

The Earth's Lower Mantle and Core

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More than 90 percent of the Earth's mass is composed of iron, oxygen, silicon and magnesium, distributed among a metal-rich core, a silicate-rich mantle and more highly fractionated crustal rocks (less than 1% of the total). Mantle and core compositions can be approximated quite easily provided the bulk-Earth composition is assumed to be the same as that of appropriate meteorites. Critical mineral-physics data, some of which are reviewed in this article, are then needed to develop viable compositional and thermal Earth models, thus leading to a better knowledge of the deepest rocks in the Earth.

KEYWORDS: mantle, core, differentiation, chondrites

INTRODUCTION

In our current understanding, the formation of the Earth took place in a few tens of millions of years, around 4.56 billion years ago (Agnor et al. 1999 and references therein). The primordial building material for the Earth is thought to correspond closely to chondrite meteorites, the least differentiated solar system materials. There exist, however, different classes of chondrites, with variable chemical compositions (e.g. Jarosewich 1990; Newsom 1995). For example, the ratio of two major elements in the Earth, silicon and magnesium, varies by as much as 20% among different chondrite classes. Strong relative variations of iron and silicon also exist. Carbonaceous chondrites are most often used to construct compositional models (see Lyubetskaya and Korenaga 2007 and references therein), but questions remain concerning which class of chondrites represents the dominant primordial material involved in the Earth's accretionary processes (see Javoy 1995; Williams and Knittle 2005). These processes involve aggregation of dust on a timescale on the order of a hundred thousand years, but the mechanisms responsible for the subsequent formation of planetesimals (bodies with sizes of a few kilometres or more) are not fully understood (see Tanga et al. 1996 and Benz 2000). Planetesimals, in turn, coalesce to form planets. A giant impact of a planetesimal during the late-stage accretion of our planet was responsible for the formation of the Moon, probably when the Earth was about 80% of its present size.

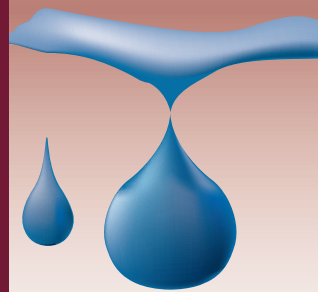
It is widely accepted that, as the Earth grew, the gravitational energy delivered by accreting planetesimals, and *a fortiori* by the giant Moon-forming impact, was enough for significant melting to occur. The Earth probably had an extensive molten outer layer, which we call the "magma

ocean". This layer was molten throughout the accretionary process, and much of the mantle was probably remelted several times due to giant impacts. In this molten system, minerals were strongly differentiated according to their density. The prevailing oxygen fugacity maintained iron (Fe) and nickel (Ni) in the liquid-metal state, so these elements merged into small droplets that were progressively extracted from the liquid silicates. These droplets settled into large pockets at the base of the magma ocean, and

then sank farther as big descending diapirs or blobs toward the centre of the Earth. These large reservoirs of core material may have carried iron from the base of the magma ocean to the growing core without significant chemical equilibration along the way. According to this scenario, a liquid metallic core formed in a total elapsed time between tens of millions of years and one hundred million years. Note that metallic cores probably formed in precursor bodies as well. Giant impacts likely triggered substantial mixing of metal and silicate liquids in the Earth's magma ocean, allowing re-equilibration to take place until the droplets reached the base of the magma ocean, where the silicate mantle material solidified (Fig. 1). It is currently accepted that the base of the magma ocean was at a depth of around 700 to 1200 km (pressures of 25 to 40 GPa), where the temperature was 2800 to 3300 K (e.g. Wood et al. 2006). This environment was likely the last where chemical equilibrium occurred between core-forming metallic compounds and surrounding silicates (i.e. the Earth's core formed with the chemical signature of equilibrium at pressures well below the actual core pressure). This equilibrium dictated the abundance of light elements in the core and the abundances of moderately siderophile (iron-loving) elements in the mantle (e.g. Walter et al. 2000). However, as mentioned by Stevenson (1990), it is reasonable to suppose that core formation involved a blending of multiple core-forming events at different T and P conditions rather than a single T and P event.

As the magma ocean cooled, the first crust formed. Degassing of some of the volatile substances that had been trapped in small amounts within the accreting planet probably formed the earliest atmosphere. Meteorites and comets also delivered volatile elements to the Earth, further modifying the composition of the atmosphere. The delivery of water to the Earth is one of the most poorly understood aspects of the Earth's formation (e.g. Morbidelli et al. 2000). Water could indeed have played an important role as a source of light elements for the core and could have had a strong influence on mantle melting temperature.

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A simple mass-balance calculation shows that the major-element compositions of the mantle and core can be obtained provided the Earth's composition is given by a specific class of meteorites (e.g. Allègre et al. 1995; Javoy 1995; McDonough and Sun 1995). In this approach, the Earth's mantle represents the silicate residue of core formation. Using the composition of chondritic meteorites, the composition of the mantle that can be inferred from least differentiated peridotites constrains the composition of the core (at least for non-volatile elements), provided the whole mantle is rather homogeneous in composition. When examined in detail, however, significant discrepancies remain unaddressed in this simple scenario. The Si/Mg ratio of mantle rocks, for example, is lower than values obtained from chondrite meteorites. This may result from the trapping and alloying of silicon in the iron core material during differentiation. Alternatively, this low ratio could indicate that the primordial materials from which our planet was built may have undergone differential evaporation that preferentially removed silicon from the region of the Earth's orbit in the protosolar nebula. Another possibility is that the Earth's mantle is not chemically homogeneous (see Anderson 1989). In this case, the composition of peridotite mantle rocks sampled at the surface may not be representative of the Earth's deep mantle. None of these hypotheses have resulted in a clear consensus, and the debate about what class of chondrites could represent the Earth's primordial bulk composition is still open.

The composition of the Earth's core and lower mantle can be estimated by combining observations from geophysics, petrology, mineral physics, cosmochemistry and mantle geochemistry; it cannot be determined from any one of these fields alone. A brief mineral-physics perspective will be given in this article.

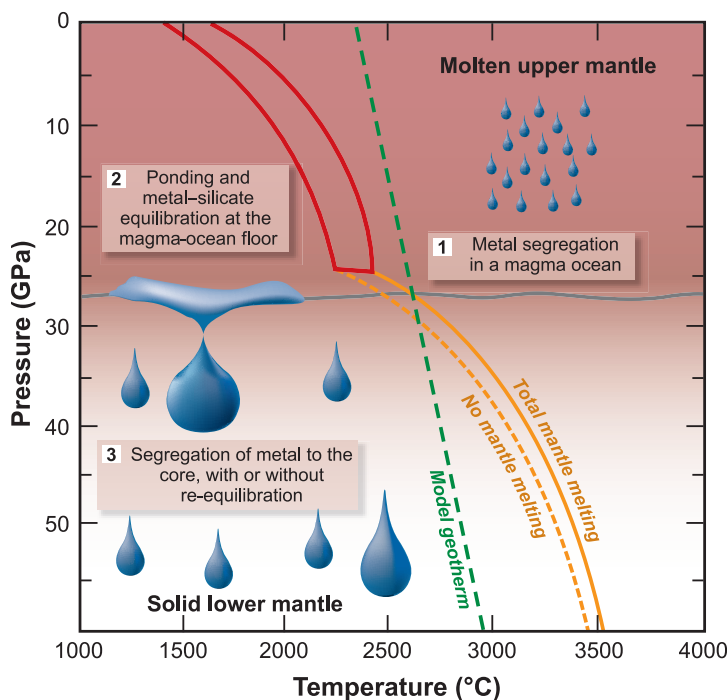


FIGURE 1 Metal segregation in a magma ocean. The ocean's depth is limited by a change in melting slope due to stabilization of silicate perovskite. Metal segregated from the magma ocean [1] may pond at its base [2] and then descend as droplets or diapirs with little equilibration with depth [3]. Alternatively, descent through a solid matrix could operate by percolation, which would enhance higher-P re-equilibration. AFTER WALTER (1999)

THE CORE

Propagating seismic waves and normal-mode oscillations are available observations to study the core, and their inversion yields a set of sound velocity, density and compressibility profiles. These measurements reveal the presence of a liquid outer core and a solid inner core, characterized by a measurable anisotropy of propagation of compressional (P) seismic waves. Using shockwave measurements on iron, Birch (1952) proposed that the Earth's core was too light to be made of pure iron. Since then, several studies have confirmed that iron is too dense to be the sole constituent not only of the core as a whole, but also of the solid inner core (e.g. Birch 1952; Jephcoat and Olson 1987). From a methodological viewpoint, high-pressure mineral physics provides sets of data that can be combined with seismic data in order to check the self-consistency of the models. In this sense, the study of Earth materials under extreme conditions (high pressure and high temperature) in recent years has unveiled information on the density (FIG. 2) and compressibility of minerals under conditions of the deep Earth from the in situ study of their crystal structure by X-ray diffraction. For example, it is widely accepted that the hexagonal close-packed structure (*hcp*) is the most likely structure for iron in the Earth's inner core. This is still an open issue, however, because theoretical calculations (e.g. Belonoshko et al. 2003) and a recent experimental observation on a nickel-iron alloy (Dubrovinsky et al. 2007) indicate that a body-centered cubic structure could be more appropriate.

The nature of the light-element component in the outer core has received considerable attention, but no consensus has emerged yet. In the last fifty years, a large number of light elements have been proposed, such as H, C, N, O, Mg, Si, S (and others), and the relative amounts of these light elements possibly alloyed in the core (both the liquid outer and the solid inner core) have been tentatively established on the basis of P-V-T equation-of-state data and petrological studies (see Poirier 1994 and references therein). Static measurements of sound velocities under extreme conditions (Fiquet et al. 2001 and references therein) have recently become available. Measurements of sound velocities of iron alloyed with lighter elements, including S, O and Si, have been carried out (Badro et al. 2007). In that study, direct high-pressure measurements of sound velocities are

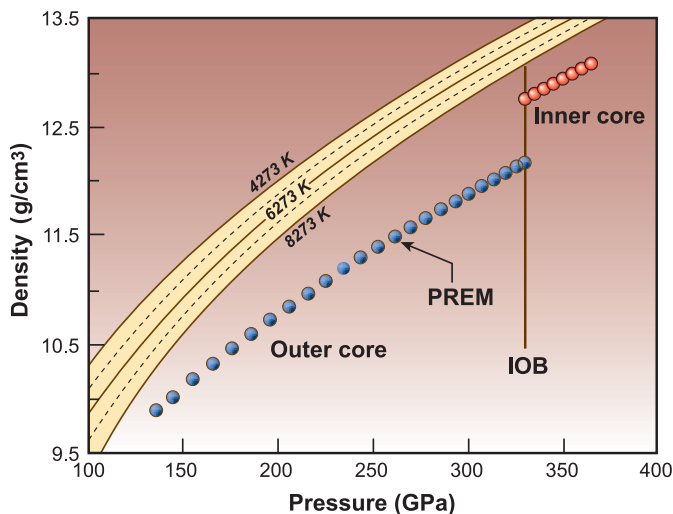


FIGURE 2 Density of pure iron (with the *hcp* structure) as obtained from X-ray diffraction as a function of pressure and temperature (yellow area). The extrapolation of these data to core conditions shows an excess density for pure iron (ca 10% in the outer core and 4% in the inner core) compared to geophysical data (after Uchida et al. 2001). PREM: preliminary reference Earth model; IOB: inner core-outer core boundary.

reported for iron compounds plausibly dissolved in the Earth's core, i.e. iron oxide (FeO, wüstite), iron sulfides (FeS, troilite, and FeS₂, pyrite) and iron silicide (FeSi) – see FIGURE 3. These measurements have been combined with the previous sets formed by the pressure–density systematics for these compounds and compared with radial seismic models such as PREM (Dziewonski and Anderson 1981). This recent mineral-physics approach shows that incorporation of significant amounts of Si or O in the core is compatible with geophysical observations and geochemical abundances. The effect of Ni on the calculated light-element contents is shown to be negligible. The preferred core model derived from these measurements is an inner core that contains a few percent Si and traces of O, and an outer core containing Si and several percent O.

This model, which is based mainly on PREM (our reference radial model for density and velocity profiles for the Earth) and which is consistent with mineral-physics data, is in good qualitative agreement with several recent cosmochemical (Allègre et al. 1995; Javoy 1995; McDonough and Sun 1995) and theoretical (Alfè et al. 2002) approaches. There are strong indications that silicon, in particular, is significantly abundant in the Earth's core – an inference that might solve, in full or in part, the aforementioned silicon deficit in the Earth's mantle. An ultimate test for such compositional models will be comparison with experimental melting phase diagrams of iron alloys at the pressure and temperature conditions of the inner core–outer core boundary, a goal as yet unachievable with existing experimental capabilities, despite recent progress at lower pressures (see, for example, Fei et al. 1997).

Anisotropy in the inner core of the Earth might be used, in the future, as a useful constraint on the composition of the Earth's core. There has been considerable progress in recent years in the detection of anisotropy in the inner core (e.g. Souriau 2007) and in its interpretation in the context of mineral physics (e.g. Antonangeli et al. 2006 and references therein). If temperature has a negligible effect on the shape of the *hcp* iron elastic anisotropy at inner-core density, these studies suggest that a preferential alignment of the *c*-axis of iron crystals parallel to the Earth's rotational axis provides the simplest explanation for the P-wave travel-time anomalies observed in the inner-core. As mentioned by Antonangeli et al. (2006), alignment of the stiffest elastic axis of the constituent crystals parallel to the Earth's spin axis would, for example, be compatible with several simple textural models obtained for *hcp* iron if convective flow is or has been present in the inner core, or if grain growth is sensitive to the strain energy associated with the non-hydrostatic stress field induced by inner-core rotation. The differential effect of alloying elements on anisotropy might thus be an additional tool for better constraining the composition of the inner core, in addition to providing data on its thermal and textural history.

Thermodynamics and kinetics of the exchange of Si, O and other elements between metal and silicate at high pressure and high temperature, presumably 15–35 GPa and 2200–3000 K (see above), are the determinants of the composition of the Earth's core inferred from approaches such as the one just discussed. There is thus a strong link between the composition of the core, the circumstances of its formation, and mineral-physics data on metal/silicate exchange as a function of pressure, temperature and oxygen fugacity. For example, laser-heated diamond anvil cell experiments¹ suggest that characteristic temperatures of metal/silicate exchange in

1 The wide-range transmittance of diamonds allows focusing high-power infrared lasers onto the sample squeezed in the diamond anvil cell, thereby subjecting it simultaneously to high temperatures of over 7000 K and pressures above 100 GPa.

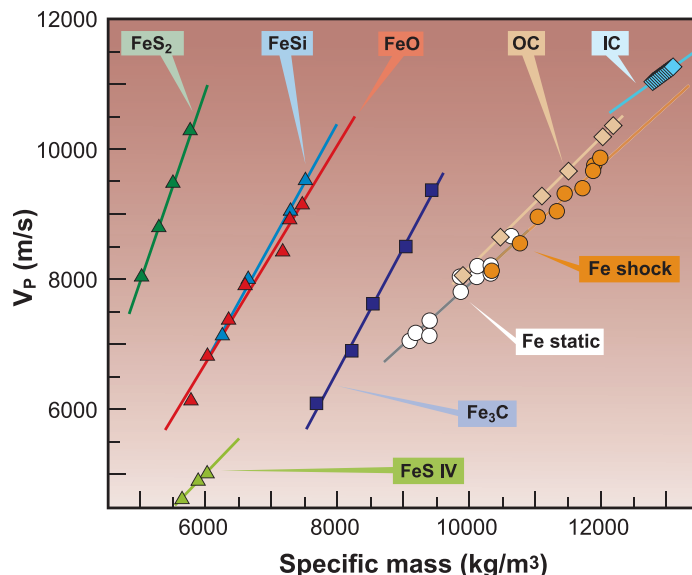


FIGURE 3 Compressional (P-wave) wave velocities in Fe, FeS, FeO, FeS₂, FeSi and Fe₃C as a function of specific mass. Seismic velocity profiles from the radial PREM model for the inner (IC) and outer (OC) core, as well as shock measurements, are also reported (see Badro et al. 2007 and references therein). Linear combinations of these data and fits to geophysical profiles then allow to propose possible core compositions.

excess of 3000 K may be required to obtain simultaneously high silicon and high oxygen abundances in the core, which might thus provide further constraints on dynamical scenarios of the Earth's formation.

THE LOWER MANTLE

Constraining both the thermal structure and the bulk composition of the lower mantle from 1-D radial profiles of density and seismic velocities (e.g. PREM; Dziewonski and Anderson 1981) is a classical problem for deep-Earth geophysics. This question has been debated intensively for several decades and still poses a considerable challenge to mineral physics. Whether the lower mantle has the same bulk composition as the upper mantle is fundamental for understanding global mantle dynamics, the thermal structure and bulk composition of the Earth, and the nature and location of various geochemical reservoirs. A homogeneous mantle of pyrolite² composition is compatible with global whole-mantle convection. It reproduces, to a first approximation, the seismic discontinuities observed at 410 and 660 km depths (e.g. Ringwood 1991), yielding a global molar Mg/Si ratio of about 1.3, quite different from any chondritic value. Alternatively, Anderson (1983) proposed a compositional model based on the mass balance of different mantle components, and Anderson and Bass (1986) introduced a piclogitic³ model for the transition zone associated with a silica-rich lower mantle, both models having a bulk Mg/Si ratio close to the value of 1 found in carbonaceous chondrites. These conflicting views influence the inventory of Mg and Si in the Earth: Is the core a major reservoir for Si? Is the Mg/Si ratio for the Earth chondritic?

2 Pyrolite is a hypothetical upper-mantle rock. It is a variety of fertile peridotite commonly assumed to be the parent of mantle basalts produced by partial melting.

3 Rocks that have less than 50% olivine plus orthopyroxene have been given the general name piclogites. Piclogites can represent garnet-rich cumulates and generate basaltic melts over a wide range of temperatures.

Although the pressures and temperatures of the lower mantle are difficult to reproduce and accurately measure in the laboratory, there has been enormous progress in synthesizing appropriate samples and in characterizing the elastic and thermal properties of lower-mantle phases. State-of-the-art laser-heated diamond anvil cell experiments coupled with synchrotron X-ray diffraction are now available, and offer unique opportunities to characterize the thermal properties of mantle minerals at all pressure and temperature conditions prevailing in the lower mantle. Moreover, such experiments are complemented by an increasing number of first-principles theoretical calculations. These approaches have led to the now widely accepted view that the lower mantle is made of an assemblage of (Mg,Fe,Al)(Si,Al)O₃ (highly predominant) and CaSiO₃ silicates with the perovskite structure, and (Mg,Fe)O oxide (ferropericlase) with the rock-salt structure. There exists no consensus on the relative amounts of these phases or on their Fe and Al contents, which are issues that touch the central problem of the bulk composition of the mantle.

Numerous studies have been dedicated to the interpretation of average radial profiles of seismic wave velocity, density and elastic properties in terms of mantle mineralogy and thermal structure (e.g. Jackson 1998). Despite significant progress in the determination of the thermal properties of relevant materials under extreme conditions of pressure and temperature, Mattern et al. (2005) emphasized that some significant irreducible trade-offs remain between temperature and bulk composition. As shown in FIGURE 4, a strong positive trade-off is observed between the magnesium silicate perovskite content of the lower mantle and temperature. As a consequence, the average lower-mantle compositional models, assuming a non-pyrolitic composition [for instance, CI chondritic or so-called cosmic models (i.e. silica rich); Anderson and Bass 1986], are also consistent with seismological observations, provided that temperatures in the lower mantle are a few hundred degrees greater than predicted by an adiabatic isentropic whole mantle. In other words, the sole use of bulk sound velocity and density as constraints does not lead to a unique solution for mantle composition and temperature. A solution might arise from precise measurements of shear velocities at high pressures and temperatures.

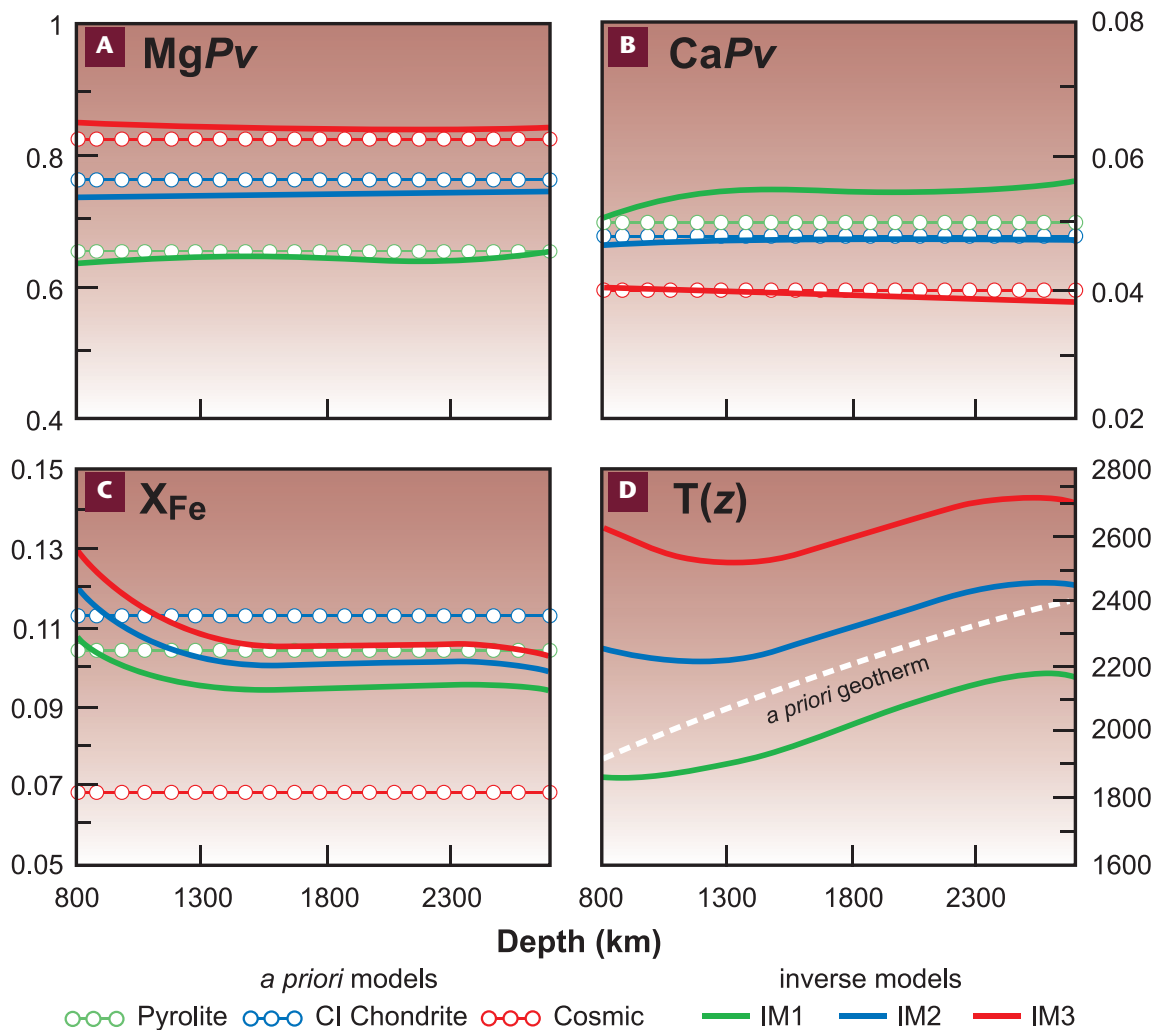


FIGURE 4 Lower-mantle compositions (IM1 to IM3) obtained from different *a priori* compositional models (pyrolite, CI chondrite, cosmic) and geotherm (dashed line in d). Phase molar fraction for magnesium-rich silicate perovskite and calcium silicate perovskite are given in (A) and (B). Temperature is in kelvin. Green circles: *a priori* pyrolite composition and associated inverted model IM1 (solid green line); blue circles: *a priori* CI-chondritic composition and associated inverted model IM2 (solid blue line); red circles: *a priori* cosmic composition and associated inverted model IM3 (solid red line). Iron content

X_{Fe} (C) and temperature (D) are the most sensitive parameters, whereas the magnesium silicate perovskite (A) and calcium silicate perovskite (B) contents remain close to their *a priori* values. There is a strong positive trade-off between the magnesium silicate perovskite content and temperature. The seismic density and bulk sound velocity profiles can be explained either by a 'cold' (i.e. 2000 K) pyrolite-like lower mantle (MgPv ≈ 0.64) or by a 'hot' (i.e. 2600 K) perovskitic lower mantle (MgPv ≈ 0.84). See Mattern et al. 2005 and references therein for more details.

Deschamps and Trampert (2004) indeed show that knowledge of these shear properties would significantly decrease the temperature and composition uncertainties. Using the most recent elastic data and pressure derivative available for the mantle magnesium silicate perovskite, Matas et al. (2007) indicate that the average lower-mantle Mg/Si ratio should be lower than 1.3 (i.e. a value that does not differ significantly from a pyrolitic one) in order to fit the 1-D seismic profile. Thus, depending on the choice made for the pressure derivative of the shear modulus of the magnesium silicate perovskite compound, it is still impossible to choose between (1) an adiabatic isentropic geotherm associated with a uniform chemical composition and (2) a larger temperature gradient associated with a depth-dependent bulk composition (with silicon enrichment between 800 and 2700 km depth). A temperature of about 2800 K at a depth of 2700 km is obtained in the first case. In the latter case, the temperature could reach 3400 K at the same depth.

Located at greater depth, the so-called D'' layer was rather enigmatic until recently, when a phase transition from perovskite to post-perovskite was discovered by Murakami et al. (2004). In addition to providing a better but still incomplete explanation for some D'' seismic features (Hirose and Lay 2008 this issue), this transition will prove to be essential for describing the deep-mantle thermal state. Until recently, the deep-mantle geotherm was obtained by combining the pressure–temperature phase diagrams of the main mantle silicates (mostly olivine) with the pressures corresponding to the seismic discontinuities at 410 and 660 km depth. The mantle geotherm was then inferred by using an adiabatic isentropic profile linking and extrapolating these two temperatures, with the remaining uncertainty that thermal boundary layers of several hundred degrees might exist within the mantle (e.g. at 660 km depth). Back extrapolation of the melting temperature of iron and/or iron alloys from the inner core–outer core boundary (IOB) using an adiabatic isentropic profile was then used to estimate temperature at the core–mantle boundary (CMB) on the core side. In a recent study, Van der Hilst et al. (2007) attribute some seismic reflectors near the CMB to the perovskite to post-perovskite transition. The appearance of post-perovskite is fundamental in that it is another thermobarometer in the mantle, bridging the enormous 4500 km wide thermometer-free gap between the 660 km discontinuity and the inner-core boundary. The points of intersection of the thermal gradient with the phase boundary associated with the depths of the reflectors provide, in principle, a way to calculate temperature and heat flow at the CMB (see FIGURE 5). Van der Hilst et al. (2007) then estimate temperatures of 3950 ± 200 K at the core–mantle boundary and about 2400 K at a depth of 2700 km on the mantle side, thus yielding a thermal boundary layer of 1600 to 1400 K at the CMB.

FINAL THOUGHTS

The most critical mineral-physics results needed for the further refinement of the compositional and thermal models of the lower mantle are the shear properties of mantle minerals and, in particular, the pressure derivatives of the shear properties. The role of constituents such as aluminum, calcium and water is difficult to constrain, and some effort should be made to acquire such information. These constituents may in addition have a significant effect on shear properties. A low-temperature estimate of about 2400 K at 2700 km depth (Van der Hilst et al. 2007), combined with the inversion of radial seismic profiles (Matas et al. 2007), favours a rather simple homogeneous compositional model and thermal structure for the mantle, which is also consistent with the pressure derivative of the shear modulus of

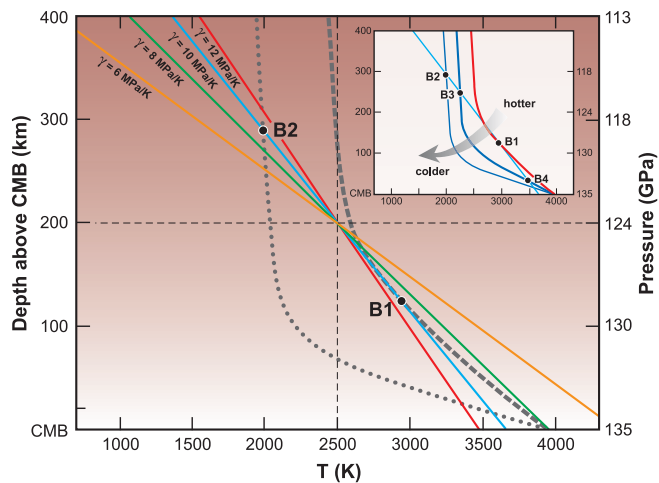


FIGURE 5 Depth of conversion (y-axis) from perovskite to post-perovskite (and reversal) as a function of temperature (x-axis). The dotted and dashed lines depict two different estimated geotherms through B1 and B2. The shallow part (shallower than 200 km above the core–mantle boundary) is adiabatic, whereas the deeper part may be described with a conductive temperature gradient toward the CMB. These temperature profiles intersect the perovskite to post-perovskite phase transition boundary (coloured lines) at different locations (B1 or B2), depending on the pressure–temperature conditions. A reference point is fixed at $P = 124$ GPa and $T = 2500$ K for the perovskite–post-perovskite transition, and different Clapeyron slopes ($\gamma = 6$ – 12 MPa/K) are represented. **Inset:** cold, intermediate and hot geotherms and Clapeyron slopes (the straight blue line stands for $\gamma = 10$ MPa/K). No transition occurs if the mantle is sufficiently hot (B1). As the mantle temperature decreases, the same perovskite to post-perovskite transition occurs at increasing distances above the CMB (B3 and B2). A reverse transition from post-perovskite to perovskite occurs along colder geotherms (double crossing) at decreasing height above the CMB (B4). See Van der Hilst (2007) and references therein for further details

magnesium silicate perovskite recently obtained by Brillouin spectroscopy (Murakami et al. 2007). However, if this low-temperature estimate for the CMB is not confirmed in the future, an iron-rich, silica-rich, high-temperature lower mantle could come back into the limelight. In addition, the mantle is not pure MgSiO_3 , and the perovskite to post-perovskite phase boundary pressure probably depends upon Fe and Al contents, which could certainly increase the CMB temperature uncertainty relative to the Van der Hilst et al. (2007) estimate. Further, it should be borne in mind that shear properties have not yet been measured under the exact pressure and temperature conditions of the lower mantle. Moreover, in our attempt to derive Earth's compositional models from the comparison between seismic and mineral-physics data, we might soon encounter the long-envisioned limitation of using exclusively 1-D average seismic profiles such as PREM instead of exploiting directly more realistic and informative 3-D seismic images. This conceptual transition will be a challenge for mineral physicists in the coming decade.

Another critical challenge will be to obtain more-precise temperature and compositional data on deep-Earth phase transformations that can be used as thermobarometers (e.g. the perovskite to post-perovskite transformation) and possibly to discover new phase transitions that could be manifested in seismic images. It is indeed possible that, at such depths, iron might assume a dominantly low-spin phase state, which would certainly affect its partitioning among lower-mantle phases, as well as the thermal conductivity (lattice and/or radiative) in the deep mantle (Badro et al. 2005). There are also preliminary indications that spin state may have strong effects on elasticity (Brown et al. 2007). These electronic transformations of iron could profoundly

alter the thermochemical state of Earth's lower mantle and its convective patterns. The transition pressures in ferropericlase and magnesium perovskite indeed correspond, respectively, to the bottom third of the lower mantle (70 GPa, 1700 km depth) and to the lowermost 300 km above the core–mantle boundary (120 GPa, 2600 km depth). Understanding the contribution of these newly discovered electronic spin phase transitions to the unique geophysical signatures of this still-mysterious region of the Earth remains an exciting challenge for the next decade of mineral physics. The same is true of the perovskite to post-perovskite trans-

formation, and both phenomena need clarification in terms of their exact relationships to the D'' layer and their temperature and compositional dependencies. All these are exciting challenges whose pursuit will dramatically improve our knowledge of the deepest rocks in the Earth.

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