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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 lowest mantle 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 region) 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 multi-phase systems (San Carlos olivine, pyrolitic, and midocean ridge basaltic compositions) at the P – T conditions of the lowest mantle, searching for candidate rocks with a sharp Pv – pPv discontinuity. Whereas the pyrolitic mantle may not have a seismologically detectable Pb – 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 lithosphere 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 aluminium (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 lowest mantle 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, pyrolite, 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 Catali et al. (4), and further discussed below and in Supporting Information.

Results

Laser heating of pyrolitic material at lowest mantle pressures produces approximately 70 mol% Mg-silicate (Pv and/or pPv) and approximately 30 mol% Fp (Fig. 1 A–C). Among the major oxide components, we do not include CaO in our pyrolitic 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 pyrolite according to Murakami et al. (17) (Supporting Information). Two samples of pyrolitic 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 pyrolite 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 pyrolitic 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 Pfp 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 Pfp + pPv (Fig. 1E). A third sample was heated to 2,500 K and 136 GPa, where pure Pfp was synthesized and remained stable throughout heating. This sample was decompressed and heated at different pressures. The Pfp → Ppv 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,
Intensities are plotted as a function of inverse interplanar distance.

Medium (Ar or Ne), and nitrogen (N). A few unidentified lines are noted by internal pressure calibrant (Au), rhenium gasket (Re), argon or neon pressure with cross), CF phase (open up triangle), Ca-Pv (open down triangle), the gold type phase at lowermost mantle conditions (Fig. 1). Approximately 20 mol% Ca-Pv, and approximately 10 mol% CF-phases were found to be stable without pPv. A third MORB sample produced pPv when heated at 115 GPa and 2,600 K. The sample was then decompressed to 95 GPa and 2,600 K where diffraction peaks grew and the pPv phase disappeared, indicating the stability of P. Separate samples heated to 118 GPa and 122 GPa and 3,000 K produced P + 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 heated amorphous starting materials within 20 min of heating (large circles), and (method B) from previously heated P, pPv, or P + 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 Cataill 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 P – pPv boundaries in the studied systems.

The uncertainties in pressure scales are important to consider for comparison between 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.

Fig. 1. X-ray diffraction patterns of (A–C) Ca-free pyrolitic, (D–F) San Carlos olivine, and (G–I) MORB compositions measured at high pressure and temperature. The major peaks are indicated for (A) pyrolite (blue circles), pPv (red circles), Fp (open circles), CaCl2-type silica (open square), α-PbO2 type silica (square with cross), Ca-Pv (open down triangle), the gold internal pressure calibrant (Au), rhenium gasket (Re), argon or neon pressure medium (Ar or Ne), and nitrogen (N). A few unidentified lines are noted by *" (Supporting Information). Backgrounds were subtracted. The diffraction intensities are plotted as a function of inverse interplanar distance.

where an unheated sample spot was located and heated at 2,700 K, forming pure P 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. P 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 P, indicating the P → P + pPv boundary. A second sample was taken to 100 GPa and 2,500 K, with P again found to be stable without pPv. A third MORB sample produced P + pPv when heated at 115 GPa and 2,600 K. The sample was then decompressed to 95 GPa and 2,600 K where P diffraction peaks grew and the P + pPv phase disappeared, indicating the stability of P. Separate samples heated at 118 GPa and 122 GPa and 3,000 K produced P + 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.
The uncertainties are: (1) the PV transition in a pyroclastic 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 > PV > pPv (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, pyrolite has a much thicker and deeper PV–pPv boundary. In pyrolite, Fe$^{2+}$ still partitions into the Fp, but the PV–pPv system is rich in Al. Therefore, the difference in these two systems indicates that Al likely makes the two phase region much deeper and wider in pyrolite. 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 pyrolite, 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. 3A), but in partial agreement with the MORB study by Ohta et al. (23). Unlike pyrolite, 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 pyroclastic 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 in 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 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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**Fig. 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 calculated 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 ±1 uncertainties.
Pressure (is 135 GPa and the gold scale we used is unlikely to overestimate than pyrolite. In addition, given that the pressure at the CMB lithosphere materials, such as MORB or harzburgite (Fig. 3 likely occurs in mantle regions rich in differentiated subducted (at least will be undetectable due to the thickness), whereas it Pv → smaller, because it relies on difference in pressure within the same scale. Fig. 2. The error bar in (pressures than the CMB with a mixed phase region too wide for 2278 ∣ vine-rich rocks such as harzburgite (4, 19). In the lower-mantle, 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 all Al 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 (Mg₀.₈₈Fe₀.₁₁)₂SiO₄ 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 preindented rhenium 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 micron-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 loaded using the gas-loading system 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 pyrolic, 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. 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 platelet 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 Fe, pMg, and a mixed phase (pMg + pFe).

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