}$  if the saturation effect is existing. To account for the possible iron saturation effects, we assumed several values of  $x_{Fe(sat)}^{Bm}$  in the range of 12.9–30% (dashed orange curves in Fig. 5). Interestingly, in all cases, the thermal conductivity remains lower than the average lower-mantle conductivity by at least 30% for  $x_{Fe(sat)}^{Bm} = 12.9\%$  and up to ~80% for  $x_{Fe(sat)}^{Bm} = 30\%$ . Finally, it is important to note that our modeling implicitly assumes that the ULVZs are regions with solid materials strongly enriched in iron. For a given material, thermal conductivity is typically lower if this material is melted or partially melted than if it is a solid. Therefore, although the thermal conductivity of partially melted iron-rich materials at the lowermost mantle conditions remains largely unknown, it is expected to be lower than that of solid iron-rich materials. If ULVZs are composed of iron-rich partial melt, their cooling would thus be further delayed.

A significant decrease in thermal conductivity due to the combination of thermal and chemical (iron enrichment) effects is thus likely to affect the evolution of ULVZs if these regions are enriched in iron and to a lesser extent, the heat flux at CMB and the evolution of the core as well as the dynamics of LLSVPs. The detailed evolution and dynamics of ULVZs and LLSVPs remain to be investigated. Incorporating our experimental data for thermal conductivity of lower-mantle minerals in simulations of mantle dynamics may, therefore, bring insight into the combined evolution of the Earth's mantle and core.

**ACKNOWLEDGMENTS.** We thank J. Yang, N. Tomioka, and S. Jacobsen for help with synthesis and preparation of the samples; S. Jacobsen for sharing experimental parameters for synthesis of ferropervskite and bridgmanite; and V. Prakapenka for his assistance with X-ray diffraction analysis of the starting crystals. The work by W.-P.H. and F.D. was supported by the Academia Sinica and Ministry of Science and Technology of Taiwan, Republic of China Contracts CDA-106-M02 (to W.-P.H.), MOST 103-2112-M-001-001-MY3 (to W.-P.H.), 105-2116-M-001-024 (to W.-P.H.), 106-2116-M-001-022 (to W.-P.H.), 105-2116-M-001-017 (to F.D.), and AS-102-CDA-M02 (to F.D.). J.-F.L. acknowledges support from the Geophysics and Cooperative Studies of the Earth's Deep Interior Programs of the US National Science Foundation, the Visiting Professorship Program of the Institute for Planetary Materials, Okayama University, and the Center for High Pressure Science and Technology Advanced Research. This work was supported, in part, by Japan Society for the Promotion of Science KAKENHI Grant 26287135. X-ray diffraction patterns of the crystal were analyzed at GeoSoilEnviroCARS (GSECARS) sector of the Advanced Photon Source. GSECARS was supported by National Science Foundation Grant EAR-0622171 and Department of Energy Grant DE-FG02-94ER14466 under Contract DE-AC02-06CH11357. The APS is supported by 263 Department of Energy–Basic Energy Sciences Contract DE-AC02-06CH11357.

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