Mineralogical effects on the detectability of the postperovskite boundary

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The discovery of a phase transition in Mg-silicate perovskite (Pv) to postperovskite (pPv) at lowestmantle pressure-temperature (P–T) conditions may provide an explanation for the discontinuous increase in shear wave velocity found in some regions at a depth range of 200 to 400 km above the core-mantle boundary, hereafter the D” discontinuity. However, recent studies on binary and ternary systems showed that reasonable contents of Fe2+ and Al for pyrolite increase the thickness (width of the mixed phase) of the Pv→pPv boundary (400–600 km) to much larger than the D” discontinuity (+70 km). These results challenge the assignment of the D” discontinuity to the Pv→pPv boundary in pyrolite (homogenized mantle composition). Furthermore, the mineralogy and composition of rocks that can host a detectable Pv→pPv boundary are still unknown. Here we report in situ measurements of the depths and thicknesses of the Pv→pPv transition in multiphase systems (San Carlos olivine, pyroilitic, and midocean ridge basaltic compositions at the P–T conditions of the lowestmantle mantle, searching for candidate rocks with a sharp Pv→pPv discontinuity. Whereas the pyroilitic mantle may not have a seismologically detectable Pv→pPv transition due to the effect of Al, harzburgitic compositions have detectable transitions due to low Al content. In contrast, Al-rich basaltic compositions may have a detectable Pv→pPv boundary due to their distinct mineralogy. Therefore, the observation of the D” discontinuity may be related to the Pv→pPv transition in the differentiated oceanic lithospheric materials transported to the lowermost mantle by subducting slabs.

The lower mantle is a multicomponent (MgO, SiO2, FeO, Al2O3, CaO, Na2O, etc.), multiphase (magnesium silicate perovskite (Pv), ferropericlase (Fp), calcium silicate perovskite (Ca-Pv), silica, calcium-ferrite-type aluminum (CF, phase, etc.) system and understanding the effects of chemistry and mineralogy on the depths and thicknesses of mantle phase boundaries is of fundamental interest. Although the discovery of the Pv→pPv transition at lowestmantle P–T conditions (1–3) has been invoked as an explanation for the D” discontinuity, the combined effect of mineralogy and chemistry remain unresolved. Some recent studies (4–14) demonstrated large effects of chemical composition on the depth and thickness of the Pv→pPv boundary. The depth range over which the Pv→pPv transition occurs in mantle-related systems is much wider (4, 5) than the seismically constrained thickness (15, 16). It also occurs close to the core-mantle boundary (CMB) (135 GPa) even at 2,500 K with a positive Clapeyron slope, making it possible that the transition may not occur at all in the hotter lowermost mantle. Although the effect of Fp on the Pv→pPv transition has been modeled (4), other mineralogical effects are not fully understood due in part to our poor understanding of Al partitioning in these systems. Direct measurements on different mantle-related compositions are critical in determining the source of the seismically detectable Pv→pPv boundary.

Here we report in situ measurements on the depth and thickness of the Pv→pPv boundary in San Carlos olivine, pyroilitic, and midocean ridge basaltic (MORB) compositions conducted in the double-sided laser-heated diamond-anvil cell at pressures up to 170 GPa and temperatures up to 3,000 K. We loaded compressible Ar or Ne as a pressure transmitting medium, which also acts as an insulation medium to reduce thermal gradients. To further decrease the radial thermal gradients, we made the size of the sample platelet comparable to the size of the laser beam focus. Samples were heated for long durations at given pressures (1–1.5 h), and the boundary was measured during compression and decompression (reversal) to reduce kinetic problems. These improvements over previous studies allow us to obtain a reliable dataset to extract chemical and mineralogical effects on the properties of the Pv→pPv boundary. The methods we used are identical to those in Catalli et al. (4), and further discussed below and in Supporting Information.

Results

Laser heating of pyroilitic material at lowestmantle pressures produces approximately 70 mol% Mg-silicate (Pv and/or pPv) and approximately 30 mol% Fp (Fig. 1A–C). Among the major oxide components, we do not include CaO in our pyroilitic starting material to avoid the diffraction peaks of Ca-Pv. Ca-Pv is not capable of influencing the depth or thickness of the Pv→pPv transition because it comprises only 5 mol% and remains chemically pure in pyroilitic according to Murakami et al. (17) (Supporting Information). Two samples of pyroilitic starting material were heated to 1,600–2,500 K at 124 and 130 GPa with the diffraction lines of Pv and Fp appearing within the first 10 min of heating (Fig. 1A). Pv remains stable up to 139 GPa at high temperature. Three pyroilitic samples were heated at 139, 145, and 165 GPa, producing Pv+pPv that remains stable throughout heating (Fig. 1B). We compressed or decompressed the samples between 130 and 158 GPa and found that Pv+pPv continues to be stable assemblage. A sixth sample heated to 2,400 K at 170 GPa crystallized pure pPv with Fp within the first 10 min of heating (Fig. 1C).

Compared with the pyroilitic sample, San Carlos olivine produces a greater amount of Fp (50 mol% Mg-silicate and 50 mol% Fp). A pressure-amorphized olivine sample heated to 2,000–3,000 K at 128–133 GPa crystallized pure Pv with Fp that remains stable throughout heating (Fig. 1D). Another sample was heated to 2,700–3,000 K at 135 GPa, producing a mixture of Pv+pPv (Fig. 1E). A third sample was heated to 2,500 K and 136 GPa, where pure Pv was synthesized and remained stable throughout heating. This sample was decompressed and heated at different pressures. The pPv→Pv boundary was inferred by the appearance of Pv lines along with the broadening and decrease in the intensity of pPv lines after decompression and heating at 117 GPa. A fourth sample was heated at approximately 3,000 K and 140 GPa, producing pure pPv. The sample was then decompressed to 123 GPa,
where an unheated sample spot was located and heated at 2,700 K, forming pure Pv together with Fp.

Based on the relative peak intensities in our diffraction patterns, electron probe microanalysis (EPMA) of the starting glass, and a previous study (18), the MORB sample should contain approximately 35 mol% Mg-silicate, approximately 35 mol% silica, approximately 20 mol% Ca-Pv, and approximately 10 mol% CF-type phase at lowermost mantle conditions (Fig. 1 G–I). Ca-Pv produces the dominant lines in the diffraction patterns of MORB at lower-mantle pressures due to its higher symmetry. Pv forms together with other phases in starting material heated to 105 GPa and 3,000 K. Pressure was then increased to 114 GPa and heated to 2,800 K, where diffractions peaks for pPv grew and coexisted with Pv, indicating the Pv $\rightarrow$ pPv + pPv boundary. A second sample was taken to 100 GPa and 2,500 K, with Pv again found to be stable without pPv. A third MORB sample produced Pv + pPv when heated at 115 GPa and 2,600 K. The sample was then decompressed to 95 GPa and 2,600 K where Pv diffraction peaks grew and the pPv phase disappeared, indicating the stability of Pv. Separate samples heated at 118 GPa and 122 GPa and 3,000 K produced Pv + pPv. Pure pPv was formed in a fresh sample at 126 GPa and 2,500 K, and remained stable throughout heating (for a detailed description on these observations refer to Supporting Information).

**Discussion**

The pressure-temperature conditions of our data points obtained through two different in situ methods are shown in Fig. 2: synthesis of stable phase assemblages (method A) from previously unheated amorphous starting materials within 20 min of heating (large circles), and (method B) from previously heated Pv, pPv, or Pv + pPv for 60–90 min of heating (triangles). Method A has been used in most pPv boundary studies, whereas no previous studies attempted method B for the multicomponent systems. Kinetic problems should be less severe from method A because the data points are obtained from a highly metastable state. Also, Soret diffusion may be less severe in the short laser heating of method A. However, laser heating of highly metastable materials in this method could result in the synthesis of a metastable phase assemblage at a local energy minimum, particularly under severe deviatoric stresses or temperature gradients. Many previous studies used a NaCl medium, which becomes much less compressible after the B1–B2 phase transition, or even no medium for pressure transmission and thermal insulation.

Although a metastable assemblage is less likely synthesized in method B where we used a crystalline phase assemblage stable in an adjacent $P - T$ field as a starting material, it may be more severely affected by kinetics under poor thermal insulation with insufficient heating duration. However, we measured the boundary along both the forward and reverse directions (reversal) and achieved more stable heating with thermal insulation and longer heating duration, which is important to reduce the kinetic issues.

Although we made efforts to reduce the experimental issues in the laser-heated diamond-anvil cell (e.g., deviatoric stresses, thermal gradients, Soret diffusion, and kinetics), problems may still exist and could introduce some error in our data points. Therefore, it is important to examine the severity of those issues. Comparison of the boundary determination results from methods A and B, which are complementary to each other, should provide an important test. As shown in Fig. 2, these two methods yield consistent depths and thicknesses of the phase boundaries within approximately 10 GPa.

Our reversal measurements (Supporting Information) also provide an estimate for kinetic effects. Difference in the boundaries determined during the forward and reverse directions is less than 8 GPa (±150 km) in these multiphase systems. Although this is larger than in the binary and ternary systems studied in Catalli et al. (4), suggesting larger kinetic effects are likely due to the sluggish redistribution of cations amongst the different phases in the multiphase systems (Supporting Information), our experiments still provide sufficient resolution for the differences in the depth and thickness of the Pv – pPv boundaries in the studied systems.

The uncertainties in pressure scales are important to consider when comparing different experimental results and for seismic applications. The uncertainty of the gold scale may be approximately 5 GPa (100 km) at the investigated $P - T$ range (Supporting Information). However, the uncertainty of the pressure difference, which is more important for the thickness and differences in transition depths between different compositions, should be less than 5 GPa.
The robust conclusions we can draw from our data considering the uncertainties are: (1) the Pv → pPv transition in a pyrolytic composition occurs deeper by 200 and 400 km than in San Carlos olivine and MORB compositions, respectively (possibly even deeper than the CMB), and (2) the Pv−pPv boundary is narrower in San Carlos olivine (<70 km) and MORB (100–300 km) compositions than pyrolite (approximately 600 km).

A calculation (4) based on an ideal solution model (19) predicted that Fe partitioning with Fp can deepen and sharpen the Pv−pPv boundary only if Fe$^{2+}$ content follows an order of Fp > pPv > Pv (20). However, other measurements suggest Fp > Pv > pPv (17), which would sharpen the boundary as well, but push the transition to shallower depths. We found that the Pv−pPv boundary in San Carlos olivine deepens by approximately 20 GPa compared to Fp-free Fe$^{2+}$-bearing samples (4) and sharpens the thickness to ≤70 km, which is in excellent agreement with the calculation and supports iron preferentially partitioning into pPv over Pv (20, 21).

Whereas both our pyrolite and San Carlos olivine have similar Fe contents and mineralogy, pyrolyte has a much thicker and deeper Pv−pPv boundary. In pyrolyte, Fe$^{2+}$-still partitions into the Fp, but the Pv−pPv system is rich in Al. Therefore, the difference in these two systems indicate that Al likely makes the two phase region much deeper and wider in pyrolyte. This interpretation helps explain the results from recent experiments (4, 5, 7, 8) and is in excellent agreement with computations (9, 10, 12, 13) on Al effects [but not all (22)] (Fig. 3 and Supporting Information). Therefore, Al appears to be the key element that determines the detectability of the Pv → pPv transition in systems without a phase that participates in Al partitioning with the Mg-silicate phases.

We find that the Pv−pPv transition in MORB is shallower and narrower than in pyrolyte, although MORB has more Al$_2$O$_3$ by a factor of 3−4. This seems to be in disagreement with some previous studies on Al-bearing binary or ternary systems (4, 5, 7, 8) (Fig. 3), but in partial agreement with the MORB study by Ohta et al. (23). Unlike pyrolyte, MORB contains separate silica phases and the CF phase that can lower the activity of Al through the partitioning into these phases. We observed that silica undergoes a gradual transition from CaCl$_2$-type to α-PbO$_2$-type at a pressure range similar to that of the Pv → pPv transition, consistent with a previous study on a similar composition (18). The Al$_2$O$_3$ content in silica increases by a factor of four at the CaCl$_2$-type to α-PbO$_2$ transition, reaching 13 wt% after the transition (18). This drastic increase in Al$_2$O$_3$ content combined with the large amount of silica in MORB would greatly affect the Pv → pPv transition. The CF phase may be a sink for both Fe and Al because it contains both FeO (10 wt%) and Al$_2$O$_3$ (37 wt%) and is a significant modal fraction (15 wt%) of MORB (18).

Previous experiments on San Carlos olivine composition (6, 24) do not constrain the thickness to a precision better than 300 km, although the data are generally in agreement with our results (Fig. 2B). A computational study (14) predicted a thickness of 100 km for San Carlos olivine composition, which is in good agreement with our result (Fig. 3B).

Two previous studies on a pyrolytic composition (17, 23) reported a much shallower and thinner Pv−pPv boundary. Although the previous studies had Ca-Pv, we did not include Ca in the system for unambiguous phase identification (Supporting Information). The presence of Ca-Pv in Ohta et al. (23) is unlikely the source of the discrepancy because of the low modal fraction of Ca-Pv and undetectably low amount of Al$_2$O$_3$ in Ca-Pv in their samples (17, 23). A modal calculation based on the reported composition indicates that our Al$_2$O$_3$ content is slightly higher (by a factor of 1.2) in the Pv−pPv system than Ohta et al. (23). However, we do not believe this slight difference can explain the factor of five smaller thickness reported in (17, 23).

Although it is difficult to understand the source of the discrepancy, there are a few important differences to consider. We use noble gas pressure medium instead of NaCl or no pressure medium, conduct forward and reverse measurements, use anhydrous starting materials, and present results from both long and short heating durations. A small amount of sodium or water (if present) may stabilize pPv as previously suggested (9, 18) (Supporting Information). However, as discussed above, our results on pyrolite are much more consistent with most of the existing experi-

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**Figure 2.** The pressure-temperature conditions for the stability of Pv, Pv + pPv, and pPv in (A) calcium-free pyrolitic, (B) San Carlos olivine, and (C) MORB compositions. The right- and left-pointing triangles represent data points measured along the forward and reverse paths, respectively, and the large circles represent the data points obtained directly from heating of amorphous starting materials. Blue, green, and red triangles represent observations of Pv, Pv + pPv, and pPv, respectively. The solid black lines are the phase boundaries determined from our data. The Clapeyron slope of the boundary was obtained from Catalli et al. (4) (Supporting Information). The black symbols are the data points from previous studies in related compositions (6, 18, 23). Error bars are ±1σ uncertainties.

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**Supporting Information.**
mental and computational results regarding the effects of Al and Fe (Fig. 3).

Our results on San Carlos olivine can be extrapolated to olivine-rich rocks such as harzburgite (4, 19). In the lower-mantle, harzburgite has slightly less Fp (40 mol%) and slightly more Al₂O₃ (≤1 wt%) than San Carlos olivine. The pPv transition in harzburgite can be calculated (4) and should begin at a pressure between 125 and 130 GPa, with a thickness between 0 and 7 GPa (Fig. 3C). Therefore, the Pᵥ − pPv boundary in harzburgite should be seismically detectable. The depth and thickness of the Pᵥ − pPv boundary in harzburgite and MORB are in better agreement with the D' discontinuity (200–400 km above the CMB) than pyrolite. In addition, given that the pressure at the CMB is 135 GPa and the gold scale we used is unlikely to overestimate pressure (Supporting Information), our results suggest that the Pᵥ − pPv transition may not occur in the pyrolitic mantle (or at least will be undetectable due to the thickness), whereas it likely occurs in mantle regions rich in differentiated subducted lithosphere materials, such as MORB or harzburgite (Fig. 3C).

Our results show that mineralogical effects play a critical role for the detectability of the Pᵥ − pPv boundary. In rocks with intermediate amounts of Al, where Al all exists in Pᵥ or pPv such as pyrolite (3–5 wt% Al₂O₃), the transition may occur at higher pressures than the CMB with a mixed phase region too wide for seismic detection due to the lack of a mineral phase that can reduce the effects of Al. Aluminum-depleted and Fp-enriched rocks, such as harzburgite, will have a detectable Pᵥ − pPv boundary. Although MORB contains much more Al, it has a narrower boundary than pyrolite due to the existence of phases that help mitigate its effects. The Pᵥ − pPv boundary in MORB may be seismologically detectable, if lattice preferred orientation (25) and/or nonlinearity in the phase fraction (4, 19) can further decrease the seismic thickness of the boundary. Although global coverage is sparse, large regions of robust lateral extension of the D’ discontinuity have been documented in the lowermost mantle beneath the Circum-Pacific (26, 27). If subducting slabs are eventually deposited at the base of the mantle (27, 28), these areas likely have subducted materials containing harzburgite and MORB.

Geochemical studies have shown that the mantle contains significant amounts of basaltic crustal materials (29) and refractory residues of melt extraction (30). Recent petrologic evidence also suggests deep subduction of ocean crust (31). In solid mantle materials, chemical diffusion is limited to a few meters even over billion year time scales (32–34), preserving chemical heterogeneities in the deep mantle. A recent dynamic simulation (35) demonstrated that although differentiated rocks represent a small fraction of subducted material, preferential deposition can occur in the CMB region if they have sufficiently higher density than pyrolite. Over geologic time scales this could result in these rocks becoming the dominant type in the region. According to our results, the observation of the D’ discontinuity resulting from the Pᵥ → pPv transition may indicate the presence of significant amounts of differentiated materials transported from the shallow mantle into the CMB by subducting slabs. Because the lowermost mantle is believed to be the source region of mantle plumes and the graveyard of subducting slabs, our results may have broad implications for the scale of mantle mixing, the nature of seismic heterogeneities, the source of hot spot volcanism, and the cycling of elements through the Earth’s mantle.

Materials and Methods

The starting materials were a natural San Carlos olivine with a composition of (Mg₉₀Fe₈₀Fe₉₄)₉₀SiO₄ and synthetic glasses with composition given in the Supporting Information. The glass starting materials were synthesized from oxide starting mixtures by the containerless method under reducing conditions to prevent iron oxidation (36). The starting materials were powdered and mixed with 10 wt% gold, used as a pressure calibrant and laser absorber. A prepressed sample + gold platelet was placed in a 35, 50, or 90 μm hole drilled into a preindentation diamond gasket using beveled diamond anvils with 75, 100, or 150 μm culets in symmetric type diamond-anvil cells, respectively. The sample platelet was separated from the diamond anvils by a few micrometer-sized grains of the sample material to allow the pressure medium (argon or neon) to flow around the sample and insulate it from the diamonds during laser heating (Supporting Information). Argon was cryogenically loaded as the pressure medium and thermal insulation, except for four MORB samples where neon was used. The pressure loading was performed at GeoSoilEnviro Center for Advanced Radiation Sources (GSECARS). The neon-loaded samples also had a approximately 5 μm ruby sphere placed at the edge of the sample chamber, well separated from the sample platelet, for pressure determination during gas loading. During X-ray diffraction measurements, pressures were determined in situ from the equation of state of gold (37). We note that the sample setup used in this study is identical to that in our previous study on mantle-related binary and ternary systems (4), facilitating an internally consistent comparison among our six different datasets on the thickness and depth of the Pᵥ − pPv boundary.
X-ray diffraction patterns were collected at beamline 13-ID-D of the GSECARS sector of the Advanced Photon Source (APS). A total of six, four, and six different samples were prepared for pyrolytic, San Carlos olivine, and MORB starting materials, respectively. The starting materials were taken up to target pressures and then heated using the double-sided, flat-top laser heating system while simultaneously collecting diffraction patterns every 2–3 min during the heating cycle (38). Gray body radiation from both sides of the sample was collected for temperature estimation. Laser heating was performed between 1,500 K and 3,000 K in cycles of approximately 30 min to prevent overheating of the diamond-anvil cell. The sample was heated for 1–1.5 h at a given starting pressure before it was determined that the sample was well crystallized and likely in the equilibrium phase assemblage. Approximate modal abundances were determined using the starting oxide composition determined by EPMA. All diffraction patterns show clear diffraction intensities from the pressure medium, ensuring quasi-hydrostaticity and good insulation between the sample plateau and the diamond anvils (Fig. 1). Diffraction images were integrated to produce diffraction patterns using the Fit2D program (39). The diffraction patterns were used to determine the stability fields of P, Pp, and a mixed phase (Pv + Pp).

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Supporting Information

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Materials and Methods.
For pyrolitic and midocean ridge basaltic (MORB) compositions, glass starting materials were synthesized with the levitation method (1) in a reducing atmosphere buffered by a CO/CO$_2$ gas mixture. We used renormalized oxide ratios of SiO$_2$, Al$_2$O$_3$, FeO, and MgO for the pyrolitic composition from McDonough and Sun (2). The expected amount of Al$_2$O$_3$ in Mg-silicate (perovskite, P$v$) or postperovskite (pP$v$) for our pyrolitic sample remains the same as that expected for the pyrolitic composition in McDonough and Sun (2) (5–6 wt% Al$_2$O$_3$). We do not include CaO in our pyrolitic starting material to avoid the diffraction peaks of Ca-silicate perovskite (Ca-P$v$). Ca-P$v$ comprises only 5 mol% of the phase assemblage in pyrolite, remains pure (3), and therefore does not influence the depth and thickness of the P$v$ → pP$v$ transition through element partitioning.

To maximize our ability to determine the effect of ferropericlase (Fp) and Al on the system, we use a natural San Carlos olivine, (Mg$_{0.90}$Fe$_{0.11}$)$_2$SiO$_4$. San Carlos olivine contains no Al whereas pyrolite does. San Carlos olivine composition produces 50 mol% Fp at lower-mantle pressures, whereas pyrolite produces approximately 30 mol% Fp.

For the MORB composition, we took the ratios among SiO$_2$, Al$_2$O$_3$, FeO, MgO, CaO, and Na$_2$O of normal MORB (4). For the synthesis of MORB glass, we used a mixture of synthetic oxides of SiO$_2$, Al$_2$O$_3$, FeO, and MgO, with a CaSiO$_3$ glass previously synthesized by laser levitation, and NaAlSi$_2$O$_6$, a natural Amelia albite (Mineralogical Museum at Harvard University, sample #126680). The compositions of the starting materials were determined by electron microprobe analysis at the Massachusetts Institute of Technology and those of pyrolitic and MORB glasses are presented Table S1. Due to some volatile loss during glass synthesis, the oxide ratios of the glass products are slightly different from the original mixtures. However, the difference does not exceed 1%.

Results.
Pyrolitic Composition. Two of the samples from pyrolitic starting material were heated to 2,000–2,500 K at 124 GPa and 1,600–2,600 K at 130 GPa with the diffraction lines of P$v$ and Fp appearing within the first 10 min of heating (Fig. 1A). Pressure in the sample chamber increased from approximately 130 GPa to approximately 139 GPa over 2.2 h of heating, with P$v$ stable throughout the heating and without the appearance of any diffraction lines from pP$v$.

A third sample was heated to 2,300 K at 139 GPa, producing P$v$ + pP$v$. P$v$ + pP$v$ persisted through subsequent heating of the sample with some increase in sample pressure over the 1.5 h heating duration (Fig. 1B). The sample was then compressed to approximately 150 GPa and heated between 1,750 K and 2,000 K for 1 h, with the mixed phase persisting throughout the heating cycles up to a pressure of 158 GPa. Heating of a fourth sample to 2,000–2,500 K at approximately 145 GPa produced P$v$ + pP$v$ that remained stable for 1.2 h at high temperature. This sample was decompressed and heated at approximately 2,200 K at 130 GPa for 1 hour, with the P$v$ + pP$v$ mixture persisting over the duration of the heating. Our fifth sample was heated to 1,750–2,500 K at 165 GPa, producing P$v$ + pP$v$ that remained stable throughout 2.2 h of heating. We heated a sixth sample to 2,400 K at 170 GPa for 1 h. Postperovskite crystallized within the first 10 min of heating without any diffraction lines from P$v$ (Fig. 1C).

San Carlos Olivine Composition. A pressure-amorphized San Carlos olivine sample was heated to 2,000 K at 128 GPa for 30 min, synthesizing P$v$ together with Fp. The temperature was increased to 3,000 K for another 30 min with P$v$ persisting throughout the heating cycle at 133 GPa (Fig. 1D). A second sample was laser heated between 2,700 K and 3,000 K at 135 GPa for a total of 2 h, producing a mixture of P$v$ + pP$v$ at all temperatures (Fig. 1E).

Our third sample was compressed to 135 GPa, with pure pP$v$ appearing after 30 min of heating at 2,500 K and 136 GPa. Pure pP$v$ remained after heating the sample for an additional 30 min at 2,700 K and 139 GPa. The sample was then decompressed and heated at 2,500 K and 134 GPa for 30 min with no evidence of pP$v$ → P$v$ transformation. The sample was further decompressed and heated to approximately 2,500 K at 132 GPa for 1 h, with only pP$v$ present over the heating duration. Back-transformation inferred by the appearance of P$v$ lines along with widening and lowering of intensity of pP$v$ lines occurred after a third decompression and heating to approximately 2,000 K at 117 GPa for 50 min.

The fourth sample was laser heated at approximately 3,000 K and 140 GPa for 1 h. pP$v$ was stabilized after 10 min of heating and persisted through the duration of the heating. The sample was then decompressed to 123 GPa, where an unheated sample spot was located and heated at 2,700 K for 10 min, forming pure P$v$ together with Fp, suggesting the stability of P$v$. The sample was then heated in the original spot (used to synthesize pure pP$v$) at approximately 2,500 K at 126 GPa for a total of 2 h, with a mixed P$v$ + pP$v$ phase appearing after the first hour of heating. This persistence of P$v$ + pP$v$ at this pressure–temperature condition is likely due to kinetics because synthesis directly from the glass starting material heated at similar pressure–temperature conditions produced pure P$v$.

MORB Composition. In a MORB sample heated at 105 GPa and 3,000 K, we found P$v$ forms together with other phases in 30 min, indicating this pressure–temperature range corresponds to the stability field of pure P$v$ (Fig. 1G). Another 30 min of heating at these pressure–temperature conditions confirmed the stability of P$v$. Pressure was then increased on this sample to 114 GPa and heated to 2,800 K, where diffractions peaks for the pP$v$ phase grew after 30 min and coexisted with P$v$, indicating a crossing of the P$v$ → P$v$ + pP$v$ boundary. A second sample was taken to 100 GPa and 2,500 K, and again P$v$ was found to be the stable phase, with no evidence for pP$v$ over 90 min of heating. Pressure was then increased to 105 GPa and 2,800 K, and the sample was still determined to be in the P$v$ field after 60 min of heating, confirming the stability of P$v$ at the pressure–temperature range measured from the first sample.

The third MORB sample was first heated at 115 GPa and 2,600 K, and found to be in the mixed-phase field. The sample was then decompressed to 95 GPa and 2,600 K where P$v$ diffraction peaks grew and the pP$v$ phase disappeared, indicating the stability of P$v$. Separate samples were also first synthesized at 118 GPa and 122 GPa and 3,000 K, producing mixed phases over a total of 120 min and 90 min of heating, respectively (Fig. 1H).

In a fresh sample, at 126 GPa and 2,500 K, pure pP$v$ was synthesized after 10 min of heating and then remained stable throughout a total of 90 min of heating (Fig. 1I). After decreasing pressure slightly, and heating the sample to 2,500–3,000 K, pP$v$ remained the stable phase. Pressure was then further decreased and then heated at 95 GPa and 2,700 K where P$v$ was found to be stable after 30 min of heating.
Although it is difficult to extract unit cell volume from the α-
PhO2 phase of SiO2 due to peak overlap, we were able to deter-
mine unit cell parameters at 108 GPa and 117 GPa based on 6–8 dif-
fraction peaks. The unit cell parameters at 108 GPa are 3.79(3) Å, 4.71(2) Å, 4.22(4) Å, with a volume of 75.24(5) Å³, and at 117 GPa are 3.76(3) Å, 4.71(4) Å, 4.20(3) Å with a volume of 74.36(6) Å³.

Sources of Uncertainty in the Measurements.
Accurate data analysis requires understanding the sources of er-
ror and making an effort to reduce them. The diamond-anvil cell
is a uniaxial device that can generate large deviatoric stress that
must be reduced for phase relation studies for the mantle. In this
study, we use Ar or Ne as a pressure transmitting medium, which
are compressible and chemically inert. Our pressure transmitting
media also act as thermal insulation for the sample. We observed
intense diffraction peaks from the media in all experiments,
indicating sufficient insulation separating the sample from the
diamond anvils (Fig. 1). This is important because diamond is
an excellent heat conductor, resulting in large thermal gradients
in the sample if it is not properly insulated. To further reduce the
thermal gradients along the radial directions, we made the size of
the sample platelet comparable to the size of laser beam focus, as
we also did in our binary and ternary study (5). We are not able to
quantify the amount of Soret diffusion in our samples because
they are loaded with noble gas and are difficult to recover upon
decompression. Results from previous studies using solid pres-
sure media indicate some chemical segregation, especially to-
wards the edges of the sample (6, 7). However, the effect has not
been quantified using argon pressure media, which may be a good
thermal insulator and is chemically inert.

In this study we crossed the boundary along both forward and
reverse directions, similar to our previous study (5). This is
particularly important to estimate the effects of kinetics on the
determined boundary thickness and depth. As shown in Fig. 2,
a few data points measured from a previously synthesized Pv +
pPv mixture persisted even at the pressure-temperature condi-
tions where pure Pv should be stable according to the data points
obtained from fresh starting materials, such as a data point in the
pyrolitic composition at 130 GPa and 2,200 K, and a data point
in the San Carlos olivine composition at 126 GPa and 2,500 K.
The offset in pressure for these data points from the general
trend is larger (8 GPa) than our measurements on the binary
and ternary systems (5), indicating that the kinetic effects are lar-
ger in the multiphase systems presented here. Although kinetics
of the Pv → pPv transition and partitioning of elements between
Pv and pPv are the main sources of uncertainty in the binary and
ternary systems, kinetics of element partitioning among Pv, pPv,
and the other coexisting phases that do not participate in the
phase transition (such as Fp, silica, and calcium ferrite-type
phase) is an important additional source in multiphase systems.

In MORB, because of the relatively small proportion of Mg-silicate (approximately 35 mol%) and its weak scattering, it
can be difficult to distinguish between samples that are in the
mixed-phase region but near the phase boundary where the frac-
tion of one phase relative to the other may be very high from
those in the pure field. This contributes to the error in the loca-
tion of the boundaries particularly in MORB.

Consideration of the uncertainties in pressure scales is impor-
tant for comparison among different experimental results and
with seismic observations. Although much effort has been made (8), significant uncertainties still exist in the thermal equations of
state of pressure standard materials at pressures over 100 GPa.
The majority of data points, including both the previous work of
other researchers and our studies in Fig. 2, are based on the gold
pressure scale. Ohta et al. (9) used a gold scale calibrated to MgO
(10) that estimates pressure about 5 GPa higher than the pressure
scale (11) used in our study. However, the existing data are not
sufficient to validate the accuracy as an absolute pressure scale
(12). Considering the discrepancy among recent studies on the
gold scale (11, 12), it is reasonable to assume that the gold scale
has an uncertainty of about 5 GPa (100 km) at pressures greater
than 100 GPa and 2,000 K.

We note that using these same techniques, we have so far in-
vestigated a total of six different systems for the depth and thick-
ness of the Pv → pPv transition, together with Catalli et al. (5).
Our methods have identified sharp boundaries (0–100 km) in
two different systems (San Carlos olivine and MgSiO3·Fe2O3),
a narrow boundary (100–300 km) in MORB, and broad
boundaries in three different systems (pyrolite, MgSiO3·Fe2O3,
and MgSiO3-Al2O3·Fe2O3), demonstrating that the method is capa-
bile of measuring a wide range of thicknesses.

Unidentified Diffraction Lines.
A few diffraction peaks in Fig. 1 were not attributable to any of
the expected phases. In pyrolite, one diffraction line at approxi-
mately 0.6 Å⁻¹ appears in the pure Pv diffraction pattern
(Fig. 1A). The unidentified peak is in all the diffraction patterns
of Pv but consists of only a few spots instead of a complete ring.

Three unidentified peaks appear in mixed-phase diffraction
patterns in the San Carlos olivine composition (Fig. 1E) at ap-
proximately 0.62 Å⁻¹, approximately 0.67 Å⁻¹, and approxi-
ately 0.73 Å⁻¹. The diffraction line at 0.67 Å⁻¹ is spotty and
not in all diffraction patterns, and the line at 0.73 Å⁻¹ is also
spotty as well. The unidentified lines are unique to the San Carlos
olivine sample and do not occur in other samples. It is possible
that these peaks are from some impurity phases in our natural
San Carlos olivine starting material. The observation of the
stishovite line in one of San Carlos olivine composition may be
due to quartz impurity in the natural sample. One unidentified
peak appears in the pure pPv diffraction patterns (Fig. 1F) at
approximately 0.63 Å⁻¹ in San Carlos olivine. This line does
occasionally appear in some mixed-phase diffraction patterns in
pyrolite and in pure pPv diffraction patterns in MORB. The un-
identified peaks in diffraction patterns with pPv could potentially
be from structural polymorphism as described in refs. 13 and 14.

In the MORB diffraction patterns, an unknown line appears
near approximately 0.36 Å⁻¹, at slightly higher d-spacing than
the 110 line of the CaCl2 phase of silica (Figs. 1 G and I). This
line consistently shows up in the diffraction patterns, independent
of the phase diagram of Pv and pPv, but always in the presence
of the CaCl2 phase. The morphology of the line in the 2D diffraction
image as well as it only being present with CaCl2, suggests that it
is likely associated with the silica phase.

Clapeyron Slope of the Pv → pPv Boundary.
The Pv – Pv + pPv boundary in the pyrolitic composition has en-
ough data coverage to estimate a Clapeyron slope of
5.6 ± 0.8 MPa/K, consistent with estimates (6.7 ± 0.5 MPa/K)
in ref. 5. Therefore, the Clapeyron slope from ref. 5 is used for
the boundaries in Fig. 2.

Effects of Al.
A computation by Tsuchiya and Tsuchiya (15) proposed that Al
decreases the depth of the Pv → pPv transition and does not in-
dcrease the thickness (Fig. 3B). However, this study assumed dif-
ferent structural effects of Al from other computational studies,
which remains to be investigated by experiments.

Effects of Fe³⁺.
Our measurements on the Pv – pPv boundary in MgSiO3-
Al2O3·Fe2O3 ternary system give a shallower boundary than
other studies on Al-bearing systems (5). However, this is likely
due to Fe2O3, which decreases the depth and thickness of the

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Pv−pPv boundary according to our results on the MgSiO$_3$-Fe$_2$O$_3$ binary system (5).

**Discrepancy with Previous Studies on Pyrolite.**

Previous studies on a pyrolitic composition (3, 9) reported a much shallower and thinner Pv−pPv boundary. A slightly shallower and thinner boundary is expected because they used KLB-1 peridotite composition with about 1 wt% less Al$_2$O$_3$ than this study. However, the discrepancy cannot be entirely attributable to the slight compositional differences. They used a different gold scale however, the discrepancy cannot be entirely attributable to the slight compositional differences. They used a different gold scale. However, the discrepancy cannot be entirely attributable to the slight compositional differences. They used a different gold scale.

A more recent study on a pyrolitic composition (17) reported pure pPv after heating to approximately 2,400 K at 135 GPa. However, the pressure was measured after laser heating. This study used silica as a pressure transmitting medium, which may support larger deviatoric stresses and elevate silica activity in the system. Therefore, it is difficult to compare with our results.

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**Table S1. Chemical compositions of glass starting materials for Ca-free pyrolite and MORB (in oxide wt%).**

<table>
<thead>
<tr>
<th></th>
<th>Pyrolite</th>
<th>MORB</th>
</tr>
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<tbody>
<tr>
<td>SiO$_2$</td>
<td>45.6</td>
<td>49.6</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>4.9</td>
<td>16.6</td>
</tr>
<tr>
<td>FeO</td>
<td>8.7</td>
<td>7.9</td>
</tr>
<tr>
<td>MgO</td>
<td>40.8</td>
<td>9.7</td>
</tr>
<tr>
<td>CaO</td>
<td>-</td>
<td>13.4</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>-</td>
<td>2.8</td>
</tr>
</tbody>
</table>

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