

Some recent advances in understanding the mineralogy of Earth's deep mantle

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Understanding planetary structure and evolution requires a detailed knowledge of the properties of geological materials under the conditions of deep planetary interiors. Experiments under the extreme pressure–temperature conditions of the deep mantle are challenging, and many fundamental properties remain poorly constrained or are inferred only through uncertain extrapolations from lower pressure–temperature states. Nevertheless, the last several years have witnessed a number of new developments in this area, and a broad overview of the current understanding of the Earth's lower mantle is presented here. Some recent experimental and theoretical advances related to the lowermost mantle are highlighted. Measurements of the equation of state and deformation behaviour of (Mg,Fe)SiO₃ in the CaIrO₃-type (post-perovskite) structure yield insights into the nature of the core–mantle boundary region. Theoretical studies of the behaviour of MgSiO₃ liquids under high pressure–temperature conditions provide constraints on melt volumes, diffusivities and viscosities that are relevant to understanding both the early Earth (e.g. deep magma oceans) and seismic structure observed in the present Earth (e.g. ultra-low-velocity zones).

Keywords: mantle; post-perovskite; silicate liquids; Earth interior; MgSiO₃

1. Introduction

Knowledge of the composition and structure of the Earth's deep mantle places important constraints on the processes involved in the Earth's formation and subsequent evolution. Our understanding of the Earth's deep interior is derived from several lines of evidence including geophysical observations (e.g. seismology), geochemical studies of natural rocks and minerals, numerical simulations of mantle dynamics and experimental and theoretical studies of the physical and chemical properties of Earth materials at high pressures and temperatures. In this work, a basic overview of our understanding of the mantle structure is given. This is followed by more detailed discussion of selected recent research related to the Earth's core–mantle boundary region and the properties of silicate liquids under deep Earth conditions.

Experimental capabilities for studying materials at extreme conditions are progressing rapidly. Advances in X-ray diffraction methods at synchrotron radiation facilities have expanded the P – T range accessible to direct

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measurements all the way up to 200 GPa and 3000 K, while, at the same time, leading to improved resolution that has resulted in dramatically better ability to recover physical and crystallographic properties (Duffy 2005). *Ab initio* theoretical studies have also made major strides in the size and scope of problems that can be addressed (Gillan *et al.* 2006). In combination with new geophysical observations of the Earth, we can now better address such fundamental questions as the origin of seismic discontinuities, chemical heterogeneity in the mantle and the nature of the core–mantle boundary region.

2. Overview of the Earth's mantle

The most detailed information about the structure of the Earth comes from analysis of seismic waves generated by earthquakes. From such studies, one-dimensional models of compressional and shear velocity with depth can be constructed for either specific regions or a global average (Kennett *et al.* 1995). The mantle is characterized by major seismic velocity discontinuities at 410 and 660 km depths and an anomalously steep velocity gradient in the transition zone between them. The uppermost mantle (above 300 km) shows strong regional variations in velocity and also exhibits considerable seismic anisotropy, especially in the upper 200 km.

The Earth's lower mantle, extending from 660 km to a depth of approximately 2900 km, is the single largest region of the Earth, containing roughly 100 times the mass of the Earth's crust. In contrast to the upper mantle, seismic profiles for the lower mantle reveal generally smooth increases in seismic velocity with depth. However, the region that lies just above the core–mantle boundary, known for historical reasons as D'', is one that exhibits significant heterogeneity and anomalous properties (Garnero 2000).

Over the last 20 years, seismologists have progressed in constraining the three-dimensional seismic structure in the mantle using seismic tomography (Romanowicz 1991). Tomographic studies are able to resolve the velocity variations associated with subducting lithospheric plates and thereby image their interaction with the 660 km seismic discontinuity. More recently, tomographic studies have examined the nature of rising plumes of hot material (hotspots; Montelli *et al.* 2004). The velocity variations imaged by tomography can mostly be ascribed to the effects of temperature (Duffy & Ahrens 1992*b*; Karato 1993; Karato & Karki 2001), but chemistry and phase may also be important, especially in regions such as the subcontinental lithosphere and the deepest mantle.

A key question is the extent to which the mantle is compositionally uniform or whether large-scale heterogeneities or compositionally distinct regions exist. Some geochemical evidence from analysis of the distribution of trace elements and radiogenic isotopes in different rock types favours the existence of long-lived chemically isolated reservoirs, perhaps associated with major seismic discontinuities (van Keken *et al.* 2002). However, evidence from seismic tomography suggests that many subducting lithospheric slabs penetrate through the 660 km discontinuity, although some slabs are impeded or deflected by the boundary (van der Hilst *et al.* 1997). This suggests that the 660 km discontinuity does not isolate the upper and lower mantle into compositionally distinct regions. There is seismic evidence of chemical heterogeneity in the deep mantle (Kellogg *et al.* 1999;

van der Hilst & Karason 1999). It has therefore been suggested that the bottom third of the mantle may be geochemically distinct, and more heterogeneous, although no global sharp discontinuity in seismic velocity has been detected there (Kellogg *et al.* 1999). While polymorphism of the major lower mantle phases is not expected until the D'' region, changes in the spin state of Fe in (Mg,Fe)O and (Mg,Fe)SiO₃ have been detected experimentally at relevant pressures (Badro *et al.* 2003), and these may have profound implications for understanding the bottom third or so of the mantle.

The chemistry of the Earth's mantle is inferred from petrological data supplemented by constraints on the bulk chemical composition of the Earth. Direct samples of the uppermost mantle provide constraints on the chemistry of the upper 200 km or so of the Earth's mantle. Less direct constraints come from the study of basalts that are derived from the upper mantle by partial melting at mid-ocean ridges. Mineral inclusions in diamond (Stachel *et al.* 2000; McCammon 2001) provide rare samples of the deeper mantle, perhaps even to the depths of the transition zone or lower mantle. Interpretation of all these samples is augmented by constraints on the Earth's bulk chemistry (McDonough & Sun 1995) largely derived from the estimation of Solar System chemical abundances (from measurements of the solar photosphere and primitive meteorites).

The overall picture that results is that the uppermost mantle is composed of a Fe- and Mg-rich rock type (pyrolite), which upon partial melting produces the basalts of the oceanic crust and the residual peridotite of the depleted uppermost mantle (Irifune & Tsuchiya 2007). Determining whether the composition of deeper regions matches that of the uppermost mantle is one of the major challenges of mineral physics research. In the upper mantle, a pyrolite composition produces four primary minerals: olivine ((Mg,Fe)₂SiO₄); orthopyroxene ((Mg,Fe)SiO₃); clinopyroxene (CaMgSi₂O₆); and pyrope-rich garnet ((Mg,Fe,Ca)₃Al₂Si₃O₁₂). Olivine is the dominant upper mantle mineral component in this model (approx. 60% by volume). Support for the model comes from the fact that, at the expected temperatures of the mantle, phase transformations in olivine occur at pressures corresponding roughly to those at depths of 410 and 660 km, the major seismic discontinuities of the upper mantle. This is a basis for expecting that the bulk chemical composition inferred from near-surface rocks may extend across the entire upper mantle, and perhaps through the Earth's mantle as a whole. However, there is also evidence that the fraction of olivine needed to satisfy seismic data in the transition zone is significantly below that of the pyrolite model (Duffy *et al.* 1995; Cammarano & Romanowicz 2007). Furthermore, the presence of phase transitions does not rule out the existence of chemical changes as well (Jeanloz 1991).

The four mineral components of pyrolite ultimately transform to assemblages that are dominated by perovskite-structured phases. These transformations occur at depths corresponding to the transition zone and the vicinity of the 660 km discontinuity. Thus, from a mineralogical viewpoint, the 660 km discontinuity plays a central role in the Earth's mantle owing to the emergence of six-coordinated, perovskite-dominated assemblages.

Experimental studies have shown that the mineral assemblage adopted by a peridotite or pyrolite lithology under lower mantle conditions consists of three main minerals: (Mg,Fe)SiO₃ perovskite; CaSiO₃ perovskite; and (Mg,Fe)O ferropericlasite (Ringwood 1991; Kesson *et al.* 1998; Lee *et al.* 2004;

Ono & Oganov 2005; Irifune & Tsuchiya 2007). In peridotite compositions, aluminium is incorporated into the perovskite structures, but, in more Al_2O_3 -rich systems such as basalt, a separate Al-rich phase as well as a SiO_2 phase is expected to be present (Irifune & Ringwood 1993; Hirose *et al.* 1999; Funamori *et al.* 2000).

3. Post-perovskite and the core–mantle boundary region

The D'' region is one of the most poorly understood parts of the planet. A seismic discontinuity marks the top of D'' and the region itself is characterized by strong lateral heterogeneity and other anomalous properties (Garnero 2000; Lay & Garnero 2007). In contrast to the bulk of the lower mantle, the core–mantle boundary region exhibits pronounced seismic anisotropy (Kendall 2000). Local regions of much reduced (more than 10%) seismic velocities (ultra-low-velocity zones, ULVZs) have also been observed. These have been attributed to partial melting at the base of the mantle (Williams & Garnero 1996). They might also arise from iron enrichment due to either chemical interactions between the mantle and the core or other causes (Mao *et al.* 2004; Dobson & Brodholt 2005; Stackhouse *et al.* 2006). Complexity in the deepest mantle should not be surprising given that it is the boundary between the silicate minerals of the mantle and the liquid iron alloy of the core. The region is also a likely source area for mantle plumes (Montelli *et al.* 2004) and a potential final repository for subducting slabs of plate tectonics. Strong temperature gradients are also expected across D'' as it represents the thermal boundary layer between the mantle and the core.

The recent discovery (Murakami *et al.* 2004; Oganov & Ono 2004) of a post-perovskite (pPv) phase (CaIrO_3 -type structure) in MgSiO_3 at 125 GPa, close to conditions expected for the D'' region, has major potential implications for understanding geophysics and geochemistry of the deep mantle. The orthorhombic CaIrO_3 -type phase consists of edge- and corner-sharing SiO_6 octahedra that form layers along the (010) plane. The octahedral sheets alternate with eightfold coordinated magnesium layers along the b crystallographic axis. The structure is anisotropic with the highest compressibility normal to layering. The new phase contrasts markedly with the perovskite structure, which consists of a three-dimensional network of corner-linked SiO_6 octahedra with eightfold coordinated Mg filling in the cavities on this framework.

Although our understanding of this phase transition and its implications is still at an early stage, the CaIrO_3 -type phase of $(\text{Mg,Fe})\text{SiO}_3$ appears to provide some of the right characteristics to match seismic observations of D'' (Wookey *et al.* 2005; Lay & Garnero 2007; Shim 2008). While there remain considerable uncertainties in laboratory pressure determinations at these extreme conditions, the transformation occurs at pressures near those found at the top of the D'' layer for expected mantle compositions (Murakami *et al.* 2004; Oganov & Ono 2004; Wookey *et al.* 2005). The strongly positive pressure–temperature or Clapeyron slope of the transition means that the observed topography of the D'' boundary is explained by a deeper transition in locally hotter regions and a shallower transition in cooler regions (Hirose 2006). This is consistent with the seismic observation which suggested that a phase transition with a strong, positive

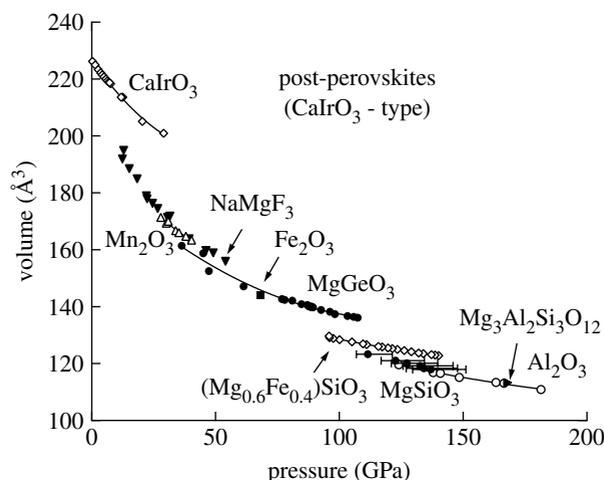


Figure 1. Representative volume–pressure relations for compounds in the post-perovskite (CaIrO_3 -type) structure. Solid lines are simple polynomial fits to the data (Oganov & Ono 2004; Ono & Ohishi 2005; Tateno *et al.* 2005; Kubo *et al.* 2006; Mao *et al.* 2006; Martin *et al.* 2006, 2007; Ono *et al.* 2006; Santillan *et al.* 2006; Hustoft *et al.* 2008).

Clapeyron slope (approx. 6 MPa K^{-1}) could explain the topography of the D'' discontinuity (Sidorin *et al.* 1999). In addition, the Earth has a steep thermal gradient near the core–mantle boundary and temperatures at the base of the mantle may become sufficiently hot that perovskite may re-emerge just above the core (Hernlund *et al.* 2005). In this case, one may expect complex structures such as localized lens of pPv. Attempts to seismically image these structures in this region have already yielded some provocative results (Lay *et al.* 2006; van der Hilst *et al.* 2007; Hutko *et al.* 2008).

A large number of compounds have now been discovered to possess the pPv structure, mostly at elevated pressures (figure 1). Owing to the high synthesis pressures required to form silicate pPvs, many experiments of interest cannot readily be performed on this material. Analogue compositions can therefore be useful by allowing measurements to be carried out at lower pressures. For example, germanates have long been known to be good structural analogues for silicates with corresponding phase transitions occurring at low pressures in germanates (Ringwood & Seabrook 1963). The pPv phase transition in MgGeO_3 occurs near 55–70 GPa (Hirose *et al.* 2005; Tsuchiya & Tsuchiya 2007*a*), compared with approximately 125 GPa in MgSiO_3 . Other materials found to crystallize in the pPv structure include various sesquioxides (Fe_2O_3 , Al_2O_3 and Mn_2O_3) and NaMgF_3 . pPv is the stable phase of CaIrO_3 at ambient conditions.

(a) Equation of state of $(\text{Mg},\text{Fe})\text{SiO}_3$ pPv

The equation of state (EOS) is one of the most fundamental parameters obtained from high-pressure studies. Using the laser-heated diamond anvil cell, the equations of state of coexisting perovskite and pPv (CaIrO_3 -type) have been investigated using phases synthesized from a natural pyroxene composition with a $\text{Fe}/(\text{Fe}+\text{Mg})$ value of 0.09, close to that expected for the lower mantle (Shieh *et al.* 2006). The measured pressure–volume data for the pPv phase from 12 to

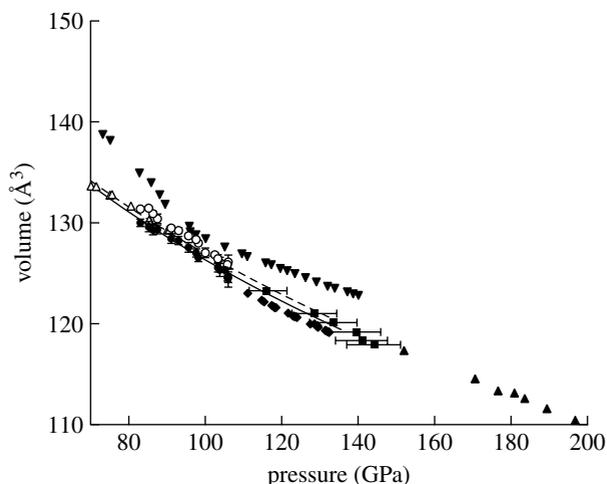


Figure 2. Selected pressure–volume compression data for perovskite (open triangles (dashed line), En100 (Fiquet *et al.* 2000); open circles, En91Fs09 (Shieh *et al.* 2006)) and CaIrO₃-type (filled squares, En100 (Ono *et al.* 2006); filled diamonds, En100 (Guignot *et al.* 2007); filled circles (solid line), En91Fs09 (Shieh *et al.* 2006); filled down triangles, En60Fs40 (Mao *et al.* 2006); filled up triangles, En85Co15 (Kubo *et al.* 2007)) phases at 300 K. En, enstatite (MgSiO₃); Fs, ferrosilite (FeSiO₃); Co, corundum (Al₂O₃). For the En100 data of Ono *et al.* (2006), pressure error bars show uncertainty in pressure depending on the choice of three different scales for the gold pressure calibrant. Also shown are representative volume error bars for a selected study (Shieh *et al.* 2006). Solid line is a Birch–Murnaghan EOS fit to the CaIrO₃-type data of Shieh *et al.* (2006) for the En91Fs09 composition. The dashed line is the EOS for MgSiO₃ perovskite (Fiquet *et al.* 2000).

106 GPa yield a zero-pressure bulk modulus of 219(5) GPa and a zero-pressure volume of 164.9(6) Å³ when $K'_0 = 4$ (figure 2). From the fitted EOS, the variation of the bulk modulus with compression can be determined (figure 3). The bulk modulus of pPv is 575(15) GPa at a pressure of 100 GPa. These results are broadly consistent with theoretical calculations (Oganov & Ono 2004) and other experimental EOS studies of (Mg,Fe)SiO₃ pPv (Ono *et al.* 2006; Guignot *et al.* 2007; Shim *et al.* 2008).

A direct comparison of volumes of coexisting perovskite and CaIrO₃-type phases at 80–106 GPa demonstrates that the pPv phase has a smaller volume than perovskite by 1.1(2) per cent (figure 2). Using measured volumes together with the bulk modulus calculated from EOS fits, we find that the bulk sound velocity decreases by 2.3(2.1) per cent across this transition at 120 GPa (figure 3), which is again consistent with theoretical predictions. Because the shear wave velocity is expected to increase across the transition, the decrease in bulk sound velocity implies that perovskite–CaIrO₃-type transition should produce a stronger shear wave signal in comparison with compressional waves. This is consistent with seismic studies that report a 2–3 per cent increase in V_S across the transition while the increase in V_P is usually smaller or even undetectable (Lay *et al.* 2006; Hutko *et al.* 2008). Quenched samples from these experiments (Shieh *et al.* 2006) were analysed by transmission electron microscopy. It was found that crystalline perovskite grains are enriched in iron (Mg/(Mg+Fe)=0.89) compared with adjacent amorphous parts (Mg/(Mg+Fe)=0.93) presumably converted from pPv (Hirose *et al.* in press). This

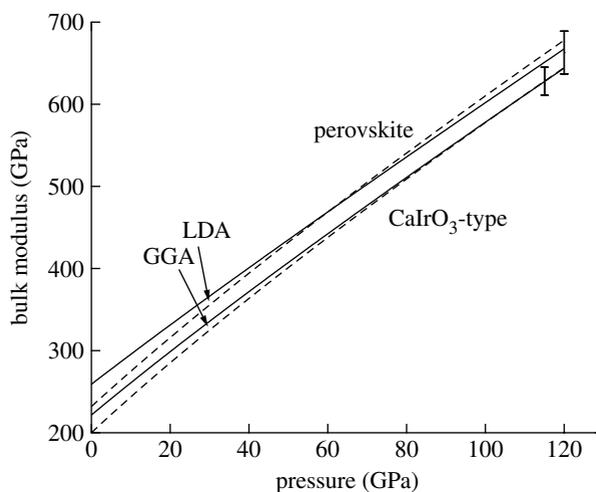


Figure 3. Bulk moduli of Fe-bearing perovskite and CaIrO_3 -type post-perovskite calculated from EOS fits (Shieh *et al.* 2006) and compared with density functional theory calculations for MgSiO_3 (Oganov & Ono 2004).

indicates that ferrous iron stabilizes perovskite to higher pressures. Simultaneous volume measurements of the perovskite and pPv forms of MgSiO_3 have also recently been reported by Komabayashi *et al.* (2008).

In another recent study, experiments using glass starting materials with compositions along the MgSiO_3 (En)– Al_2O_3 (Co) join have recently been carried out to investigate the effects of Al content on the EOS, transformation pressure and stability limits of the new phase (Kubo *et al.* 2007). The pPv phase was synthesized for compositions with 0, 5, 15 and 20 mol% corundum at pressures above 120 GPa. The effect of Al_2O_3 incorporation is to increase the transition pressure and lead to the formation of a potentially broad two-phase coexistence region containing perovskite and pPv. Sensitivity of the phase transition pressure and thickness to compositional variables such as FeO and Al_2O_3 may also contribute to D'' boundary topography. Determining the width of the coexistence region is challenging due to potential metastability and sluggish reaction kinetics. However, for the $\text{En}_{85}\text{Co}_{15}$ composition, the perovskite and pPv phases were observed to coexist between 127 and 152 GPa. The increases in transition pressure and width of the mixed phase region are qualitatively consistent with theory (Akber-Knutson *et al.* 2005). Dissolution of Al_2O_3 into MgSiO_3 pPv also appears to have a major effect on the pressure–volume relationship (figure 2), which is again consistent with theoretical predictions (Caracas & Cohen 2005; Stackhouse *et al.* 2005a).

(b) Deformation studies of germanate and silicate post-perovskites

One of the most interesting properties of the D'' region is that it possesses relatively strong (and variable) seismic anisotropy (Kendall 2000; Lay & Garnero 2007). The velocities of horizontally polarized shear waves (V_{SH}) are approximately 3 per cent faster than vertically polarized shear waves (V_{SV}) in some well-studied regions such as the circum-Pacific. The anisotropy, however,

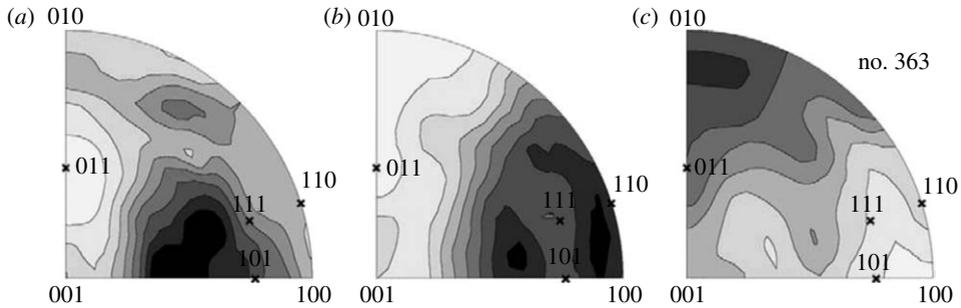


Figure 4. Inverse pole figures from deformation experiments on CaIrO_3 -type post-perovskites with compositions (a) $(\text{Mg,Fe})\text{SiO}_3$ (157 GPa, 300 K; Merkel *et al.* 2007), (b) MgGeO_3 (130 GPa, 300 K; Merkel *et al.* 2006) and (c) CaIrO_3 (6 GPa, 800 K; Miyagi *et al.* 2008). MgGeO_3 and $(\text{Mg,Fe})\text{SiO}_3$ post-perovskites are best explained by dominant slip on the (100) and (110) planes, while CaIrO_3 itself is best explained by slip on (010)[100]. Adapted from Miyagi *et al.* (2008).

is complex and varies from region to region. Understanding seismic anisotropy can yield clues to mantle dynamics at the base of the mantle. However, interpretation of seismic anisotropy in the deep Earth is challenging as it requires an understanding of mineral deformation mechanisms, the anisotropic elastic properties of the relevant phases and the strain history of materials in the deep mantle.

Measurement of the deformation behaviour of silicate pPv within its pressure–temperature stability field is not possible at present. However, using the diamond anvil cell and X-ray diffraction measurements in a radial geometry (Duffy *et al.* 1999), the deformation behaviours of MgGeO_3 and MgSiO_3 pPvs have been constrained at room temperature and pressures of 104–157 GPa, a pressure range directly relevant to the deep mantle (Merkel *et al.* 2006, 2007). Figure 4 shows inverse pole figures from these deformation experiments, showing the distribution of crystal planes relative to the loading axis of the diamond anvil cell. For both the silicate and germanate pPvs, polycrystalline plasticity simulations were performed and show that the observed textures can be explained by deformation with (110) and (100) as the primary slip planes. These results are consistent with a recent theoretical study, which found that slip along (110) could produce a series of stacking fault structures between perovskite and pPv and proposed that such planes were likely candidates for slip planes in CaIrO_3 -type pPv (Oganov *et al.* 2005).

Plastic strains in pPv and the corresponding contribution to seismic anisotropy in D'' were calculated using mantle convection models, polycrystalline plasticity simulations and constraints on the anisotropic elastic moduli of CaIrO_3 -type MgSiO_3 under D'' conditions (Merkel *et al.* 2007). The shear wave anisotropy pattern that results from this model is highly variable with azimuth, and the fast polarization direction is generally inclined to the vertical. Horizontally polarized shear waves are typically slower than vertically polarized shear waves, in contrast to many seismic observations.

There are several possible explanations that may be able to reconcile the deformation experiments with seismic observations. The elastic moduli of CaIrO_3 -type $(\text{Mg,Fe})\text{SiO}_3$ under deep mantle conditions remain uncertain as available

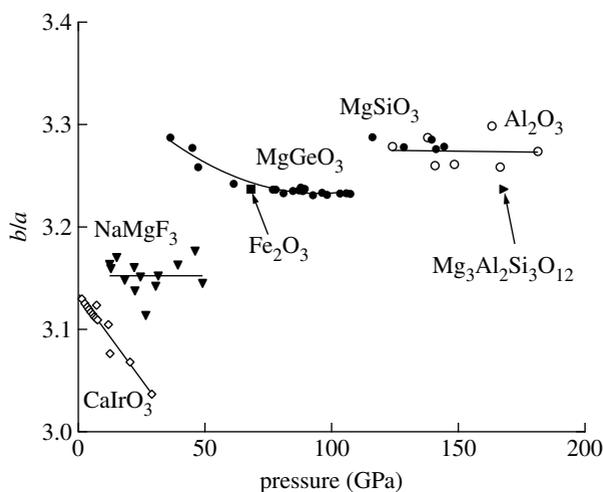


Figure 5. Crystallographic b/a ratio for selected post-perovskites from figure 1. Lines are least-squares fits.

theoretical calculations at high P - T conditions show significant differences (Stackhouse *et al.* 2005b; Wentzcovitch *et al.* 2006). A detailed analysis of the anisotropy patterns resulting from various combinations of slip systems and sets of elastic constants can be found elsewhere (Stackhouse & Brodholt 2007). Other phases such as (Mg,Fe)O are also highly anisotropic under D'' conditions and may contribute to or even dominate the seismic anisotropy signal even if they are not the volumetrically most abundant phase (Long *et al.* 2006). Another possibility is that high-temperature deformation mechanisms in (Mg,Fe)SiO₃ are different from the measured room-temperature values, or the experimental textures observed in (Mg,Fe)SiO₃ and MgGeO₃ are textures that result from a phase transformation rather than deformational textures (Santillan *et al.* 2006).

Based on the layered nature of the crystal structure of the CaIrO₃-type phase, it has been suggested that (010) slip (i.e. parallel to the octahedral sheets) may instead be a likely deformation mechanism for this structure. A number of deformation experiments have been performed at relatively low pressures and high temperatures on the analogue material CaIrO₃ pPv (Miyajima *et al.* 2006; Yamazaki *et al.* 2006; Walte *et al.* 2007; Miyagi *et al.* 2008), and these consistently find that, indeed, [100](010) slip is the dominant slip mechanism at both room temperature and high temperatures. Theoretical studies have provided support for both (110) slip and (010) slip in MgSiO₃ pPv (Oganov *et al.* 2005; Carrez *et al.* 2007). Some modelling studies have suggested that [100](010) slip could provide a plausible explanation for observations of lowermost mantle seismic anisotropy (Yamazaki *et al.* 2006).

A key question in evaluating the results for MgGeO₃ and CaIrO₃ pPvs is whether these materials represent good analogues for the silicate (figure 1). The relevance of an analogue material can be tested by examining a range of structural properties (axial ratios, compressibility, bond distances, polyhedral distortions, etc.) in the analogue and the real material. Figure 5 shows a comparison of crystallographic b/a ratios for different compositions in the CaIrO₃-type structure. Silicates, germanates and sesquioxides exhibit similar b/a

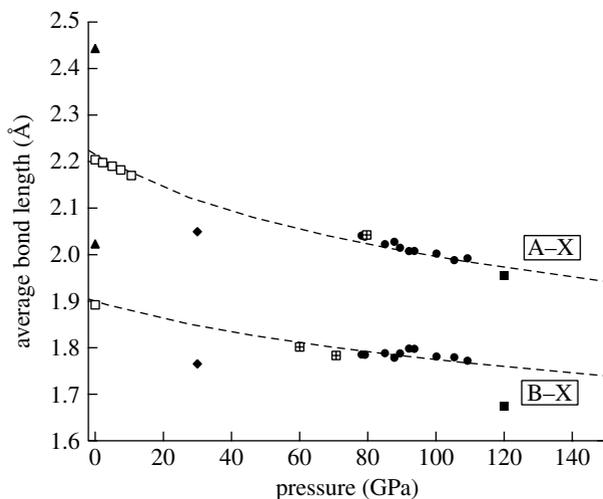


Figure 6. Average bond lengths from single-crystal X-ray diffraction, powder X-ray diffraction analysed by the Rietveld method and theoretical studies of ABX_3 post-perovskites and other phases. Filled circles indicate experimental data (Rietveld method) for $MgGeO_3$ (Kubo *et al.* 2008). Dashed line shows the results of 0 K theoretical calculations for $MgGeO_3$ (Kubo *et al.* 2008). Filled squares, $MgSiO_3$ post-perovskite at 120 GPa (theory; Tsuchiya *et al.* 2004); filled diamonds, $NaMgF_3$ pPv at 30 GPa (theory; Umemoto *et al.* 2006); filled triangles; single-crystal X-ray diffraction for $CaIrO_3$ pPv at ambient conditions (experiment; Rodi & Babel 1965); open squares, single-crystal X-ray diffraction for $MgSiO_3$ and $CaGeO_3$ perovskites (Sasaki *et al.* 1983; Ross & Hazen 1990); squares with plus, powder X-ray diffraction (Rietveld method) for α - PbO_2 -type GeO_2 and $MgSiO_3$ perovskite (Fiquet *et al.* 2000; Prakapenka *et al.* 2003; Shiraki *et al.* 2003).

ratios but the value for $CaIrO_3$ is considerably lower than that for the other materials. Rietveld structure refinements of X-ray diffraction data and/or density functional theory (DFT) calculations can be used to evaluate atomic-level structural parameters such as bond distances, angles and polyhedral volumes and distortion. A comparison of various structural parameters for diffraction studies of $MgGeO_3$, $MgSiO_3$, $NaMgF_3$ and $CaIrO_3$ pPvs has been reported (Kubo *et al.* 2008). This study found some similarities between $MgSiO_3$ and $MgGeO_3$ pPvs in axial ratios, averaged Mg–O distance, MgO_8 polyhedral volume and degree of octahedral distortion as well as consistency in elastic systematics and generally similar behaviour in axial compressibilities. Surprisingly, the $NaMgF_3$ pPv phase shows even closer similarities in structural parameters with $MgSiO_3$ pPv. As one example, figure 6 shows average A–X and B–X bond distances for these ABX_3 pPvs. Both $MgGeO_3$ and $NaMgF_3$ possess average distances similar to $MgSiO_3$, whereas $CaIrO_3$ differs markedly with considerably longer bond distances for both polyhedral sites. Considerable differences between the elastic properties of $CaIrO_3$ and $MgSiO_3$ have also been reported from theoretical calculations (Tsuchiya & Tsuchiya 2007b). Consideration of all these differences raises serious questions about the relevance of measurements on $CaIrO_3$ for understanding silicate pPvs. Further studies are needed to evaluate whether the deformational properties of this compound can be used reliably to make inferences about the behaviour of the corresponding silicate under deep Earth conditions.

4. MgO–SiO₂ liquids at deep mantle pressures

(a) Deep mantle melting

Melting is a ubiquitous process during early planetary evolution and a primary mechanism of planetary differentiation. The properties of silicate liquids are thus essential for understanding a wide range of geophysical phenomena related to the deep Earth and its origin and evolution. Energy deposited into the growing Earth by impacting planetesimals is likely to have produced strong heating and the presence of magma oceans at or below the Earth's surface during accretion appears inevitable (Tonks & Melosh 1993). There is evidence that early magma oceans were prevalent on Mars, the Moon and even many asteroids (Warren 1985; Righter & Drake 1996; Greenwood *et al.* 2005). On Earth, the subsequent cooling and crystallization of a magma ocean might have led to the chemical differentiation of the mantle (Ohtani 1985). Understanding the dynamics of a terrestrial magma ocean is essential to understand the initial conditions for the thermal and chemical evolution of the Earth (Tonks & Melosh 1993; Labrosse *et al.* 2007). The liquid viscosity and its depth dependence are among the important parameters that characterize an early (liquid-rich) magma ocean (Solomatov 2000). Viscosity controls the thermal state and dynamic processes in the magma ocean and influences its subsequent evolution and crystallization (Solomatov 2000). In the present mantle, partial melting may explain the ULVZs found in the D'' layer near the core–mantle boundary (Williams *et al.* 1998; Lay *et al.* 2004). Small degrees of partial melt distributed throughout the lower mantle could also provide an explanation for the high relative values of seismic shear anomalies compared with compressional anomalies (Duffy & Ahrens 1992a). Gravitationally stable partial melt layers have also been proposed in the upper mantle such as atop the 410 km discontinuity (Revenaugh & Sipkin 1994; Song *et al.* 2004; Matsukage *et al.* 2005), and this could help explain the geochemical differences between basalts from mid-ocean ridges and those from island arcs (Bercovici & Karato 2003).

One key question about melting in the deep Earth involves the density contrast between the solid and the melt. The buoyancy of the melt relative to the coexisting solid will be controlled by the molar volume change on melting, as well as compositional differences (i.e. Fe enrichment) between the melt and the solid. Enhanced compressibility of melts relative to solids can lead to density crossovers under mantle P – T conditions. Densities of silicate liquids have been studied using shock wave techniques (Rigden *et al.* 1984; Miller *et al.* 1991; Mosenfelder *et al.* 2007) or by sink–float methods in multi-anvil apparatus (Agee & Walker 1993; Ohtani & Maeda 2001; Agee 2008), and density inversions between silicate melts and equilibrium liquidus crystals have been identified (Rigden *et al.* 1984; Agee 1998). However, there are few constraints on possible density inversions under conditions of the Earth's lower mantle. While it has been proposed based on laboratory measurements to 15 GPa that basaltic melts may become denser than mantle peridotite at conditions near the base of the mantle (Ohtani & Maeda 2001), these results are subject to considerable uncertainty due to the long extrapolation involved. The existence of a dense magma ocean near the base of the mantle early in Earth's history could provide a means to generate the geochemical heterogeneities observed in the present-day mantle (Labrosse *et al.* 2007).

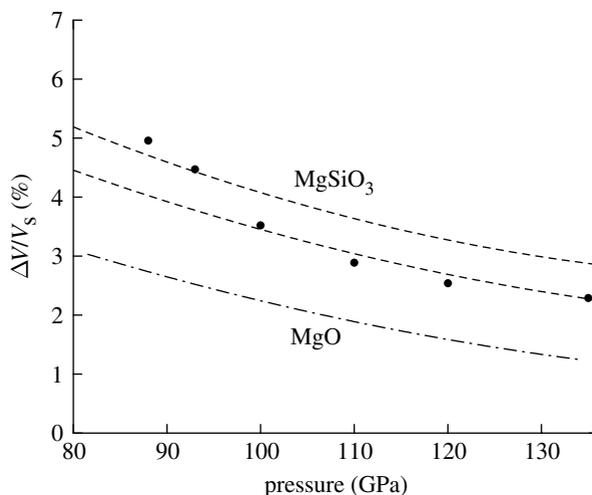


Figure 7. Molar volume difference between the liquid and the solid normalized to molar volume of the solid for MgSiO₃ and MgO liquids from recent first-principles simulations. For MgSiO₃, circles are from Wan *et al.* (2007) and correspond to 3500 K; dashed curves are from Stixrude & Karki (2005) for 3000 and 4000 K, respectively. Results for MgO (dot-dashed curve) are from Karki *et al.* (2006b).

Experimental studies of silicate liquids at deep mantle pressures are challenging. An alternative approach to the study of high-pressure liquid properties is to use computer simulations. Molecular dynamics (MD) simulations using semi-empirical intermolecular potentials have been used to compute densities and other properties of silicate melts (Wasserman *et al.* 1993; Lacks *et al.* 2007). These have the advantage that the semi-empirical potentials allow for long simulation times that are important for constraining transport properties. However, the reliability of the potentials used at high P and T must be evaluated carefully.

Recently, several studies (Stixrude & Karki 2005; Karki *et al.* 2006a,b; Wan *et al.* 2007; de Koker *et al.* 2008) have reported simulations of the properties of liquid silicates at deep mantle pressures using *ab initio* molecular dynamics simulations and DFT (Car & Parrinello 1985). These simulations allow for theoretical study from the first principles, i.e. without empirical or adjustable parameters of the properties of solid and liquid silicates at arbitrary conditions of pressure and temperature. DFT, in the local density approximation (LDA), or with its generalized gradient approximation (GGA) improvements, is the most advanced theoretical tool to predict the microscopic properties of materials. While many DFT studies have focused on static (zero-temperature) properties such as crystal structures and low-temperature elastic constants, it is now possible to carry out sufficient long runs at high temperatures using molecular dynamics to compute the required thermal averages necessary to obtain the structural and dynamic properties of high-temperature silicate liquids. For example, one recent simulation on MgSiO₃ liquid carried out runs for approximately 10 ps on a system containing 80 atoms (16 MgSiO₃ units; Wan *et al.* 2007).

Figure 7 compares the results of recent *ab initio* simulations of liquid MgSiO₃ and MgO. The plot shows the difference, ΔV , between the liquid molar volume, V_L , and the solid molar volume, V_S , normalized to the volume of the solid as a

function of pressure at 85–135 GPa. Temperatures in these simulations were between 3000 and 4000 K, and the pressures correspond to depths from approximately 1950 km to the core–mantle boundary. For both MgO and MgSiO₃, the volume difference between the liquid and the solid decreases with depth owing to the higher compressibility of the liquid than the solid. At 3500 K and 88 GPa, the density of crystalline MgSiO₃ in the perovskite structure is 5 per cent greater than liquid MgSiO₃, whereas the density excess is reduced to 2.9 per cent at 120 GPa and 5000 K (Wan *et al.* 2007). The absolute volumes calculated for liquid or solid MgSiO₃ are approximately 3–4 per cent different in the two recent studies (Stixrude & Karki 2005; Wan *et al.* 2007), and this is mostly due to the different approximations (LDA versus GGA) used in the DFT. The volume or density differences between the liquid and the solid are more directly comparable since both phases are calculated using the same DFT approximations.

The *ab initio* simulations to date for MgSiO₃ indicate that volumes of liquid MgSiO₃ remain 2–3 per cent greater than those of solid perovskite up to D'' conditions (Stixrude & Karki 2005; Wan *et al.* 2007). The transformation to a pPv structure is expected to further reduce the solid volume by 1–1.5 per cent (Oganov & Ono 2004; Shieh *et al.* 2006). For MgO, the volume excess of the liquid is approximately 1 per cent at the core–mantle boundary. A density crossover in MgSiO₃ relative to perovskite densities is not expected to occur until 180 GPa, and this would be even higher relative to pPv (Wan *et al.* 2007). These results imply that density crossovers due solely to the enhanced compressibility of the liquid relative to the solid are not expected for these compositions in the MgO–SiO₂ system. However, the convergence of solid and liquid volumes and densities with pressure will make it more plausible that chemical differences between the melt and the solid can lead to neutral or negatively buoyant liquids in the deep Earth. Fe is known to partition preferentially into the melt. Estimates of the solid–liquid partition coefficients for Fe needed to achieve neutral buoyancy in (Mg,Fe)SiO₃ compositions appear to be plausible based on very limited experimental data at lower mantle conditions (Wan *et al.* 2007).

Recent shock experiments on Mg₂SiO₄ forsterite and wadsleyite starting materials have been interpreted as producing melts that are denser than the corresponding solids (MgSiO₃ pPv and MgO) by 3.7 ± 3.0 per cent at 142 GPa and by 2.2 ± 1.8 per cent at 151 GPa, respectively, along the Hugoniot (Mosenfelder *et al.* 2007). These experimental results do not appear consistent with the molecular dynamics simulations discussed above, and further work is needed to understand these differences.

(b) Diffusivity and viscosity of MgO–SiO₂ liquids

Molecular dynamics simulations of liquid properties using either *ab initio* methods or semi-empirical potentials allow for determination of diffusivities from the mean-square displacements of the ions. Diffusivities control chemical reaction rates and are relevant to phenomena such as magma mixing, and crystal growth and dissolution. As with molar volumes, *ab initio* calculations provide insights into liquid behaviour over a much wider range of conditions that can be studied with current laboratory techniques alone.

Table 1. Diffusivities of selected oxide and silicate liquids from theory and experiment.

	P (GPa)	T (K)	D ($\text{cm}^2 \text{s}^{-1}$)	reference
<i>experiment</i>				
CaMgSi ₂ O ₆	15	2573	9.1×10^{-6}	Reid <i>et al.</i> (2003)
<i>theory</i>				
MgSiO ₃	5	4500–5000	$2\text{--}4 \times 10^{-5}$ (Si,O), $7\text{--}10 \times 10^{-6}$ (Mg)	Wasserman <i>et al.</i> (1993)
MgSiO ₃	47	3000	$2\text{--}3 \times 10^{-6}$ (Si,O), 7.3×10^{-6} (Mg)	Lacks <i>et al.</i> (2007)
MgSiO ₃	120	4000	4.6×10^{-6}	Wan <i>et al.</i> (2007)
MgSiO ₃	120	5000	3.3×10^{-5}	Wan <i>et al.</i> (2007)
MgO	19	3000	5.0×10^{-5} (O), 9.2×10^{-5} (Mg)	Lacks <i>et al.</i> (2007)
MgO	20	3000	$2\text{--}4 \times 10^{-5}$	Karki <i>et al.</i> (2006a)
MgO	105	3000	$1.5\text{--}6.5 \times 10^{-6}$	Karki <i>et al.</i> (2006a)
MgO	121	5000	$2\text{--}3 \times 10^{-5}$	Karki <i>et al.</i> (2006a)

Table 1 compares diffusivities of selected mantle-relevant compositions (CaMgSi₂O₆, MgSiO₃ and MgO) from experiment and theory over a range of P – T conditions. Comparison of data using different techniques and over different P – T ranges must be approached with caution. Nevertheless, a broad picture of the behaviour of diffusivities in these simple liquid systems is beginning to emerge from theoretical calculations. Results above 1 Mbar for both MgSiO₃ and MgO indicate that the temperature dependence of diffusivity remains strong at deep mantle conditions as a temperature change of 1000 K produces approximately an order of magnitude change in diffusivity (Karki *et al.* 2006a; Wan *et al.* 2007). This is a consequence of a stronger pressure dependence of diffusivity at lower temperatures (e.g. 3000 K) than at higher temperatures (e.g. 5000 K) (Karki *et al.* 2006a). Secondly, the diffusivities in MgSiO₃ and MgO liquids are broadly similar at these deep conditions. At approximately 120 GPa and 4000 K, the diffusivities range from approximately $5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ decreasing to $2\text{--}3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at the same pressure and 5000 K (Karki *et al.* 2006a; Wan *et al.* 2007).

A direct comparison of empirical potentials and *ab initio* results can be made at approximately 19 GPa and 3000 K for MgO (Karki *et al.* 2006a; Lacks *et al.* 2007). Under these conditions, Karki *et al.* (2006a) obtained diffusivities of approximately $2\text{--}4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ compared with values of $5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (for O) and $9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (for Mg) from the empirical calculations, which indicate that the MD simulations using empirical potentials are producing diffusivities about twice as large as the *ab initio* simulations. A direct comparison of theory and experiment is not possible at present. The *ab initio* simulations on diopside-composition liquids would be useful in order to compare theory more directly with experiments (Reid *et al.* 2001) and to constrain the pressure dependence of diffusivity in this system.

The viscosities of silicate liquids control melt transport. Estimates of viscosities can be obtained from mean diffusion coefficients from the Debye–Stokes–Einstein formula or Eyring equation. Viscosities of oxide and silicate liquids from experiment are compared with *ab initio* and semi-empirical molecular dynamics in table 2. Estimated viscosities in MgSiO₃ liquids at D''

Table 2. Viscosities of silicate liquids from theory and experiment.

	P (GPa)	T (K)	η (Pa s)	reference
<i>experiment</i>				
CaMgSi ₂ O ₆	8–13	2200–2470	0.028–0.51	Reid <i>et al.</i> (2003)
peridotite	3–13	2041–2523	0.019–0.13	Liebske <i>et al.</i> (2005)
peridotite	10 ⁻⁴	1850	0.126	Dingwell <i>et al.</i> (2004)
<i>theory</i>				
peridotite	10 ⁻⁴	5000	3 × 10 ⁻⁴	Dingwell <i>et al.</i> (2004)
MgSiO ₃	14	3000	0.013	Lacks <i>et al.</i> (2007)
MgSiO ₃	47	3000	0.178	Lacks <i>et al.</i> (2007)
MgSiO ₃	120	4500–5000	0.019–0.031	Wan <i>et al.</i> (2007)

conditions (120 GPa, 4000–5000 K) are broadly similar to values obtained at low pressures (approx. 10 GPa, 2400 K) from falling sphere experiments on a peridotite liquid and from empirical MD simulations (at approx. 14 GPa, 3000 K) on MgSiO₃ liquids (Liebske *et al.* 2005; Lacks *et al.* 2007). To the extent that these results are comparable, this implies that pressure and temperature effects are of roughly equal importance in controlling how viscosity changes at great depth. It may be that viscosities in the deep mantle are similar to values in the shallow mantle because the competing effects of pressure and temperature roughly balance. However, changes in melt structure with P and T mean that the viscosity may behave non-monotonically with depth. Again, *ab initio* calculations can yield important insights into how properties such as the coordination number vary over a wide range of P – T conditions (Stixrude & Karki 2005).

The use of theoretical molecular dynamics simulations to study silicate liquids in the deep Earth is still in its infancy. Nevertheless, the promise of the method has been demonstrated. Improvements in experimental methods have also been rapid, but it is not likely that experiments will approach conditions of the Earth's deep mantle in the near future. However, it is important that the theoretical calculations be tested and benchmarked by comparison with experimental studies at lower P – T conditions.

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