Sharp 660-km discontinuity controlled by extremely narrow binary post-spinel transition

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The Earth’s mantle is characterized by a sharp seismic discontinuity at a depth of 660 km that can provide insights into deep mantle processes. The discontinuity occurs over only 2 km—or a pressure difference of 0.1 GPa—and is thought to result from the post-spinel transition, that is, the decomposition of the mineral ringwoodite to bridgmanite plus ferropericlase. Existing high-pressure, high-temperature experiments have lacked the pressure control required to test whether such sharpness is the result of isochemical phase relations or chemically distinct upper and lower mantle domains. Here, we obtain the isothermal pressure interval of the Mg–Fe binary post-spinel transition by applying advanced multi-anvil techniques with in situ X-ray diffraction with the help of Mg–Fe partition experiments. It is demonstrated that the interval at mantle compositions and temperatures is only 0.01 GPa, corresponding to 250 m. This interval is indistinguishable from zero at seismic frequencies. These results can explain the discontinuity sharpness and provide new support for whole-mantle convection in a chemically homogeneous mantle. The present work suggests that distribution of adiabatic vertical flows between the upper and lower mantles can be mapped on the basis of discontinuity sharpness.

The 660-km seismic discontinuity (D660) is the boundary between the upper and lower mantles. Seismological studies based on short-period P-wave reflections (P’660P–P’P‘ ratio; where P’P‘ is high frequency P wave reflection, and P’660P‘ is its precursor reflected at the 660-km discontinuity) have demonstrated that D660 is extremely sharp and less than 2 km thick, which is in striking contrast to the 7-km-thick 410-km discontinuity. Understanding the nature of D660 from a perspective of mineral physics provides important clues to open questions about the structure and dynamic processes in Earth’s mantle, such as slab subduction and upwelling of hot plume.

Geochemical studies suggest that Earth’s upper mantle consists of ~60% atom-proportion of the (Mg,Fe)SiO\textsubscript{3} polymorphs with Mg/Mg+Fe ratios around 0.9, including olivine (Ol), wadsleyite and ringwoodite (Rw), with the remaining 40% consisting primarily of ortho- and clinopyroxenes and garnet. By contrast, the lower mantle consists of ~70 atom% (Mg,Fe)SiO\textsubscript{3} compounds, such as bridgmanite (Brg) and post-perovskite, with ~20 atom% ferropericlase (fPc) and 10 atom% calcium perovskite. Because the discontinuity depth is close to the pressure of the post-spinel (PSP) transition, Rw decomposes to Brg + fPc in the Mg–Fe (pseudo)binary PSP transition, this binary loop must be extremely narrow and less than 0.1 GPa in pressure. However, such a narrow binary loop has never been demonstrated by mineral physics data. Reference 1 first attempted to determine the transition interval through a conventional multi-anvil experiment, in which pressures were determined with a precision of ~0.5 GPa. The experiment was based on the spatial dimension of Rw + Brg + fPc coexistence along a temperature gradient obtained by microfocused X-ray diffractometry and the Clapeyron slope of the PSP transition that they determined. The strategy was invalid, however, because of the limited spatial resolution of laboratory microfocused X-ray diffractometry and controversial Clapeyron slope of the PSP transition. Reference 1 attempted to determine the interval by precise multi-anvil experiments in combination with in situ X-ray diffraction, obtaining a pressure interval of ≤1 GPa. However, they determined pressures with a precision of ~0.2 GPa and observed pressure drop despite constant press load and temperature. The pressure drop may have led to serious overestimation of the pressure interval because the PSP phase remains even in a Rw stability field due to the sluggish reverse reaction. Furthermore, a thermodynamic

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 Articles Nature Geoscience

Phase relations in the system Mg$_2$SiO$_4$–Fe$_2$SiO$_4$. $X_{Mg}$ is the Mg/(Mg + Fe) ratio. Compositions of three phases (Rw, Brg and fPc) are shown by solid lines. Dashed lines are a rough drawing of phase boundaries in this system. a. The phase relations at 1,700 K. Open and solid circles indicate stable phases at $X_{Mg}$ = 100 are Rw and Brg + fPc, respectively. Open and solid triangles indicate that stable phases at $X_{Mg}$ = 70 are Rw + fPc + St and Brg + fPc + St, respectively. Blue and red colours indicate Mg$_2$SiO$_4$ and (Mg$_{0.7}$Fe$_{0.3}$)$_2$SiO$_4$ starting compositions, respectively. Error bars originate from the pressure uncertainty of the equation of the state of MgO suggested by Tange et al.24. b. Estimated shift of the phase boundaries from 1,700 (blue) to 2,000 K (red).

Determination of the binary post-spinel transition

The binary phase relations determined at 1,700 K are shown in Fig. 1. A striking feature is that the transition pressure in the Fo$_{90}$ composition (between 23.86(6) and 24.00(5) GPa; pressure errors in parentheses) is higher than that in the Fo$_{100}$ composition (between 23.72(5) and 23.86(6) GPa) by 0.14 GPa, beyond the present uncertainty (0.11 GPa). The higher transition pressure with more iron-rich composition differs from the consensus regarding the phase relations in this system after ref. 2. Note that the run at 23.86(6) GPa (M2268) shows that Brg + fPc is stable in a Fo$_{100}$ composition and Rw is stable in a Fo$_{90}$ composition (Fig. 1 and Supplementary Fig. 4b). The geometry of the phase diagram shows that the pressure interval of the binary loop at (Mg$_{0.5}$Fe$_{0.5}$)$_2$SiO$_4$ (Fo$_{90}$) should be much smaller than this pressure difference (0.14 GPa).

The pressure intervals at Fo$_{90}$ were quantitatively estimated at 1,700 and 2,000 K using compositions of the three phases (Brg, fPc and Rw) between the magnesium endmember and the four-phase coexistence boundary calculated with thermodynamic data because it is impossible to reach chemical equilibrium within limited experimental hours in the synchrotron radiation facility due to small diffusion coefficients (refs. 14–15) and because very small grain sizes (<3 μm) of recovered phases were too small for compositional analysis by electron microprobe (Methods and Supplementary Tables 2 and 3). We calculated compositions of Brg and Rw for a given fPc composition by using the Gibbs energy changes by Mg–Fe exchange and interaction parameters of the three phases14–17. We changed the fPc composition step by step from the magnesium endmember and repeated this calculation until the iron content in Brg reached the maximum solubility reported by ref. 14. The pressures for these three-phase coexistences were calculated by the phase compositions, their volume at pressures and temperatures of interest and the interaction parameters to depict the binary loop.

Extremely narrow binary post-spinel transition

The binary loop thus obtained is curved and has very close magnesium and iron contents between Rw and Brg + fPc, which agrees with previous thermodynamic calculations14–15. The pressure interval is 0.012 ± 0.008 GPa at a bulk composition of Fo$_{90}$ at 1,700 K, as shown in Fig. 1. This interval is one order of magnitude smaller than the previous estimation (0.15 GPa) (ref. 2). This pressure interval corresponds to a depth interval of only 100–500 m, which is also one order of magnitude smaller than the observable thickness of D660 using 1 Hz seismic waves (<2 km) (ref. 1). The pressure interval at an expected mantle temperature, namely, 2,000 K (ref. 22), was evaluated by the same procedure. The Clapeyron slope reported by ref. 23 was used and modified using the MgO scale suggested by ref. 24 to estimate transition pressures at the magnesium endmember and the four-phase coexistence. We obtained a pressure interval at 2,000 K of 0.003 ± 0.002 GPa, which is even smaller than that at 1,700 K.

One consideration is that incorporation of secondary components such as FeO$_3$, Al$_2$O$_3$ and water may change the pressure interval by changing the compositions of Rw and Brg and by stabilizing garnet. Our thermodynamic calculations show that the pressure interval in more natural compositions will be less than or similar
to that in the present Mg–Fe$^{2+}$ binary system. In particular, garnet has the important role of buffering the Fe$^{3+}$ and Al$^{3+}$ contents of Brg, which would otherwise broaden the transition (Supplementary Information). The reducing effect of a non-transforming phase such as garnet was also discussed in ref. 25. Thus, the seismically observed sharpness of D660 is in excellent agreement with our experimental results. This circumstance does not require chemical stratification of the upper and lower mantle, supporting a compositionally homogenous mantle throughout the present-day mantle and whole-mantle convection.

**Variation of the transition width in the adiabatic mantle**

Reference 26 suggested a potential expansion of the discontinuity thickness due to latent heat associated with a phase transition in an adiabatic mantle flow (Verhoogen effect) (Fig. 3), which was also reported by a geodynamic study27. The existing thermodynamic data suggest that the thickness of the present PSP transition could be expanded by ~7 km at most due to the latent heat of the PSP transition (Methods). This expansion should lower reflectivity of short-wavelength P-waves at D660 (ref. 28). Reference 29 reported a decrease in short-wavelength P-wave reflectivity at D660 approaching the Mid-Atlantic Ridge axis, which might be caused by possible vertical adiabatic flow under the ridge. Therefore, a global mapping of sharpness of D660 can be used to assess presence of vertical flows faster than thermal diffusion. The present study encourages global seismologists to revisit this topic to obtain new insights regarding mantle dynamics.

**Online content**

Any methods, additional references, Nature Research reporting summaries, source data, statements of code and data availability and associated accession codes are available at https://doi.org/10.1038/s41561-019-0452-1.
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Acknowledgements
We appreciate H. Fischer, S. Ubelhack, R. Njul, H. Schulze, U. Trenz and S. Limhardt at Bayerisches Geoinstitut for their technical assistance. We acknowledge N. Tomioka, A. Slatkoff, G. Manfudike, S.-M. Zhai, K. Saito, K. Kawai, J. Ito, A. Kubo, S. Okita, T. Okishio, M. Sugita, M. Matsui, A. Kowata, M.-S. Song and S. Yoskosi for their participation in the early stage of this study (2003–2004). This work was supported by the research project approved by DFG (KA 3434/7–1, KA3434/8–1, KA3434/9–1) and BMBF (OSK16WC2) to T. Katsura and DFG (IS 350/1–1) to T.I. This project has also been supported by the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (proposal no. 787 572). T.I. has been supported by a research fellowship for scientific research from the Japan Society for the Promotion of Science (JSPS) for Young Scientists, an overseas research fellowship from the Scientific Research of the JSPS for Young Scientists and an Alexander von Humboldt Postdoctoral Fellowship. The synchrotron X-ray diffraction experiments were performed in the beamline BL04B1 at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (proposal no. 2003A0087, 2003B0638, 2004A0366, 2004B0497, 2015A1359, 2015B1196, 2016A1172, 2016A1274, 2016A1434, 2016B1094, 2017A1150, 2018A1071, 2018B1218).

Author contributions
T.I. conducted most of the experiments, analysed all the samples and data, conducted thermodynamic analysis in the Mg₂SiO₄–Fe₂SiO₄ system and wrote the manuscript. T.Katsura directed this project. R.H. and T.Katsura conducted trial runs of preliminary experiments. R.H. and H.F. helped in starting sample preparations. I.K. helped to establish the cell assembly. R.M. conducted thermodynamic calculations to discuss effects of secondary components. F.M., L.Y., Z.L., D.D., T.Y., S.B., R.F., T.Kawazoe, N.T., E.K., Y.H. and Y.T. operated synchrotron radiation experiments at the beamline BL04B1 at SPring-8. All authors discussed the results and commented on the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41561-019-0452-1.
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Peer review information Primary handling editor(s): Melissa Plail; Rebecca Neely.

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Methods

Preparation of starting materials. We used two starting materials with MgSiO₃ (Fo₀⁺) and (MgFe)₀.₆SiO₃ (Fo₀⁺) bulk compositions. To examine the phase stability of Rw and Brg + IpC by normal (Rw + Brg + IpC) and reverse (Brg + IpC + Fe3Pc) reactions, these starting materials were prepared as fine powders with a grain size of 1–3 μm of MgSiO₃. MgSiO₃ enstatite (En) + reagent-grade MgO and (MgFe)₀.₆SiO₃ (Ol + MgSiO₃) sinters by using a Kawai-type multi-anvil press. The sintered samples were cut in the shape of disks 1.2 mm in diameter and 0.5 mm thick, which were cut into half or quarter disks.

In situ X-ray diffraction experiments under high pressure and temperature. High-pressure and high-temperature experiments combined with in situ X-ray measurement were conducted using the 15 MNK multianvil press, speed-MK-II, at the synchrotron radiation facility, Spring-8 (the beamline BL04B1)³¹. Tungsten carbide anvils (grade TF05 produced by Fuji Die) with a 4 mm anvil opening were used. The pressure media were prepared from reagent-grade MgO with a grain size of 1 μm. The starting samples and the pressure marker were sintered for 1 h at 2 GPa and 800 K near Fe–FeO conditions (in the case of the Fe₀.₇ sample) made with a molybdenum foil capsule using a Kawai-type multi-anvil press. The sintered samples were cut in the shapes of disks 1.2 mm in diameter and 0.5 mm thick, which were cut into half or quarter disks.

Patterns of the Fo₀.₇ sample (M2268). The samples were first compressed to a sample pressure of ~23 GPa, which is the target pressure at 1,700 K (Supplementary Fig. 5a (III)). The samples were then heated to 1,700 K within 5 min. Just after reaching this temperature, the pressure load was immediately increased at a rate of ~0.05 MN m⁻² for the first 5 min and then slowly at a rate of 0.01–0.02 MN m⁻¹ to maintain the sample pressures (forced pumping) (Supplementary Fig. 5a (IV)). The increasing rate of press load was determined on the basis of our experiences of the pressure variation while keeping the temperature stable in preceding runs. The pressure variation and progress of the reaction in the samples were checked by collecting X-ray diffraction patterns of the pressure marker and samples alternately while the temperature was kept constant. The samples were kept at the temperature for 0.5–2.0 h. They were then immediately cooled by cutting off the electric supply to the heater and slowly returned to ambient conditions. Because the average temperature at the 660-km discontinuity is expected to be 2,000 K (ref. ²), we also attempted experiments at 2,000 K. However, we had extreme difficulty in keeping a target pressure constant at this temperature because of irreproducible pressure drop and lowering of pressure precision due to the disappearance of peaks of the MgO pressure marker caused by grain growth. For these reasons, the experimental temperature of 1,700 K for the present setup (Supplementary Figs. 2 and 3) was adopted.

Phase identification in situ X-ray observation and analyses of recovered samples. In the Fo₀.₇ sample, Rw coexisted with a small amount of Brg + IpC below 23.8 GPa, whereas only Brg + IpC was present at higher pressures. The relatively fast and slow kinetics of the Ak–Brg transition ²⁷ and formation of Rw from Brg plus Pcem²⁷,²³,²⁶,²⁷,³⁷,³⁸, respectively, suggest that the assemblage of Rw + Ak + Pcem formed at 1,100 K should have first transformed to Rw + Brg + IpC during increasing temperature, and then most Brg and Pc were consumed to form pure Rw in the Rw stability field. Therefore, we conducted not only the normal run (Rw = Brg + IpC) but also the reverse run (Brg + IpC = Rw) using the same starting material in each run. We conducted the runs with the mineral assemblage of Rw + Brg + IpC to be the result of Rw stability. The coexistence of Brg + IpC was because each of their grains is isolated by Rw grains, as already reported by ref. ². (Supplementary Fig. 4). Since Brg and Pc were stable in each system (that is, Brg in the MgSiO₃ system and Pc in the MgO system) at our investigated pressure range (23–25 GPa)²³,³⁸, the complete reverse reaction was hampered due to this separation. However, no Rw was found in the stability field of Brg + Pc due to destabilization of Rw above the transition pressure and its fast kinetics ². In the Fo₀.₇ sample, the assemblages of Brg + IpC + St and Rw + IpC + St were observed above and below 23.76 GPa, respectively. In contrast to the Fo₀.₇ sample, no Brg was observed at lower pressures. The absence of Brg was due to decomposition of Brg to the Rw + St with iron-rich compositions ².

Microphotographs of starting and recovered samples were observed using a field-emission-type scanning electron microscope (Zeiss LEO 1530 Gemini) with an energy-dispersive X-ray spectrometer (Oxford X-Max⁴). Phases present in the starting and recovered samples were confirmed with a laboratory microfocused X-ray diffractometer (Bruker AXS Discover 8). We had difficulty determining compositions of phases in the recovered samples because each grain in the recovered samples was too small and conducted electron microprobe analysis. X-ray diffraction analysis, and Rw grains contain inclusions of IpC and St due to fine-grain mixing in the starting materials. We therefore estimated an Mg–Fe partition coefficient between the magnesium endmember and the boundary of four-phase coexistence by the following thermodynamic calculation. We also emphasize that it is unlikely that equilibrium compositions are obtained at this temperature due to the inertness of Brg ².

Estimation of the widths of the post-spinel transition binary loops at 1,700 and 2,000 K in (Mg₀.₆Fe₀.₄)SiO₃. Compositions of Brg and Rw for a given IpC composition were calculated by Mg–Fe partitioning between Brg and IpC and between Rw and IpC as follows. Note that no Fe³⁺ is assumed in this calculation because of reduced conditions produced by the molybdenum tubes and diamond–epoxy rods. The Mg–Fe exchange equilibrium between Brg and IpC can be written as:

\[
\text{MgSiO}_3 + \text{FeO} \leftrightarrow \text{FeSiO}_3 + \text{MgO}
\]

The free energy change of pure components, \(\Delta G^\circ_{\text{pure}}\), for equation (1), can be written as:

\[
\Delta G^\circ_{\text{pure}} = -RT \ln \left( \frac{\text{FeO}}{\text{MgO}} \right)
\]

where \(a_i^C\) is the activity of the \(i\) component in phase A, \(R\) is the gas constant, \(P\) is pressure and \(T\) is temperature. The activity is expressed as:

\[
a_i^C = X_i^A \times T_i
\]
where $X_i$ and $y_i$ are the mole fraction and the activity coefficient of the $i$ component in phase $A$, respectively. $X_{iMg}$ is described as:

$$X_{iMg} = \frac{Fe^{2+} \text{Fe}^{2+} + Mg^{2+}}{Fe^{2+} + Mg^{2+}}$$

The partition coefficient $K_{DiPc}$ for this reaction is described as:

$$K_{DiPc} = \frac{W_{Pc}^{Di} X_{Di}^{Pc}}{W_{Di}^{Pc} X_{Pc}^{Di}}$$

Using equations (3) and (5), equation (2) can be rewritten as:

$$\Delta_{DiPc} G_{Di}^{Pc} = -RTln K_{DiPc} = -RT ln \left( \frac{W_{Pc}^{Di} X_{Di}^{Pc}}{W_{Di}^{Pc} X_{Pc}^{Di}} \right)$$

Here, we assume that both solid solutions are regular symmetric solutions, which allows writing activity coefficients for each solid solution as:

$$RTln Y_{i} = W_{Di}^{Pc} (1 - X_{Di}^{Pc})$$

where $W_{Di}^{Pc}$ is a symmetry interaction parameter of component $i$ in phase $A$. By substituting equation (7) into equation (6) and rearranging, we obtain the following equation:

$$RTln Y_{i} = W_{Di}^{Pc} (1 - X_{Di}^{Pc})$$

Similarly, the Mg–Fe exchange equilibriums between Brg and Ppc can be expressed as:

$$MgSiO_3^{Pc} + FeO^{Pc} = MgSiO_3^{Brg} + MgO^{Pc}$$

In the same way as the Mg–Fe exchange equilibriums between Brg and Ppc, we have:

$$RTln K_{DiPc} = -RTln K_{DiPc}^{Pc} = -RTln K_{DiPc}^{Brg} = -RTln K_{DiPc}^{Pc}$$

The compositions of Brg and Ppc for a given $f_{Pc}$ composition are obtained using the partition coefficients given by equations (8) and (10), respectively. The necessary thermochromic parameters in equations (8) and (7) are given in Supplementary Table 2.

To depict a binary loop of the PSP transition, equilibrium of magnesium and iron components should be considered as follows:

$$MgSiO_3^{Pc} = MgSiO_3^{Brg} + MgO^{Pc}$$

In usual ways, equilibrium compositions and transition pressures should be obtained by equality of chemical potentials between the right and left sides of equations (11) and (12). However, consistent results between equations (11) and (13) based on the partition coefficients given by equations (8) and (10) are not obtained. This is certainly due to lack of reliable thermochromatic parameters, especially of the iron endmember of bridgmanite. In this study, therefore, the binary loop is depicted by estimating the pressures that three phases with compositions estimated from the partition coefficients coexist, which are evaluated using the equation of the magnesium components (equation (11)).

The Gibbs energy change for equation (11) is given as:

$$\Delta_{DiPc} G_{Di}^{Pc} = \Delta_{DiPc} H_{Di}^{Pc} - \Delta_{DiPc} S_{Di}^{Pc} + \int_{1_{Di}}^{1_{Pc}} \Delta_{DiPc} H_{Di}^{Pc} + RTln K_{DiPc} = 0$$

$$\Delta_{DiPc} H_{Di}^{Pc} = \Delta_{DiPc} H_{Di}^{Pc} - \Delta_{DiPc} S_{Di}^{Pc} + \int_{1_{Di}}^{1_{Pc}} \Delta_{DiPc} H_{Di}^{Pc} + RTln 1 = 0$$

where $P_{Di}$ is the PSP transition pressure of the magnesium endmember.

By substituting equation (14) into equation (13) and assuming that $\Delta_{DiPc} H_{Di}^{Pc}$ is constant due to the very narrow experimental pressure interval, we have:

$$\left( P-P_{Di} \right) \Delta_{DiPc} V_{Di}^{Pc} + RT ln \left( \frac{W_{Di}^{Pc}}{W_{Di}^{Pc}} \right) = 0$$

Using equations (3) and (7), equation (15) can be written as:

$$\left( P-P_{Di} \right) \Delta_{DiPc} V_{Di}^{Pc} + RT ln \left( \frac{W_{Di}^{Pc}}{W_{Di}^{Pc}} \right) = \left( 1 - X_{Di}^{Pc} \right) \frac{W_{Di}^{Pc}}{W_{Di}^{Pc}} \frac{W_{Di}^{Pc}}{W_{Di}^{Pc}}$$

Equation (16) gives a pressure by inputting equilibrium compositions of the three phases. Note that the compositional width of the binary loop at each pressure is assured by the Mg–Fe partitioning among the three phases.

We started this calculation from $X_{Di}^{Pc} = 0.002$ and increased $X_{Di}^{Pc}$ by 0.002 step by step. The compositions of the other two phases and pressure were calculated at each step. Reference 14 reported that the maximum FeSiO$_3$ solubility in bridgmanite is 0.093 at 1,700 K. The calculation was terminated when $X_{Di}^{Pc}$ reached this value. It is noted that ref. 14 claimed that they conducted their experiments at a pressure of 26 GPa. However, we consider that they underestimated their pressure values because (1) they did not sample pressure only at ambient temperature and (2) they extrapolated the pressure values from data points below 22.5 GPa. Since it is unknown at what pressure they conducted their runs, we assume that their pressure would have been also 24 GPa.

The errors in these calculations were evaluated from the errors in published thermochromical data, which are also shown in Supplementary Table 2, based on the law of propagation of errors. We estimated the pressure intervals at a bulk composition of $(\text{Mg}_0.85\text{Fe}_{0.15})_2\text{SiO}_3$ and temperatures of 1,700 and 2,000 K to be $0.012 \pm 0.008$ and $0.003 \pm 0.002$ GPa, respectively.

Effect of geotherm on discontinuity thickness. If the geotherm is nearly isothermal around the phase boundary ($G_i$ in Fig. 3), the PSP transition occurs over a narrow interval of $D_i$. However, if the geotherm is adiabatic, temperatures in the Rw region should be higher than in the Brg–Ppc region because of the endothermicity of the PSP transition. As a result, the geotherms in the Rw and Brg–Ppc regions intersect at points A and B; therefore, the PSP transition occurs over an interval of $D_i$, which is called the Verhoogen effect. If the flow is very slow, and the temperature profile is diffused as the geotherms $G_i$ and $G_i$ in Fig. 3, the intervals $D_i$ and $D_i$ will be between $D_i$ and $D_i$ (ref. 14).

Estimation of thickness increment due to the Verhoogen effect. Latent heat ($\Delta T_{lat}$) by the PSP transition of Rw with $f_{Pc}$ was calculated as follows. If a phase transition occurs at adiabatic conditions, the geotherm is delocated along an equilibrium phase boundary because of latent heat associated with the phase transition. The temperature change by the latent heat ($\Delta T_{lat}$) is calculated from:

$$\Delta T_{lat} = \frac{T \Delta V (dP/dT)}{C_P}$$

where $T$ is temperature, $\Delta V = \left( V_{Brg} - V_{Ppc} - V_{Pc} \right) + \left( V_{Brg} - V_{Ppc} - V_{Pc} \right)$, and $P$ and $T$ were 23.4 GPa and 2,000 K, respectively. Our calculation shows the $\Delta T_{lat}$ was 30–90 K, leading to the thickness increment due to the Verhoogen effect being 0.03–0.27 GPa. Thus, we obtained the maximum thickness increase of $6.7$ km.

Data availability
Details of the cell assembly used, representative X-ray diffraction patterns, a backscattered electron image of MgSiO$_3$ recovered sample, parameters for the thermodynamic calculations and supplementary discussion of thermodynamic calculations regarding the effects of secondary components can be found in the Supplementary Information. Any additional data can be requested by e-mailing the corresponding author.

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