Post-perovskite

Rocks in the Earth’s crust and mantle are composed of minerals: crystalline structures having elements in ordered lattices. For a common mineral, such as olivine \([(Mg,Fe)\text{SiO}_4]\), there is a stable crystal form that exists for the pressure and temperature conditions present near the Earth’s surface. The physical properties of a mineral like olivine are determined by its composition and crystal structure. At higher pressures and temperatures, below 410 km (255 mi) deep in the mantle, olivine is not stable in its near-surface form, and \((Mg,Fe)\text{SiO}_4\) occurs in different mineral polymorphs, with denser packing of the elements. An olivine-composition mineral form, called wadsleyite, exists below 410 km deep in the mantle. Below 520 km (320 mi) depth, there exists an even more densely packed mineral form of olivine, called ringwoodite. If an olivine-bearing rock sinks in the mantle in a subducting lithospheric plate, the olivine minerals undergo phase transitions over narrow pressure (depth) ranges, transforming from one mineral form to the next with increasing pressure and temperature conditions. At 690 km (420 mi) depth, olivine composition in the ringwoodite structure undergoes a different type of phase transition, called a disassociative transition, which forms two distinct minerals—magnesium-silicate perovskite \([(Mg,Fe)\text{SiO}_3]\) and ferropericlase \([(Mg,Fe)\text{O}]\). Rising mantle material undergoes the reverse sequence of phase transformations. At each phase transition, physical properties of the olivine-bearing rock, such as the density, bulk modulus (incompressibility), and shear modulus (rigidity), abruptly change. This causes corresponding rapid increases in elastic (seismic) wave velocities at depths of 410, 520, and 690 km.

The predominant upper-mantle minerals all transform to the remarkably stable magnesium-silicate perovskite form at lower-mantle conditions, with no further phase changes occurring over a several-thousand-kilometer depth range. Thus, \((Mg,Fe)\text{SiO}_3\) perovskite is believed to be the most abundant mineral in the Earth, making up 70–80% of the vast lower mantle. The physical properties of magnesium-silicate perovskite have been extensively studied by experiments and theory. In 2004, high-pressure experiments in Japan first demonstrated that for pressures greater than about 120 gigapascals, corresponding to depths in the lowermost mantle within a few hundred kilometers of the core–mantle boundary, magnesium-silicate perovskite undergoes a transition to a new mineral structure, assigned the inelegant name post-perovskite.

Physical properties. The phase transition from perovskite to post-perovskite does not affect mineral composition, but the post-perovskite phase is 1–1.2% denser and has higher shear modulus than perovskite. X-ray diffraction studies of experimental samples at high pressure established the existence and the change in volume of the post-perovskite phase and provided constraints on the atomic
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Fig. 1. Crystal structure change. (a) Orthorhombic structure of magnesium-silicate perovskite and (b) base-centered orthorhombic polymorph post-perovskite structure. Large spheres represent Mg ions, and octahedrals represent SiO$_6$ units. There is about a 1.0–1.5% density increase from perovskite to post-perovskite. (T. Lay et al., 2005, Reproduced by permission of American Geophysical Union)

lattice for theoretical modeling of the precise crystal structure of the mineral. Figure 1 shows the change in crystal structure from perovskite to post-perovskite, based on molecular dynamic modeling. The theoretical calculations provide many important physical characteristics of post-perovskite that have not yet been directly confirmed by experiments. This includes prediction of the slope of the phase boundary in pressure–temperature (P–T) space: the Clapeyron slope. The computed Clapeyron slope for the pure magnesium (Mg) end-member composition, MgSiO$_3$, is about 7.5 MPa/K, a rather large positive value. This indicates that the phase boundary should occur at lower pressure (shallower in the mantle) in regions that are relatively lower in temperature. Large variations in the depth of the phase transition could thus result from the strong thermal heterogeneity expected to exist in the vicinity of the thermal boundary layer in the lowermost mantle.

Numerical calculations also predict the crystal elasticity of post-perovskite at P–T conditions likely to exist in the deep mantle, providing estimates of the seismic pressure-wave (P-wave) and shear-wave (S-wave) velocities. The P-wave velocity changes little relative to that for perovskite as a result of competing effects of increasing shear modulus, increasing density, and decreasing bulk modulus; however, the S-wave velocity is about 2% faster than for perovskite. If the transition from perovskite to post-perovskite is confirmed to occur over a small pressure (depth) range, the resulting rapid increase in S-wave velocity is expected to produce a velocity discontinuity that can reflect shear-wave energy. The theoretical models of elasticity also predict anisotropic properties (such as the directional dependence of the wave velocity) of the post-perovskite crystals. These differ significantly from those for perovskite in low-temperature calculations, with increasing temperature reducing the differences but still allowing a
The pioneering experimental and theoretical work on post-perovskite was performed for the pure Mg end-member, but effects of the presence of iron (Fe) and aluminum (Al) have recently been explored experimentally and theoretically. It is believed that lower-mantle silicates probably contain 10–15% iron substitution for magnesium. Initial work suggested that having iron in the post-perovskite mineral should reduce the pressure of the phase transition, such that it may occur hundreds of kilometers shallower in the mantle than for an iron-free mineral. These results have been contested in very recent experiments that find less pressure effect due to inclusion of Fe. Theoretical predictions of the effects of Al substitution for both Mg and silicon (Si) in the crystal lattice suggests that there may a significant depth range (a few hundred kilometers) over which perovskite and post-perovskite can coexist, which would reduce any velocity discontinuity, weakening seismic-wave reflections from the transition.

Lower-mantle rocks, like all rocks in the Earth, will involve an assemblage of mineral phases with variations in crystal size and rock fabric because of solid-state convection. While there has been some experimental work done on real rock samples at lower-mantle pressures and temperatures (with the post-perovskite phase being observed), full assessment of coexisting multiple phases is just beginning. For example, the properties of ferropericlase [(Mg,Fe)O] are important, especially the partitioning coefficient of iron between perovskite and ferropericlase. Recent experimental work indicates that at high pressure, Fe, normally in its high-spin state (Fe$^{3+}$) in the lower mantle, will prefer to be in a low-spin state (Fe$^{2+}$) in the lowermost mantle, which will favor iron partitioning into ferropericlase rather than perovskite. This Fe spin-transition may occur at depths similar to the post-perovskite phase boundary, so iron partitioning may affect the post-perovskite composition. Thermal, electrical, and mechanical transport properties of lower-mantle rocks will be influenced by iron distribution. Thus, future work on realistic assemblages under high pressure-temperature conditions is very important for assessing the effects of the precise composition of post-perovskite in the Earth.

Seismological evidence for post-perovskite in deep mantle. The experimental discovery of the perovskite-to-post-perovskite phase transition may offer an explanation for a long-standing seismological observation. In 1983, S-wave reflections from a velocity increase in the deep mantle were first observed in several regions, and there has been extensive mapping of the reflecting interface in subsequent studies. Figure 2 shows examples of seismological S-wave-velocity models for the lowermost mantle, indicating the presence of an abrupt 2-3% increase in shear velocity about 200–300 km (120–190 mi) above the core-mantle boundary. Global mapping of three-dimensional S-wave velocity variations in the deep mantle indicates that the lowermost
Fig. 2. Models of seismic S-wave velocity in the deep mantle. PREM is an average Earth model. The other models, determined for the localized regions shown on the map in Fig. 3 by analysis of seismic waves, all indicate the presence of a 2–3% shear velocity discontinuity 200–300 km (120–190 mi) above the core–mantle boundary (2891 km or 1796 mi deep). This is well explained by the presence of post-perovskite in the lowermost mantle in these regions.

300 km of the mantle has strong, large-scale patterns of heterogeneity, with relatively high S-wave velocities underlying the margins of the Pacific Ocean (Fig. 3). This coincides with the regions where large volumes of oceanic lithosphere have subducted during the past 200 million years, and there are indications of slab material extending downward throughout the mantle, possibly connecting to large provinces of relatively high-S-wave-velocity material at the base of the mantle.

Subducted oceanic slab material should be relatively low in temperature, compared to surrounding ambient mantle, so that at lowermost mantle pressures this material may preferentially undergo transition to post-perovskite, resulting in a reflecting surface at the phase change. Figure 3 indicates that the models in Fig. 2 are found for regions with higher-than-average S-wave velocity in the lowermost mantle, where it is plausible that slab material has descended. If the patterns of heterogeneity in Fig. 3 truly indicate relative temperatures (rather than a compositional change), low-velocity regions should
be hotter, and therefore any post-perovskite phase transition may occur at greater depth or not at all in the hotter regions. Seismologists are seeking to establish whether the lowest-velocity regions have any S-wave-velocity discontinuity, but so far there is little evidence for this. Thus, post-perovskite may exist in large patches of lower-mantle material that have been cooled by recently subducted slab material, and as it heats up over time the material may change back to perovskite. The core–mantle boundary is likely to be at a temperature too high for post-perovskite to be stable, so there may be a thin basal layer, with rapidly increasing temperature below regions cooled by slab material, in which the minerals transform back to perovskite.

The anisotropic properties of post-perovskite may further explain why seismologists find a strong association between regions with a lower-mantle S-wave-velocity discontinuity and regions with strong S-wave splitting, which is not observed in lower-velocity regions. S-wave splitting into two waves (a fast and a slow) is caused by wave propagation through a region with anisotropic rock properties, which can result from alignment of anisotropic post-perovskite crystals by shearing flow of the rock in the lower-mantle boundary layer.

**Dynamical consequences.** The large positive Clapeyron slope of the post-perovskite phase boundary in the presence of lateral temperature differences at the base of the convecting mantle may influence the generation of boundary layer instabilities. Warmer regions of the boundary layer will have a thinner layer of dense post-perovskite mineralogy, while colder regions of the boundary layer will have a thicker layer of the denser material. This thermally induced topography on the phase boundary is like that near the 410km olivine–wadsleyite phase transition. And in both cases, the pattern promotes flow of material across the boundary layer (as the elevated dense material sinks and pulls down over-
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lying material that transforms to the denser phase). Because the Clapeyron slope for the deep-mantle transition is about twice that of the upper-mantle transition, the effect is enhanced. Convection models that include the post-perovskite transition have quite unstable lower thermal boundary layers that tend to generate vigorous deep-mantle flow. Seismological mapping of the phase boundary can thus provide a probe of the thermal and dynamical processes in the deep mantle.

For background information see EARTH INTERIOR; ELASTICITY; GEOPHYSICS; HIGH-PRESSURE MINERAL SYNTHESIS; MINERAL; OLIVINE; PEROVSKITE; SEISMOLOGY; SUBDUCTION ZONES in the McGraw-Hill Encyclopedia of Science & Technology.

Key Words: D region; lower mantle; perovskite; phase transition


URLs

http://olivine.ethz.ch/∼artem/Post-perovskite.html
Discovery of a post-perovskite phase of MgSiO₃