A phase transition of MgSiO$_3$ perovskite, the most abundant component of the lower mantle, to a higher-pressure form called post-perovskite was recently discovered for pressure and temperature conditions in the vicinity of the Earth’s core–mantle boundary. This discovery has profound implications for the chemical, thermal, and dynamical structure of the lowermost mantle (called the D” region). Several major seismological characteristics of the D” region can now be explained by the presence of post-perovskite, and the specific properties of the phase transition provide the first direct constraints on absolute temperature and temperature gradients in the lowermost mantle. Here we discuss the current understanding of the core–mantle boundary region.

KEYWORDS: post-perovskite, phase transition, D” layer, seismic discontinuity

INTRODUCTION

Large anomalies in seismic wave velocities have long been observed in the deepest several hundred kilometers of the mantle (the D” region) (see Lay and Garnero 2007) (FIG. 1). Since these anomalies were difficult to account for with the known properties of the primary phase in the lower mantle, MgSiO$_3$ perovskite, the D” region has remained enigmatic. The existence of a phase transition in this region has been a subject of conjecture (e.g. Sidorin et al. 1999), but only recently has a major mantle constituent been shown to undergo a phase transition at pressure and temperature (P–T) conditions corresponding to the D” region. A phase transition from MgSiO$_3$ perovskite to a higher-pressure structure called post-perovskite was experimentally discovered in 2004 (Murakami et al. 2004). Rapid developments in experimental and theoretical mineral physics, seismology, and geodynamics have ensued, resulting in significant progress in our understanding of the lowermost mantle. Several long-term enigmas may be reconciled by the properties of this new phase, including the presence of an abrupt seismic velocity increase at the top of D” (the D” discontinuity), seismic anisotropy in the D” region, and anticorrelation between anomalies in S-wave and bulk-sound velocities (a hypothetical wave velocity calculated from the P- and S-wave velocities).

By virtue of its location, the D” region is a thermal, chemical, and mechanical boundary layer separating the liquid iron core from the rocky silicate mantle. Strong radial and lateral temperature gradients caused by heat flowing upward from

DISCOVERY OF THE POST-PEROVSKITE PHASE TRANSITION

For several decades, MgSiO$_3$ perovskite has been recognized as a principal constituent of the upper part of the lower mantle, but its stability and the possible occurrence of phase transitions at greater depth have remained uncertain. The properties of perovskite experimentally constrained at pressures less than 50–80 GPa have been extrapolated over great depth ranges to the CMB in order to interpret seismological observations of the D” region. At the Earth’s CMB, P–T conditions are 135 GPa and 3500–4000 K. Recent developments
at synchrotron radiation facilities, combined with advances in laser-heated diamond anvil cell (LHDAC) techniques, have enabled the generation of such high P-T conditions and the acquisition of in-situ X-ray diffraction (XRD) data necessary for the experimental investigation of perovskite under lowermost mantle conditions.

A phase transition to MgSiO$_3$ post-perovskite was discovered through a significant change in the XRD pattern (Fig. 2) (Murakami et al. 2004), with thirteen new peaks appearing when perovskite samples were heated to 2500 K above 125 GPa. Its crystal structure was determined with the aid of computer simulations of atomic positions using this XRD pattern. Post-perovskite has orthorhombic symmetry (space group: Cmcm) with a sheet-stacking structure along the b-axis (Fig. 3). It is isostructural with UFeS$_3$ and CaIrO$_3$, which are mineral forms stable under ambient conditions. The Mg$^{2+}$ site in post-perovskite is smaller than in perovskite, resulting in a volume reduction of 1.0–1.5%. A post-perovskite phase transition has now been reported in pyrolite (a supposed typical bulk silicate mantle composition) and mid-ocean ridge basalt (MORB) compositions when subjected to the lowermost mantle conditions (Ohta et al. 2008).

The transition was confirmed by ab initio calculations (calculations that do not depend on any experimental results) (Tsuchiya et al. 2004; Itaka et al. 2004; Oganov and Ono 2004) soon after the experimental discovery. Theory has also played an important role in determining the elasticity of post-perovskite, especially because experimental determinations remain very challenging. The elastic constants calculated for T = 0 K by several different groups are consistent with each other. However, some inconsistencies are found in estimates of the high-temperature elasticity of post-perovskite (Wentzcovitch et al. 2006; Stackhouse and Brodholt 2007). This complicates the interpretation of seismic velocity jumps and seismic anisotropy with lattice preferred orientation (LPO) (i.e. the crystallographic direction of a mineral is not random in the rock) of post-perovskite.

**POST-PEROVSKITE PHASE TRANSITION IN THE LOWERMOST MANTLE**

The experimentally determined MgSiO$_3$ post-perovskite transition boundary is located at 119 GPa and 2400 K, when using the most reliable MgO pressure scale (Hirose et al. 2006) (Fig. 4). Theory first demonstrated that this transition has a large positive Clapeyron slope (pressure/temperature slope of the phase boundary) of +7.5 to +10 MPa/K (Tsuchiya et al. 2004; Oganov and Ono 2004). Experiments show a slope of +11.5 ± 3 MPa/K (Fig. 4). Phase relations in a pyrolitic sample have been also determined up to CMB conditions (Ohta et al. 2008). Al-bearing (Mg,Fe)SiO$_3$ perovskite transforms to post-perovskite between 116 and 121 GPa (2550 to 2640 km deep) at a temperature of 2500 K on the basis of the MgO scale. The pyrolitic sample at lowermost mantle

![Figure 2](https://example.com/figure2.png)  
**Figure 2** XRD patterns of (A) MgSiO$_3$ perovskite and (B) post-perovskite (after Murakami et al. 2004). P, perovskite; Pt, platinum; N, new phase (post-perovskite). In (B), the powder XRD pattern of post-perovskite simulated by molecular dynamics (MD) calculations, and the peak positions of MgO and SiO$_2$ (both α- PbO$_2$-type and CaCl$_2$-type structures) are shown.

![Figure 3](https://example.com/figure3.png)  
**Figure 3** Crystal structure of the post-perovskite phase projected along (A) (001), (B) (100), and (C) (010) directions, and (D) a stereoscopic view showing the layer-stacking structure (after Murakami et al. 2004). Coordination polyhedra of oxygen atoms around Si atoms are shown as octahedra, and the Mg$^{2+}$ ions are shown as spheres. The lines indicate the unit cell. Note that the octahedral sheets are stacked along the b-axis with interlayer Mg$^{2+}$ ions.
conditions consists of approximately 72% post-perovskite, 21% ferropericlase, and 7% CaSiO₃ perovskite by weight. Al-bearing (Mg,Fe)SiO₃ perovskite is also the most abundant phase in a MORB composition above 26 GPa, coexisting with an SiO₂ phase, CaSiO₃ perovskite, and Ca-ferrite-type Al-phase (e.g. Hirose et al. 2005). The perovskite to post-perovskite phase transition takes place in MORB between 112 and 118 GPa at 2500 K (Ohta et al. 2008), lower by 3 to 4 GPa than for a pyrolitic mantle composition. The SiO₂ phase transition from CaCl₂-type to -PbO₂-type structure also occurs at very similar pressures in MORB.

**IMPLICATIONS FOR SEISMOLOGY**

**Origin of the D″ Discontinuity**

Observations of seismic wave velocity discontinuities in the lowermost mantle have been reported for decades (see Lay and Garnero 2007 for a review). The most robust observations involve an S-wave velocity increase of 2–3% in the depth range 2550–2700 km (116–125 GPa) (Lay and Helmberger 1983), which has become known as the D″ discontinuity. Corresponding increases in P-wave velocity of 0.5–3% have been observed intermittently, coinciding in a few locations with S-wave velocity increases; however, some locations have no detectable P- or S-wave velocity increase. Abrupt P- and S-wave velocity reductions are also observed at various depths above the CMB. Overall, there is no single characterization of D″ velocity structure that holds on a global scale.

The D″ velocity increases have been interpreted as the effect of thermal or chemical anomalies (e.g. Wyssession et al. 1998), or of an unspecified phase change (e.g. Sidorin et al. 1999). The discovery of post-perovskite provides the first specific explanation for the D″ discontinuity and establishes an entirely new basis for quantifying thermal and petrological variations in the lowermost mantle by interpreting seismic observations in terms of independently constrained attributes of the phase change. Most importantly, it provides a thermometer indicating the absolute temperature at the depth of an observed discontinuity (Fig. 5). However, the structure in the lowermost mantle is heterogeneous, and post-perovskite may exist only in localized regions where the temperatures are relatively low, or it may be widespread but strongly affected by thermal and chemical heterogeneity.

The large positive Clapeyron slope of the phase transition should result in thermally modulated depths of the velocity discontinuity in the lower mantle. This expectation can generally be reconciled with observed large-scale variations in the depth of the D″ discontinuity: regions of higher than average shear velocities above and within D″ (presumably relatively low temperature) tend to have somewhat shallower D″ discontinuities than regions of lower than average shear velocity (presumably higher temperature) (e.g. Sidorin et al. 1999). If the Clapeyron slope of the phase transition is well determined and the causal connection to the D″ discontinuity is accepted (Fig. 5), observed topography of the discontinuity on all scales can be used to determine lateral temperature variations in the lowermost mantle, as is done for the transition zone discontinuities.

The large-scale patterns of velocity heterogeneity in the deep mantle involve S-wave velocity variations of ±5% and P-wave velocity variations of ±2–3%, and are often attributed to cooler regions where oceanic slab is descending in subduction zones. These patterns circumscribe two large low-shear-velocity provinces (LLSVPs) beneath the central Pacific and Africa that may be associated with upwellings. Given the strong decrease in the thermal expansion coefficient with pressure expected in the lower mantle, very large temperature variations are required to account for the velocity heterogeneity if no other factors contribute. Quantifying contributions to the velocity heterogeneity from the presence of post-perovskite is thus critical to separating thermal, chemical, and phase-change contributions to the observed variations.

The elasticity parameters of MgSiO₃ perovskite and post-perovskite give estimated S-wave velocity contrasts of 1.5–4% and P-wave velocity contrasts of ±0.5% (see Lay and Garnero 2007). The predicted strength of the S-wave velocity discontinuity is similar to the observed 2–3% contrast of the D″ discontinuity. The greater size of the predicted S-wave velocity increase relative to the P-wave velocity
increase may explain why lower-mantle S-wave triplications (concentration of seismic energy due to multiple arrivals at the same distance) are more spatially extensive and readily observable than P-wave triplications (Wyssession et al. 1998). Observationally, it is very difficult to detect lower-mantle discontinuities with velocity contrasts less than ±0.5%, even when large data sets can be stacked to enhance the signal. However, the observed P-wave velocity jump in a few localized regions is as large as 3%, much greater than the mineral-physics predictions.

Assuming that the post-perovskite phase is present in at least the lowest-temperature regions of D′, the elasticity effect of the phase will combine with the thermal effect to produce high S-wave velocities unless there is a competing compositional effect. Thus, it is very important to improve constraints on the elasticity predictions for realistic compositions to isolate the thermal effect. If post-perovskite is present in only a thin layer, or not present at all, in warmer regions of D′, there is a large range of velocity variations that still has to be attributed to thermal or compositional effects. Unless partial melting occurs or very large temperature variations are present, it is likely that compositional effects play a significant role. The LLGBP regions, which have several percent lower than average S-wave velocities, are widely thought to involve compositional anomalies that may control their distinct velocities and densities. Even in these compositionally distinct regions, S-wave velocity increases several hundred kilometers above the CMB have been detected (Lay et al. 2006), which raises the possibility of post-perovskite being present even in a partially warm, low-velocity region. If the phase-boundary depth is insensitive to compositional variations (Hirose et al. 2006), either the inference of warmer temperatures in low-velocity regions is wrong (the D″ discontinuity should be much deeper than observed), or there is a distinct cause of the D″ discontinuity within the LLGBP.

Waveform modeling has shown that the D′″ velocity jump occurs over a depth extent of less than 30 km (Lay and Garners 2007). Experiments demonstrate that the post-perovskite transition occurs within a 5 GPa pressure range in a pyrolitic mantle (Ohta et al. 2008), corresponding to a lower-mantle mantle depth range of 90 km. This is much narrower than the >10 GPa width observed in the systems MgSiO 3–Al 2O 3 and MgSiO 3–FeSiO 3. However, a 5 GPa pressure interval is still larger than estimates of the sharpness of the seismic discontinuity. The discrepancy may be due to the uncertainty of pressure, typically 2 GPa, in the LHDAC experiments. Alternatively, the effective width of the transition may be much less than the two-phase coexisting region because phase proportions change nonlinearly with pressure (Stixrude 1997).

Seismic wave spreading (the procedure of shifting and summing seismograms to determine the strength of arrivals having a target phase velocity) and migration methods (the procedure involving reverse propagation of seismic waves observed at seismometers back along their paths through a velocity model for the Earth) using large data sets are beginning to resolve more-detailed velocity structures in D″. Several studies indicate the presence of an S-wave velocity decrease below the velocity increase, with about the same size of velocity jump. The depth of this feature appears anticorrelated with the depth of the velocity increase (Lay et al. 2006). The notion of a double intersection of the geotherm with the phase boundary caused by a strong temperature increase in the thermal boundary layer (a region in which heat transport is primarily by thermal conduction rather than material circulation) above the CMB with post-perovskite retransforming to perovskite at the base of the mantle (Hernlund et al. 2005) (Fig. 5) may explain this structure. In the presence of strong lateral temperature variations, this can lead to lenses of post-perovskite in D″ (Fig. 6). Using simple thermal boundary layer temperature profiles in conjunction with a specific Clapeyron slope for the post-perovskite phase transition, these depth vs. velocity increase/decrease pairs can constrain thermal models for the lowermost mantle more tightly than a single discontinuity. Lay et al. (2006) and van der Hilst et al. (2007) applied this concept to interpret seismic models under the central Pacific and Caribbean, respectively, and for a assumed thermal conductivity, they estimated local heat flux through the CMB. Improved estimates of the phase-change Clapeyron slope and thermal conductivity in both perovskite and post-perovskite for D″ conditions are needed in order to reduce uncertainty in such heat flux estimates, but this is the most direct and promising approach to constraining CMB heat flux yet developed.

### Anisotropy in D″

S-waves traverse the mid-lithosphere with little shear wave splitting (S-waves “split” into two arrivals as a consequence of propagating in an anisotropic medium; they are then comprised of two different waves, with orthogonal particle displacements, that travel at slightly different velocities). However, splitting does occur if they traverse the D″ region. It appears that the D″ layer has large-scale anisotropic structure, especially under the circum-Pacific regions, where the horizontally polarized S-wave velocity (V SH ) is faster by 1 to 3% than the vertically polarized S-wave velocity (V SV ). Since such polarization anisotropy tends to correspond to regions with a clear D″ S-wave discontinuity, the differences between the anisotropic properties of perovskite and post-perovskite are important.

Theory has shown that post-perovskite has larger single-crystal elastic anisotropy than perovskite. Acquisition of LPO by post-perovskite within D″ may be a consequence of deformation in the boundary layer above the CMB. The LPO of a mineral depends on its deformation mechanisms, particularly the slip systems. On the basis of crystal structure considerations (Fig. 3), the layering plane (010) in the post-perovskite structure has been suggested to be a dominant slip plane (Yamazaki and Karato 2007). This slip mechanism is indeed dominant for CaIrO 3 with the post-perovskite structure. This means that a lattice plane (010) would trend to be aligned parallel to horizontal shear flow in the D″ region. In this case, horizontally polarized S-waves would propagate faster by 3 to 4% than vertically polarized ones (V SV /V SH = 1.04) at T = 0 K (Itaka et al. 2004; Oganov and Ono 2004). This is consistent with the seismic observations, although a high degree of preferred orientation of post-perovskite is required. This is supported by the experimental observation that the preferred orientation is developed more strongly in CaIrO 3 post-perovskite than in perovskite (Niwa et al. 2007). It is noted, however, that the temperature effect on anisotropy is controversial. Wentzcovitch et al. (2006) calculated a large effect of temperature and argued that post-perovskite aggregates with the (010) slip plane yield S-wave polarization with V SV > V SH at high temperature for horizontal flow. In contrast, Stackhouse and Brodholt (2007) found that S-wave splitting is generally temperature independent and that the polarization expected assuming the (010) slip plane is consistent with seismic observations. Other slip mechanisms for post-perovskite have also been proposed, but they are still controversial.
**Anticorrelation between S-wave and Bulk-Sound Velocities**

Large-scale seismic tomography models show an anticorrelation between lateral anomalies in S-wave and bulk-sound velocities in the lowermost mantle (e.g. Masters et al. 2000). Since this is not caused by thermal perturbations alone, it has been argued that this is strong evidence for large-scale chemical heterogeneity in the lowermost mantle, possibly involving heterogeneities in Fe and Ca content.

Such anticorrelation, however, can be partly reconciled with the perovskite to post-perovskite phase transition. Assuming that lateral temperature variations modulate the thickness of post-perovskite material in D”, the differences in S-wave velocity and bulk-sound velocity for perovskite and post-perovskite will be manifested in the seismic velocity patterns. Theoretical calculations show that S-wave velocity is faster and bulk-sound velocity is slower in post-perovskite than in perovskite at equivalent pressure. The negative correlation between S-wave and bulk-sound velocities can thus be partially attributed to the lateral change in mineralogy between perovskite and post-perovskite, at least in regions away from LLSVPs. For the LLSVPs, which tend to dominate the global anticorrelation patterns, the S-wave velocity reductions are much stronger than P-wave velocity reductions (thus there are bulk-sound velocity increases in these regions), and the anomalous regions extend 800 to 1000 km above the core-mantle boundary, well above any likely post-perovskite domain. The absence of post-perovskite and a high-temperature anomaly cannot account for this behavior quantitatively, so some additional compositional or partial melting effect is still needed.

**SYNTHESIS OF D” REGION PROPERTIES**

As noted above, some seismological observations of D” structure may be reconciled with the recently discovered post-perovskite without the need for chemical heterogeneities. However, the D” region probably has very complex thermal and chemical structures (Fig. 6). In particular the LLSVPs appear to involve chemically distinct dense piles beneath Africa and the central Pacific. Chemical heterogeneity is a natural consequence for a thermochemical boundary. Contributions can come from deep subduction of oceanic lithosphere, partial melting, and chemical reaction with the core. Iron-rich oceanic crust subducted in early Earth history (>4 Ga) has also been proposed as a geochemically hidden reservoir in D”, although its presence and chemical composition are still highly uncertain.

**Deep Subduction of MORB Crust**

Subduction of MORB crust gives rise to strong chemical heterogeneity in the Earth’s mantle, possibly extending down to the CMB if at least some subducting slabs penetrate into the lower mantle. The thermally equilibrated subducted MORB crust is denser than the average mantle at any depth except between the 660 km boundary and 720 km depth (Hirose et al. 2005). Some MORB material from relatively warm slabs may pond in the transition zone; however, geodynamic models incorporating realistic phase changes, depth-dependent material properties, and viscosity increases in the lower mantle often display significant deep slab penetration, usually with strong slab deformation and sometimes in avalanches. In the lowermost mantle, MORB crust is denser than PREM density by about 3% (Hirose et al. 2005). Geodynamical simulations indicate that a 3% density contrast can induce a segregation of dense MORB crust from the balance of the slab at the base of the mantle, and separated MORB crust then accumulates into piles underneath lower-mantle upwellings (e.g. Christensen and Hofmann 1994). The current large-scale pattern of deep-mantle heterogeneity may thus be a natural consequence of the configuration of mantle downwellings for the past 200 Ma (McNamara and Zhong 2004). The LLSVPs plausibly represent large accumulations of dense MORB-enriched materials (Fig. 6).

**MgSiO$_3$ perovskite transforms to post-perovskite at shallower depths, by about 70 km, in a material of MORB composition than a similar phase transition in pyrolite at the same temperature (Ohta et al. 2008). If MORB has separated and accumulated into substantial piles, a phase boundary could exist laterally over a large region, and seismology may be able to detect the small velocity effect of the phase changes in MORB. The post-perovskite and SiO$_2$ phase transitions in a MORB-enriched pile could account for a shallow negative discontinuity in D” observed at the northern margin of the Pacific LLSVP (Ohta et al. 2008).**

**Partial Melting in the ULVZ**

Thin layers or mounds of strong seismic wave velocity reductions (>5% for P-wave velocity, >15% for S-wave velocity) have been detected in the ULVZ right above the CMB. It is generally believed that the ULVZ represents partially molten silicates (see review by Garnero et al. 1998), although other possibilities, such as lateral infiltration by core material and strong enrichment of Fe in post-perovskite, have been proposed (e.g. Mao et al. 2006). The ULVZ is not observed in all localities. This implies a chemically heterogeneous D” because the CMB temperature should be isothermal. Regions where the ULVZ is observed may have distinct chemical compositions with lower melting temperatures.

An extensive ULVZ is found in the Pacific LLSVP, although the correlation between ULVZ presence and a D” slow-velocity anomaly is not universal (e.g. Garnero et al. 1998). As discussed above, MORB-enriched dense materials may have accumulated in the Pacific LLSVP (Fig. 6). MORB has a lower melting temperature by several hundred degrees than pyrolite at lower-mantle pressures (Hirose et al. 1999). These observations suggest that partial melting of subducted MORB crust might be responsible for the ULVZ.
Chemical Reaction with the Outer Core

Chemical reaction between the mantle and liquid outer core may also produce chemical heterogeneities in D”. Knittle and Jeanloz (1991) suggested that the D” layer is a chemical reaction zone including SiO₂, FeO, and FeSi phases formed by reaction between (Mg,Fe)SiO₃ perovskite and molten iron. More-recent experimental study by Takafuji et al. (2005) using TEM demonstrated that these oxide and metal phases are not stable. Instead, these crystals form by quenching the (O, Si)-rich molten iron. In addition, Takafuji and coworkers suggested that the bottom of the mantle just in contact with the outer core is extremely depleted in iron (less than 1% FeO) if local equilibrium is attained between perovskite and iron-rich metal at the CMB; otherwise the outer core should contain more oxygen and silicon than required to reconcile the <10% core density deficit relative to pure iron. It has been proposed that the bottom of the mantle is enriched in iron as a result of chemical reaction with the core (e.g. Mao et al. 2006). However, the mantle-core reaction experiments suggest the opposite. Such a volume of iron-depleted mantle should be very thin, formed only at the very bottom of the mantle.

SUMMARY AND UNSOLVED PROBLEMS

Major characteristics of the D” layer may be attributed to the recently discovered MgSiO₃ post-perovskite phase. However, some features remain unexplained. The deep-mantle phase change is likely to be the origin of the D” seismic discontinuity observed at 2550 to 2700 km depth. The pressure of the post-perovskite phase transition in both MgSiO₃ end-member and pyrolite mantle composition matches the depth range of the D” discontinuity at a plausible mantle temperature of 2500 K if results obtained by using the MgO pressure scale are applied (Fig. 4). However, these experimental results include a large ambiguity in pressure determination due to uncertainty of the pressure scale. An accurate pressure scale needs to be established.

The seismically inferred S-wave velocity increase at the D” discontinuity is consistent with mineral-physics predictions for the post-perovskite phase transition, but in some regions P-wave velocity increases are larger than predicted. The sharpness of the D” discontinuity appears to be less than 30 km, which is narrower than the experimentally predicted width of a perovskite and post-perovskite two-phase field in a pyrolitic mantle composition (~90 km). The effective width of the phase transition in natural multicomponent systems needs to be further refined by experimental and theoretical mineral physics.

The onset of S-wave anisotropy at the D” discontinuity may be consistent with preferred orientation of post-perovskite. However, the slip mechanism of post-perovskite and the nature of LPO are currently controversial. In addition, inconsistencies are found in the theoretical calculations, which predict different polarizations of S-wave splitting for the same post-perovskite aggregate.

Constraining the amount and nature of chemical heterogeneities in the mantle is a key to understanding the chemical evolution of this planet. The accumulation of ancient MORB crust is one of the possible sources of chemical heterogeneity in D”. The LLSPVs in the lowermost mantle beneath Africa and Pacific appear to be dense, chemically distinct regions and may represent large accumulations of dense MORB-enriched materials. A shallow negative S-wave velocity jump in the D” layer may be due to the combined effects of post-perovskite and SiO₂ phase changes in MORB. We need to determine the high P-T elastic properties of MORB crust to further understand the nature of the LLSPV.

The origin of the ULVZ near the base of the mantle is generally attributed to partial melting. Since subducted MORB crust has a lower melting temperature than pyrolite, partially molten former basaltic crust may be responsible for the ULVZ. This is consistent with the fact that extensive ULVZ is found at the base of the Pacific LLSPV, which possibly represents a large accumulation of dense MORB-enriched materials. However, the chemical consequences of such melting process are not known. We need to obtain more data on element partitioning in the deep mantle.

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