2.03 Mineralogy of the Earth – Phase Transitions and Mineralogy of the Lower Mantle

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2.03.1 Introduction

Until recently, experimental high-pressure mineral physics studies mainly focused on materials in the upper part of the mantle, because of technical restrictions in pressure and temperature generation and also in precise measurements of crystal structures and physical properties under the lower-mantle conditions. However, developments in technologies of both laser-heated diamond-anvil cell (LHDAC) and large-volume Kawai-type multianvil apparatus (KMA), combined with synchrotron radiation, have enabled us to quantitatively study phase transitions and some key physical properties of mantle minerals under the \( P,T \) conditions encompassing those of the whole mantle.

Progress in computational mineral physics based on \textit{ab initio} calculations has also been dramatic in the last decade in conjunction with the rapid advancement of computer technologies. Classical molecular dynamics calculations required \textit{a priori} assumptions on the...
parameters for interatomic model potentials, which largely rely on available experimental data. Quantum mechanical Hamiltonians of many-body electron systems can be efficiently and quantitatively evaluated on the basis of the density functional theory (DFT) (Hohenberg and Kohn, 1964; Kohn and Sham, 1965). Practical calculations of minerals having complex crystal structures can be achieved using various methods and techniques developed following the DFT. As a result of such advancement in \textit{ab initio} calculations, it is now possible to predict stability and some physical properties of high-pressure forms quantitatively with uncertainties that are even comparable to those attached in experimentally derived data, as was dramatically shown in a series of recent articles relevant to the postperovskite phase transition (Tsuchiya et al., 2004a, 2004b; Oganov and Ono, 2004; Iitaka et al., 2004).

Another reason for the relatively scarce mineral physics studies for the lower part of the mantle may originate from the fact that there has been no indication of the occurrence of major phase transitions under these conditions, except for those corresponding to uppermost (~660–800 km) and lowermost (~2700–2900 km; the D\textsuperscript{\textgamma} layer) parts of the lower mantle. This is in marked contrast to the nature of the mantle transition region, best described as “the key to a number of geophysical problems” by Birch (1952). Recent seismological studies, however, demonstrated that there are regions that significantly scatter seismic waves, which may be related to some unknown phase transitions and/or chemical boundaries at certain depths in the upper to middle regions of the lower mantle (e.g., Niu and Kawakatsu, 1996). In addition, both geochemical considerations and mantle dynamics simulations suggest that the mantle may be divided into chemically distinct regions by a boundary at 1500–2000 km depths in the lower mantle (e.g., Kellogg et al., 1999; Tackley, 2000; Trampert et al., 2004). Moreover, seismological studies with various methods of analysis have shown detailed structures in the D\textsuperscript{\textgamma} layer, demonstrating marked heterogeneity in both horizontal and vertical directions (Lay et al., 2004). Thus, there is growing evidence that the lower mantle is not featureless any more, and many mineral physicists have started to develop experimental and computational techniques for higher pressure and temperature conditions (with improved accuracy) in order to elucidate the mineralogy of the lower mantle.

In spite of the great efforts in both experimental and theoretical studies (mostly conducted in the last decade), our knowledge on the stability and mineral physics properties of high-pressure phases relevant to the lower mantle is still very limited compared with that on the shallower parts of the mantle. Although LHDACs are now capable of generating pressures and temperatures corresponding to, or even beyond, the mantle–core boundary, there remain a number of disagreements in phase equilibrium studies using this method with various techniques in heating, temperature/pressure measurements, phase identification, etc. Mineral physics parameters that constrain densities of high-pressure phases in the lower mantle have been accumulated thanks to the intense synchrotron sources, particularly those available at third-generation synchrotron facilities, such as ESRF, APS, and SPring-8, combined with both LHDAC and KMA, but those related to elastic wave velocities are scare to date.

In the present chapter, we briefly review recent progress and limitations in experimental and computational techniques in studying phase transitions and some key physical properties under the lower-mantle conditions. Then we summarize current knowledge on these properties obtained experimentally and/or theoretically using these techniques. We rather focus on the phase transitions and phase relations in simple silicates, oxides, carbonates, and hydrous systems closely related to the mantle and slab materials, because experimental measurements or theoretical predictions of other properties such as shear moduli and their pressure/temperature dependency are still limited for lower-mantle conditions. In contrast, equation of state (EoS) parameters, that is, zero-pressure densities, bulk moduli, and their pressure/temperature dependencies of some of the high-pressure phases are summarized, as far as reliable data are available. We also review the phase transitions and density changes in lithologies associated with the subduction of slabs and also those in the surrounding model mantle materials on the basis of experimental results on multicomponent systems. Some implications for the mineralogy of the lower mantle are discussed based on these data and those obtained for the simpler systems.

### 2.03.2 Experimental and Theoretical Backgrounds

#### 2.03.2.1 High-Pressure Technology

Two kinds of high-pressure devices, LHDAC and KMA, have been used to realize static high-pressure and high-temperature conditions of the lower mantle in the laboratory. The upper limit of high-pressure generation in LHDAC has been dramatically
expanded using a smaller anvil top (culet) with various shapes for utilizing the potential hardness of single-crystal diamond. As a result, generation of pressures of multimegabars can now be comfortably produced in some laboratories. Moreover, quasi-hydrostatic pressures are also available by introducing gas pressure media, such as Ar or He, which also serve as thermal insulators in heating samples with laser beams.

The quality of heating of samples in LHDAC has also been substantially improved using various laser sources, such as YAG, CO\textsubscript{2}, and YLF, with higher powers and more sophisticated computer-controlled feedback systems, as compared with the laser heating in early stages of its development in the 1970s and 1980s. These can now yield stable high temperature in a sample as small as \(~-100\) to several tens of micrometers in diameter and even smaller thickness.

Pressures produced in KMA studies (Kawai and Endo, 1970) using conventional tungsten carbide anvils have long been limited to 25–30 GPa, although the relatively large sample volume in this apparatus made it possible to precisely determine the phase transitions, some physical properties, melting temperatures, element partitioning, etc., of high-pressure phases. Temperatures up to 3000 K are also produced stably for hours or even a few days using various forms of heaters, such as C, LaCrO\textsubscript{3}, TiC, WC, and some refractory metals. In addition, both temperature and pressure gradients within the sample in KMA are believed to be far smaller than those in LHDAC.

Introduction of harder materials, that is, sintered bodies of polycrystalline diamonds (SD) with some binders, such as Co and Si, as the second-stage anvils of KMA has dramatically changed this situation. Using relatively large SD anvil cubes of over 10 mm in edge length, some laboratories are now able to produce pressures approaching 60 GPa at high temperatures using KMA (e.g., Ito et al., 2005), without sacrificing the advantage of the relatively large sample volumes in this apparatus. It is expected that pressures as high as \(~-100\) GPa may be produced in KMA, if SD anvils with larger dimensions are supplied on a commercial basis.

Applications of synchrotron radiation to both LHDAC and KMA started in the mid-1980s, when the second-generation synchrotron sources became available worldwide (e.g., Shimomura et al., 1984). A combination of white X-ray and an energy-dispersive system has been used for KMA experiments at synchrotron facilities, because geometrical constraints imposed by the tungsten carbide anvils and surrounding guide-block systems make it difficult to conduct angle-dispersive diffraction measurements. Use of the energy-dispersive method combined with a multi-channel analyzer has the merit of rapid acquisition and analysis of X-ray diffraction data, so that realtime observations of phase transitions are possible under high pressure and high temperature. Although this method is not very suitable for the precise determination of crystal structures (due to relatively low spatial resolutions in the diffraction peak position and also to significant variations in background X-ray with the energy range), some attempts have been successfully made to make crystal structure refinements using a combined step scanning and energy-dispersive measurements (Wang et al., 2004).

Identification of the phases present and precise determinations of the lattice parameters, and hence unit-cell volumes, of the high-pressure phases can be made by \textit{in situ} X-ray diffraction measurements. The \textit{in situ} pressure can also be monitored by the unit-cell volume changes in some reference materials, such as NaCl, Au, Pt, and MgO, using an appropriate EoS. Thus the phase boundaries and the \(P,V,T\) relations of a number of high-pressure phases relevant to lower-mantle mineralogy have been determined by \textit{in situ} X-ray measurements using KMA, although there remain some uncertainties in the estimated pressures due to the lack of reliable pressure scales, as reviewed later, particularly at pressures of the deeper parts of the lower mantle. The effect of pressure on the electromotive force of a thermocouple is another unresolved issue, which may yield an additional uncertainty in the pressure estimation based on these EoS’s.

Corresponding \textit{in situ} X-ray observations have also been made using LHDAC. As the geometrical restrictions on the X-ray paths are not so severe in this device, X-ray diffraction is measured with an angle-dispersion method using monochromatized X-ray. The X-ray beam is focused to generally \(~10–20\) \(\mu\m\) with collimating mirrors, and directed to the disk-shape sample with diameters of \(~20–200\) \(\mu\m\), depending on pressure ranges. YAG or ILF lasers with beam sizes of \(~10\) to several tens of micrometers are used in most of the synchrotron facilities. By adopting imaging plates (IPs) for X-ray exposure combined with data processing systems, rapid data acquisition and reductions are also possible. Thus, the phase identification and measurements of unit-cell parameters of high-pressure phases can be made by the combination of LHDAC and
synchrotron radiation at pressure and temperature conditions corresponding to the entire mantle (e.g., Murakami et al., 2004a).

The major uncertainty in the in situ X-ray observations with LHDAC arises from the possible large temperature gradients in the small thin sample. Some studies demonstrated that variations of temperature are not very large in the radial direction of the disk-shape sample, suggesting that the temperature uncertainty may be of the order of \(\sim 10\%\) or less of the nominal values, if the diameter of the laser beam is significantly larger than that of the X-ray beam (Shen et al., 2001). However, the temperature gradient in the axial direction of the sample can be substantially larger than this estimation (Irifune et al., 2005), depending on the nature and thickness of the thermal insulator or pressure medium, as diamond has very high thermal conductivity. It should also be noted that the high thermal conductivity of diamond makes it difficult to maintain high temperatures greater than \(\sim 2000\) K at pressures of the Earth’s core \((P > 300\) GPa\) in LHDAC, as the thickness of the thermal insulator becomes so thin that the sample cannot be efficiently heated by laser.

### 2.03.2.2 Ab Initio Calculation

*Ab initio* approaches are those that solve the fundamental equations of quantum mechanics with a bare minimum of approximations. DFT is, in principle, an exact theory for the ground state and allows us to reduce the interacting many-electron problem to a single-electron problem (the nuclei being treated as an adiabatic background). A key to the application of DFT in handling the interacting electron gas was given by Kohn and Sham (1965) by splitting the kinetic energy of a system of interacting electrons into the kinetic energy of noninteracting electrons plus some remainder, which can be conveniently incorporated into the exchange-correlation energy.

The local density approximation (LDA) replaces the exchange-correlation potential at each point by that of a homogeneous electron gas with a density equal to the local density at the point. The LDA works remarkably well for a wide variety of materials, especially in the calculations of EoS’s, elastic constants, and other properties of silicates. Cell parameters and bulk moduli obtained from well-converged calculations often agree with the experimental data within a few percent and \(\sim 10\%\), respectively. Agreement with the laboratory data is not perfect, however, and some systematic discrepancies are noted for some materials.

Attempts to improve LDA via introducing nonlocal corrections have yielded some success. The generalized gradient approximation (GGA; Perdew et al., 1992, 1996) is a significantly improved method over LDA for certain transition metals (Bagno et al., 1989) and hydrogen-bonded systems (Hamann, 1997; Tsuchiya et al., 2002, 2005a). There is some evidence, however, that GGA improves the energetics of silicates and oxides but the structures can be underbound. The volume and bulk modulus calculated with GGA tend to be larger and smaller, respectively, than those measured experimentally (Hamann, 1996; Demuth et al., 1999; Tsuchiya and Kawamura, 2001). Considering the thermal effect with zero-point motion, LDA provides the structural and elastic quantities much closer (typically within a few percent) to experimental values than those obtained with GGA. In addition, a discrepancy of about \(10 \sim 15\) GPa is usually seen in transition pressures calculated with LDA and GGA (Hamann, 1996; Tsuchiya et al., 2004a, 2004c), which provide lower and upper bounds, respectively. Experimental transition pressures are usually found between the values obtained with LDA and GGA, although GGA tends to provide the pressure with better fit to the experimental value than LDA (Hamann, 1996; Tsuchiya et al., 2004a, 2004c). The main source of computational error can be attributed to how to treat the exchange-correlation potential.

The standard DFT has limitations in applying to Fe-bearing oxides and silicates in the following case. One-electron approximation with the standard DFT approaches fails to describe the electronic structure of Fe–O bonding correctly due to its strongly correlated behavior. Both LDA and GGA usually produce metallic bands for Fe–O bonding in silicates. They also do not provide the correct crystal field effects that break the d-orbital degeneracy. More sophisticated classes of technique, such as LDA + U, LDA + DMFT (dynamical mean-field theory), multi-reference configurational interaction, etc., are needed to treat the many-body effect of electrons more accurately and to investigate geophysically important iron-bearing systems.

Among these schemes, LDA + U (Anisimov et al., 1991) is the most practical method for minerals under the current state of computer technology. The main problem of applying LDA + U to materials under pressure is the determination of the effective
Hubbard U parameter, meaning screened on-site Coulomb interaction. Tsuchiya et al. (2006) computed the effective U in magnesiowüstite (Mg$_{1-x}$Fe$_x$)O in a nonempirical and internally consistent way based on a linear response approach for the occupancy matrix (Cococcioni and de Gironcoli, 2005). Thus, the ab initio LDA + U technique appears to open a new way to explore the mineral physics properties of iron-bearing systems relevant to the Earth’s deep interior (see Chapter 2.13).

### 2.03.2.3 Pressure Scale

The construction of an accurate pressure standard is a critical issue in the quantitative measurements of mineral physics properties under high pressure. The pressure ($P$)–volume ($V$)–temperature ($T$) equation of state (PVT-EoS) of materials is most useful in evaluating the experimental pressures under the $P,T$ conditions of the Earth’s deep mantle. The EoS of a pressure standard is usually derived on the basis of a conversion of dynamical shock Hugoniot data to isothermal compression data. In principle, some parameters specifying the thermal properties of a solid are necessary for this conversion process of the Hugoniot. However, measurements of these parameters without any pressure and also temperature standards are virtually impossible. In all EoS’s presently used as primary pressure standards, the conversion of the Hugoniot was therefore performed with some simple assumptions about the unknown high-pressure behavior of the conversion parameters. The most critical issue on the validity of such assumptions is the volume dependence of the thermal Grüneneisen parameter, which is a fundamental quantity characterizing the thermal effect on the material.

The characteristic properties of gold (Au), namely its low rigidity, simple crystal structure, chemical inertness, and structural stability, make it particularly suitable as a pressure standard under high $P,T$ conditions, and it has therefore been used as a primary standard in many in situ X-ray diffraction studies (e.g., Mao et al., 1991; Funamori et al., 1996). However, some recent in situ experiments noted that the pressure values estimated by different thermal EoS’s of gold show significant discrepancies. Using the EoS of gold proposed by Anderson et al. (1989), which is frequently used as the pressure scale in experiments using multianvil apparatus, Irifune et al. (1998a) first reported that the postspinel phase boundary of Mg$_2$SiO$_4$ shifted to about 2.5 GPa lower than the pressure corresponding to the depth of the 660 km seismic discontinuity (~23.5 GPa and ~2000 K). Similar results were obtained for other various minerals as summarized in Irifune (2002).

Tsuchiya (2003) predicted the thermal properties and the PVT-EoS of gold based on the ab initio theory including thermal effect of electrons. The state-of-the-art ab initio calculation showed that the relationship $\gamma/\gamma_0 = (V/V_0)^q$, assumed in some studies, is adequate for gold, at least up to $V/V_0 = 0.7$ and the predicted value of $q$ was 2.15, which is intermediate between the values used in Heinz and Jeanloz (1984) and Anderson et al. (1989). According to this study, the ab initio EoS model reduced the discrepancies between the observed phase boundaries of spinel, ilmenite, and garnet, and the seismic discontinuity. However, a gap of about 0.7 GPa still remains between the postspinel transition pressure and that of the 660 km discontinuity. The similar conclusions with a slightly larger (1.0–1.4 GPa) discrepancy have also been obtained by an experimental study using an empirical PVT-EoS model of MgO to determine pressure (Matsui and Nishiyama, 2002).

Even for gold, there are several PVT models derived by different groups, which are still not mutually consistent. Such a problem is also found in EoS’s of platinum (Jamieson et al., 1982; Holmes et al., 1989). Moreover, platinum appears to be unsuitable for the pressure scale in some cases, because of its reactivity with the sample or materials of the experimental cell at high $P,T$ conditions (Ono et al., 2005a). A similar problem is also encountered with the pressures obtained using MgO. The pressures obtained using EoS’s of different materials therefore show a significant scatter. Akahama et al. (2002) determined the pressures based on room-temperature EoS’s of several materials compressed simultaneously in a diamond-anvil cell and reported that the EoS of platinum proposed by Holmes et al. (1989) provided pressures more than 10 GPa higher than those calculated using EoS of gold as proposed by Anderson et al. (1989) at pressures of a megabar even at 300 K. A similar inconsistency has also been reported in pressure determination based on gold and silver EoS’s (Akahama et al., 2004).

Examples of the difference in pressures based on different EoS’s of gold and platinum are shown in Figure 1, along a temperature (2300 K) close to the typical lower-mantle geotherm. The pressures evaluated based on various EoS’s of gold differ by ~2–3 GPa at the pressures of the uppermost parts of the lower mantle (25–30 GPa), and are within...
the following section. As the experimental data on the phase transitions are still limited and controversial at \( P, T \) conditions of the lower mantle, we have tried to construct the most likely phase diagrams for the minerals with simple chemical compositions based on available laboratory data and \textit{ab initio} calculations. Thermoeelastic properties of some key high-pressure phases are also reviewed and summarized here, as far as experimental data or theoretical predictions are available.

\subsection{MgSiO\textsubscript{3}}

The high-pressure orthorhombic perovskite polymorph of MgSiO\textsubscript{3} (Mg-Pv) is believed to be the most abundant mineral in the Earth’s lower mantle. The possibility of a further phase transition of this phase under the lower-mantle \( P, T \) conditions has been controversial. Some studies suggested that Mg-Pv dissociates into an assemblage of SiO\textsubscript{2} and MgO at \( 70–80 \text{ GPa} \) and \( 3000 \text{ K} \) (Meade \textit{et al.}, 1995; Saxena \textit{et al.}, 1996) or that it undergoes a subtle phase change above \( 83 \text{ GPa} \) and \( 1700 \text{ K} \) (Shim \textit{et al.}, 2001b), while others claimed that Mg-Pv is stable almost throughout the lower mantle (e.g., Fiquet \textit{et al.}, 2000). However, more recent studies suggested that the result of Shim \textit{et al.} (2001b) were due to misidentification of the diffraction peaks of a newly formed platinum carbide (Ono \textit{et al.}, 2005a). The dissociation of Mg-Pv into the oxides is also unlikely to occur in the Earth’s mantle according to the subsequent experimental (Murakami \textit{et al.}, 2004a, 2005; Oganov and Ono, 2004) studies. Theoretical investigations also suggest that the dissociation should occur at extremely high pressure above \( 1 \text{ TPa} \) (Umemoto \textit{et al.}, 2006).

Recently, the Pv to postperovskite (PPv) transition in MgSiO\textsubscript{3} was found to occur by \textit{in situ} X-ray diffraction experiment using LHDAC and \textit{ab initio} calculations at \( \sim 2500 \text{ K} \) and \( \sim 125 \text{ GPa} \) (Murakami \textit{et al.}, 2004a; Murakami \textit{et al.}, 2004a; Oganov and Ono, 2004) (Figure 2), close to the \( P–T \) conditions of the \( D_0^\ast \) layer near the core–mantle boundary (CMB). The Mg-PPv phase has a crystal structure identical to that of CaIrO\textsubscript{3} with a space group Cmcm. This structure consists of silica layers stacking along the \( b \)-direction and intercalated Mg ions. In the silica layers, SiO\textsubscript{6} octahedra connect sharing edges along the \( a \)-direction and sharing corners along the \( c \)-direction. Thus, this structure is more favorable at high pressure than the Pv structure, although the cation coordinations are basically same in both structures.
The PPv structure is expected to be highly anisotropic. It is more compressible along the b-direction perpendicular to the silica layers because only ionic Mg–O bonding exists in the interlayer spacing. The Pv and PPv structures therefore look very different in this respect. However, the structural relationship between Pv and PPv is quite simple and by applying shear strain ε_b, Pv can change to PPv directly (Tsuijita et al., 2004a). According to this relation, the ε-direction remains unchanged via the structural transition. This suggests that nonhydrostaticity could significantly affect the transition kinetics of the Pv-to-PPv transition.

PPv’s thermodynamic properties and the position and slope of the phase boundary were investigated by means of ab initio quasiharmonic free energy calculations (Tsuijita et al., 2004a, 2005b). The predicted Clapeyron slope of the Pv–PPv transition was ~7.5 MPa K⁻¹, which is remarkably close to that required for a solid–solid transition to account for the D’ discontinuity (Sidorin et al., 1999). Thus the results of both experimental and theoretical studies suggest that the PPv should be the most abundant high-pressure phase in the D’ region.

Over the past decades, there have been a number of experiments to determine elastic property of Mg-Pv (e.g., Yagi et al., 1982; Mao et al., 1991; Yeganeh-Haeri et al., 1989; Ross and Hazen, 1990; Funamori et al., 1996; Fiquet et al., 2000). Among these experiments, early studies yielded relatively large variations for zero-pressure bulk modulus K₀ of Mg-Pv ranging from 254 GPa (Ross and Hazen, 1990) to 273 GPa (Mao et al., 1991). However, more recent experiments of static compression and Brillouin spectroscopy yielded mutually consistent K₀ values of ~253–264 GPa. Density functional calculations have reported similar but slightly smaller room-temperature bulk modulus for Mg-Pv of about 250 GPa (Wentzcovitch et al., 2004; Tsuijita et al., 2004b, 2005b). This underbinding tendency for Mg-Pv is seen in standard density functional calculations but is much more prominent in GGA than in LDA (Wentzcovitch et al., 2004).

In contrast to the extensive investigations of the EoS of Mg-Pv, the EoS of Mg-PPv has not been well constrained experimentally. According to a density functional prediction, the zero-pressure volume of Mg-PPv is very close to that of Mg-Pv (Tsuijita et al., 2004a, 2005b). However, K₀ and its pressure derivative of Mg-PPv are significantly smaller and larger than those of Mg-Pv, respectively, which implies the volume of Mg-PPv should be smaller than that of Mg-Pv at the relevant pressure range. The volume decrease associated with the Pv–PPv transition is estimated to be ~1.5% on the basis of ab initio calculations (Tsuijita et al., 2004a), which is consistent with those estimated based on LHDAC experiments.

2.03.3.1.2 MgSiO₃–FeSiO₃

Mg-Pv is supposed to incorporate 5–10 mol.% of FeSiO₃ in peridotitic compositions in the lower mantle (Irfune, 1994; Wood and Rubie, 1996; Katsura and Ito, 1996). However, experimental studies for the system MgSiO₃–FeSiO₃ have been limited to the pressures of the uppermost part of the lower mantle, except for an LHDAC study (Mao et al., 1991). Recent developments in KMA with sintered diamond anvils substantially extend the pressure and temperature ranges for phase equilibrium studies (as reviewed earlier), and Tange (2006) extensively studied the phase relations and the Mg–Fe partitioning between coexisting Mg-Pv and magnesiowüstite (Mw) at pressures up to ~50 GPa and temperatures to 2300 K.

Immediately after the discovery of the Pv–PPv transition in MgSiO₃, the effects of iron on this transition were studied using LHDAC (Mao et al., 2004, 2005). It was noted that the presence of iron significantly reduces the stability pressure of PPv, and PPv with up to ~80 mol.% of the FeSiO₃ component was synthesized at a pressure of ~140 GPa and at temperatures of ~2000 K (Mao et al., 2005). Thus the phase relations in the system MgSiO₃–FeSiO₃ at pressure up to ~130 GPa and at a typical lower-mantle temperature can be drawn as illustrated in Figure 3, according to the results of these and
transition pressure of ~50 GPa (Ono et al., 2005b). This transition pressure is significantly lower than the Pv–PPv transition pressure in MgSiO$_3$. Thus the presence of iron in the trivalent state is also suggested to lower the pressure of the Pv–PPv transition, as is found for divalent iron.

2.03.3.1 $\text{MgSiO}_3$–$\text{Al}_2\text{O}_3$

Irifune (1994) demonstrated that Mg-Pv is the major host of aluminum in a pyroelite composition at pressures and temperatures of the uppermost parts of the lower mantle, possessing ~4 mol.% of Al$_2$O$_3$. Phase relations in the system MgSiO$_3$–Al$_2$O$_3$ under the lower-mantle conditions have since been studied (Irifune et al., 1996a; Ito et al., 1998) with an emphasis on the MgSiO$_3$–Mg$_3$Al$_2$Si$_3$O$_{12}$ system. Irifune et al. (1996a) showed that majorite garnet with less than ~15 mol.% Al$_2$O$_3$ transforms to the Pv structure via a mixture of these two phases, while this assemblage further changes to an assemblage of majorite plus corundum at pressures about ~28 GPa, at 1800 K. This assemblage with the Mg$_3$Al$_2$Si$_3$O$_{12}$ composition was later shown to form almost pure Pv at ~38 GPa using KMA with SD anvils (Ito et al., 1998).

Phase transitions in Al$_2$O$_3$ corundum under the lower-mantle condition were first studied by Funamori and Jeanloz (1997) using LHDAC based on earlier ab initio predictions (Martin and Cohen, 1994; Thomson et al., 1996), which demonstrated that corundum transforms to a new phase with the Rh$_2$O$_3$($\mathrm{ii}$) structure at ~100 GPa and at ~1000 K. More recently, it has been predicted by ab initio studies that Al$_2$O$_3$ has a similar high-pressure phase relation to Fe$_3$O$_3$ (Caracas and Cohen, 2005a; Tsuchiya et al., 2005c; Stackhouse et al., 2005b). The Pv-to-PPv transition was thus suggested to occur in Al$_2$O$_3$ at about 110 GPa at 0 K, although the Pv phase is eclipsed by the stability field of the Rh$_2$O$_3$($\mathrm{ii}$) phase. This Pv-to-PPv transition pressure in Al$_2$O$_3$ is about 10 GPa higher but fairly close to that in MgSiO$_3$, though Akber-Knusen et al. (2005) predicted a much larger effect of Al by estimating the solid solution energy. In situ X-ray diffraction experiments on pyroelite compositions by LHDAC (Tateno et al., 2005) demonstrated a consistent result about the effect of aluminum incorporation on the PPv transition pressure. Therefore, we expect that though aluminum tends to increase the PPv transition pressure in MgSiO$_3$, the effect is not very significant.

The plausible phase diagram of the system MgSiO$_3$–Al$_2$O$_3$ in the lower-mantle $P,T$ condition is illustrated in Figure 4.
2.03.3.1.4 MgO–FeO

MgO–FeO is believed to be the next major mineral phase in Earth’s lower mantle after ferrosilicate Pv, (Mg$_{1-x}$Fe$_x$)SiO$_3$ (e.g., Helffrich and Wood, 2001). The magnesium end member of Mw, periclase, possessing the B1 (NaCl) structure is known to be an extraordinarily stable phase. No phase transitions in this material have been observed or predicted under the $P$, $T$ conditions of the entire mantle (Duffy et al., 1995; Alfe et al., 2005), primarily due to substantially smaller ionic radius of magnesium relative to that of oxygen. FeO wüstite, on the other hand, transforms to an antiferromagnetic phase accompanied by a small rhombohedral distortion. This transition is a typical magnetic order–disorder transition and therefore the transition temperature corresponds to the Neel point. Although the rhombohedral B1 (rB1) phase is stable at low temperatures up to about 110 GPa, at higher pressure over 65 GPa and high temperatures, the rB1 phase transforms to the normal or inverse B8 (NiAs) structure, as shown in Figure 5 (Fei and Mao, 1994; Murakami et al., 2004b; Kondo et al., 2004). However, several important properties of this high-pressure phase such as high-temperature stability, structural details, and electronic property are still in debate (Fei and Mao, 1994; Mazin et al., 1998; Murakami et al., 2004b).

For the compositions between these two end members, some controversial experimental results have emerged: Mw with $X_{Fe} = 50\%$ was reported to dissociate into two components, Fe-rich and Mg-rich Mw’s at 86 GPa and 1000 K (Dubrovinsky et al., 2000). In contrast, another study using LHDAC found no dissociation of Mw with even higher $X_{Fe}$ of 0.61 and 0.75 up to 102 GPa and 2550 K, though the sample with $X_{Fe} = 0.75$ showed a displacive transition to the rB1 structure at low temperature similar to FeO wüstite (Lin et al., 2003). Thus, further experimental and theoretical studies are required to address the possible dissociation of Mw.

Another issue relevant to Mw, as well as the ferrosilicate Pv, which should affect thermoelastic properties of these phases, is the occurrence of electron spin transitions under the lower-mantle conditions. High spin (HS) to low spin (LS) transitions in iron have been observed by in situ X-ray emission spectroscopy (XES) and Mössbauer spectroscopy from 40 to 70 GPa in Mw containing about 18\% of iron (Badro et al., 2003; Lin et al., 2005) and from 70 and 120 GPa in (Mg,Fe)SiO$_3$ Pv (Badro et al., 2004; Li et al., 2004; Jackson et al., 2005) at room temperature. Several significant effects on thermochemical state of the lower mantle can be inferred by the spin transition of iron. The spin transition in Mw is accompanied by significant volume reductions (Lin et al., 2005; Tsuchiya et al., 2006) and changes in these

Figure 4 A predicted phase diagram for the system MgSiO$_3$–Al$_2$O$_3$ at lower mantle pressures and at 2300K. The phase relations below ~40 GPa are based on KMA experiments (Irifune et al., 1996a; Ito et al., 1998), while those on Al$_2$O$_3$ are from Funamori et al. (1998) using LHDAC and ab initio calculations by Tsuchiya et al. (2005c). The results of Tateno et al. (2005) and Tsuchiya et al. (2005c) were also taken into account to illustrate the phase relations at 120-130 GPa. Cor, corundum; Rh, Rh$_2$O$_3$(II).

Figure 5 High $P$, $T$ phase diagram for FeO at lower-mantle pressures summarized based on the in situ measurement by Fei and Mao (1994), Murakami et al. (2004b), and Kondo et al. (2004). B1, NaCl structure; B8, NiAs structure; Rhomb, rhombohedral B1 phase.
minerals' optical absorption spectrum (Badro et al., 2004). These can produce (1) seismic velocity anomalies, (2) variations in Mg–Fe$^{2+}$ partitioning between Mw and Pv, (3) changes in radiative heat conductivity, and (4) compositional layering (Gaffney and Anderson, 1973; Badro et al., 2003, 2004). The elastic signature of this transition in Mw has been partially explored (Lin et al., 2005), but there is still much uncertainty. In contrast, anomalous compression behavior has not yet been observed in $(\text{Mg,Fe})\text{SiO}_3$ Pv.

The strongly correlated behaviour of iron oxide has deterred the quantification of these changes by density functional calculations based on the local spin density (LSDA) and spin polarized generalized gradient approximations ($\sigma$-GGA). These approaches incorrectly predict a metallic HS ground state and then successive spin collapses across the transition as reported for FeO (Sherman and Jansen, 1995; Cohen et al., 1997). More recently, a new model explaining the mechanism of HS-to-LS transition of iron in Mw has been proposed based on calculations using more sophisticated LDA + U technique that describe the electronic structure of strongly correlated system more correctly (Tsuchiya et al., 2006). In this study, the effective Hubbard U parameter has been optimized at each volume and at each iron concentration up to $X_{Fe}$ of 18.75% in an internally consistent way. As a result, it has been demonstrated that the large stability field of HS/LS mixed state appears at high temperatures instead of the intermediate spin state, due to the contributions of coexisting HS/LS mixing entropy and magnetic entropy. According to this transition mechanism, Mw is expected to be in this HS/LS mixed state for almost the entire range of lower-mantle $P,T$ conditions, with the proportion of HS iron decreasing continuously with increasing pressure (Figure 6). No discontinuous change in any physical properties would appear associated with the spin transition in Mw within this range.

It has been reported that the spin transition pressure significantly increases with increasing $X_{Fe}$. A volume decrease associated with the spin transition was observed in $(\text{Mg}_{0.4}\text{Fe}_{0.6})\text{O}$ at 95 GPa (Lin et al., 2005), while no spin transition has so far been reported in pure FeO up to 143 GPa (Badro et al., 1999). Iron–iron interactions, which are no longer negligible at $X_{Fe}$ higher than 20%, might also reinforce the magnetic moment significantly, although the mechanism of this tendency has not been fully understood to date.

![Figure 6](image_url)  
**Figure 6** High $P,T$ spin transition diagram for Mw with iron concentration of 18.75% at lower-mantle pressures predicted on the basis of LDA + U calculations by Tsuchiya et al. (2006). HS, high spin; LS, low spin.

### 2.03.3.1.5 CaSiO$_3$

The lower mantle is believed to consist mainly of $(\text{Mg,Fe})\text{SiO}_3$ Pv and Mw, with some CaSiO$_3$ perovskite (Ca-Pv) up to 7–8 vol.% (e.g., Irifune, 1994). Despite its importance, there are many unanswered questions about the structure, stability, the EoS, and other physical properties of Ca-Pv under pressure and temperature, which complicate some attempts to model the mineralogy of the lower mantle (Stacey and Isaak, 2001).

CaSiO$_3$ crystallize to the Pv structure over 10–13 GPa, depending on temperature, and is known to be unquenchable at ambient conditions. At lower-mantle conditions, CaSiO$_3$ has an ideal cubic Pv structure, while at lower temperatures it is suggested to be slightly distorted. The small degree of the possible distortion is hardly observed by current high-temperature and high-pressure X-ray techniques, and several orthorhombic and tetragonal structures have been proposed, based on *in situ* X-ray diffraction measurements (Shim et al., 2002b; Kurashina et al., 2004; Ono et al., 2004) or theoretical calculations (Stixrude et al., 1996; Chizmeshya et al., 1996; Magyari-Köpe et al., 2002; Caracas et al., 2005).

EoS of Ca-Pv has been determined up to CMB pressures by different groups (e.g., Mao et al., 1989; Tamai and Yagi, 1989; Wang et al., 1996; Shim et al., 2000a, 2000b, 2002b; Kurashina et al., 2004; Ono et al., 2004; Shihe et al., 2004). The fitting of the experimental results by third-order Birch–Murnaghan EoS, yielded a unit-cell volume, $V_0 = 45.54$ Å$^3$, bulk modulus, $K_0$, ranging from 232 to 288 GPa, and its pressure derivative, $K'_0$, within 3.9–4.5. Most of the recent results with careful removing of the effect of deviatoric stress on the produced pressure, however, yielded the lower end values (232–236 GPa; Wang...
molecular dynamics studies (Li et al., 2006a, 2006b) reported very different results. They found the tetragonal phase stable even at the mantle temperatures in addition to the low-temperature stability of the orthorhombic phase. Their calculated elasticity of Ca-Pv is also very different from earlier results (Karki and Crain, 1998), particularly with respect to the shear modulus. The cause of the discrepancies is unclear.

### 2.03.3.1.6 SiO₂

Recent theoretical studies suggested that a second-order displacive phase transition from stishovite to the CaCl₂-type structure occurs at 50–60 GPa at room temperature (Kingma et al., 1995). It has also been predicted that the CaCl₂-type silica undergoes a further structural transition to the α-PbO₂ phase (Dubrovinsky et al., 1997; Karki et al., 1997a). The results of the experimental studies on these issues, however, have been controversial. LHDAC studies reported that the CaCl₂-type phase persists at least up to 120 GPa (Andrault et al., 1998), and the transition to the α-PbO₂ phase occurs at 121 GPa and 2400 K (Murakami et al., 2003). In contrast, another similar experiment showed that the α-PbO₂-like phase was formed from cristobalite above 37 GPa at room temperature, and that stishovite directly transformed to the α-PbO₂-type structure above 64 GPa at 2500 K with a negative Clapeyron slope (Dubrovinsky et al., 2001). In addition, Sharp et al. (1999) found the α-PbO₂-type phase in a natural meteorite sample, which would have experienced very low shock pressure below 30 GPa. These discrepancies may come from various difficulties in LHDAC experiments, such as associated with kinetic problems, temperature or pressure uncertainties, effect of different starting materials, etc.

During the last decade, a series of theoretical studies (Kingma et al., 1995; Dubrovinsky et al., 1997; Karki et al., 1997a) also addressed this issue of the post-stishovite phase transitions in the framework of the ab initio calculations. These early theoretical studies were limited to static conditions, the calculations being performed at \( T = 0 \) K, without considering the zero-point energy. To investigate the contradictory experimental results on the high-temperature phase stability of SiO₂ under high pressure, finite temperature thermal effect on the transitions obtained by these static calculations should be taken into account.

Tsuchiya et al. (2004c) predicted the high-pressure and high-temperature phase equilibrium of
three ordered modifications of SiO$_2$ using *ab initio* density functional perturbation theory and the quasiharmonic approximation. The predicted stishovite–CaCl$_2$ phase transition boundary is $P = 56 + 0.0059 T$ (K) GPa, which is consistent with the results of LHDAC experiment by Ono et al. (2002). This predicted slope of the stishovite–CaCl$_2$ boundary of about $5.9 \text{MPa K}^{-1}$ is close to but slightly larger than the earlier rough estimate of $4 \text{MPa K}^{-1}$ (Kingma *et al*., 1995). The LHDAC experiment resulting in a stishovite–α-PbO$_2$ boundary with a negative Clapeyron slope (Dubrovinsky *et al*., 2001), which disagrees with the phase diagram based on Tsuchiya *et al*. (2004c), as shown in Figure 8. This disagreement may be due to experimental uncertainties and/or to kinetic problems in the former LHDAC experiment. These are supported by later calculations by Oganov *et al*. (2005), though they proposed substantially lower transition pressures primarily due to the application of LDA (see Section 2.03.2.2).

On the other hand, the phase transition boundary between CaCl$_2$ and α-PbO$_2$ in SiO$_2$ is predicted to be $P = 106.3 + 0.00579 T$ (K) GPa based on *ab initio* calculations (Tsuchiya *et al*., 2004c), which locates near the lowermost-mantle $P, T$ conditions. This calculation also indicates that the α-PbO$_2$-type phase is the stable form of silica at depths down to the CMB, consistent with the result of an LHDAC experiment (Murakami *et al*., 2003). These theoretical and experimental results also suggest that the α-PbO$_2$-type phase silica recently discovered in the meteorite sample might have been formed by a metastable reaction.

2.03.3.1.7 *Al-rich phase*

Majorite garnet is the main host of aluminum in the mantle transition region in both pyrolite and basaltic compositions. It transforms to an assemblage of Mg-Pv + Ca-Pv at pressures corresponding to the uppermost lower mantle. Aluminum is incorporated mostly in Mg-Pv in pyrolite composition (Irifune, 1994), whereas a separate aluminous phase is formed in basaltic compositions under the $P, T$ conditions of the lower mantle, as demonstrated by Irifune and Ringwood (1993).

The aluminous phase, named as ‘Al-rich phase’ by these authors, was suggested to have a crystal structure similar to but not completely identical to the calcium ferrite structure. This Al-rich phase was later proposed to have a hexagonal structure or NAL-phase (Miyajima *et al*., 2001; Akaogi *et al*., 1999; Sanheira *et al*., 2005), whereas others proposed that this phase possesses the calcium ferrite structure (Kesson *et al*., 1998; Hirose *et al*., 1999; Ono *et al*., 2005d). Although the stability relations of these two phases in MORB compositions are not very clear to date, only very minor effects on the mineralogy and dynamics in the lower mantle is expected by the possible misidentification of these two phases under the lower-mantle conditions (Sanheira *et al*., 2005; Shinmei *et al*., 2005), as the crystal structures of these two phases are quite similar and yield only slight difference in densities.

2.03.3.2 Minor Minerals

2.03.3.2.1 *MgAl$_2$O$_4*, NaAlSiO$_4$*

MgAl$_2$O$_4$ spinel is known to decompose to simple oxides of MgO and Al$_2$O$_3$ at pressure and temperatures of mantle transition region, which recombine to form a calcium ferrite (CaFe$_2$O$_4$, CF) type phase at about 25 GPa (Irifune *et al*., 1991; Funamori *et al*., 1998; Akaogi *et al*., 1999). Although the formation of an unknown phase named ε-phase (Liu, 1978) was reported at a similar pressure at 1300 K in LHDAC experiments, none of the subsequent LHDAC and KMA experiments using both quench and *in situ* X-ray measurements have confirmed this phase. Instead, it has been shown that the CF-phase further transforms to a calcium titanate (CaTiO$_4$, CT) phase at pressures of ~40–45 GPa (Funamori *et al*., 1998). An *ab initio* periodic LCAO (linear combination of atomic orbitals) calculation by Catti (2001) demonstrated that the calcium titanate structure is indeed stable.
relative to the calcium ferrite structure at pressures greater than $\sim$39–57 GPa.

NaAlSi$_4$O$_8$ also adopts the calcium ferrite structure at pressures above 25 GPa (Liu, 1977; Akaogi et al., 1999), but the formation of the complete solid solutions between this and MgAl$_2$O$_4$ has not been reported, as there is a region of the hexagonal phase in the intermediate region of these end-member compositions (Akaogi et al., 1999; Shinmei et al., 2001). It was demonstrated that the CF-type NaAlSi$_4$O$_8$ is stable at least at pressures up to 75 GPa and temperatures to 2500 K on the basis of LHDAC experiments (Tutti et al., 2000).

2.03.3.2.2 KAAlSi$_2$O$_8$, NaAlSi$_2$O$_8$

KAAlSi$_2$O$_8$-rich feldspar, an important mineral in K-rich basalt (e.g., Wang and Takahashi, 1999) and continental crust and marine sediment lithologies (Irifune et al., 1994), transforms to the hollandite structure via a mixture of K$_2$Si$_3$O$_5$ wadite + Al$_2$O$_3$ kyanite + SiO$_2$ coesite at about 9 GPa. KAAlSi$_2$O$_8$ hollandite plays an important role in fractionation of some trace elements because of its peculiar tunnel structure that accommodates large ion lithophile elements (Irifune et al., 1994). Although an LHDAC study suggested that this structure is stable almost throughout the lower-mantle $P,T$ conditions (Tutti et al., 2001), recent in situ X-ray diffraction studies using DAC with a helium pressure medium at room temperature (Ferroir et al., 2006) and KMA at high pressure and high temperature demonstrated that the hollandite transforms to an unquenchable phase, named as hollandite II (Sueda et al., 2004), at about 22 GPa at room temperature with a positive Clapeyron slope. Although only a slight modification in crystal structures between these phases was noted (Ferroir et al., 2006), this transition may significantly affect partitioning of some trace elements between the K-hollandite and coexisting melts in the lower mantle.

NaAlSi$_2$O$_8$-rich hollandite was found in shock veins of some meteorites (e.g., Tomioka et al., 2000; Gillet et al., 2000). However, attempts to reproduce the hollandite with such compositions by high-pressure experiments have failed (Yagi et al., 1994; Liu, 2006), as the solubility of this component is limited to about 50 mol.% at pressures of $\sim$22 GPa and at temperatures up to 2500 K. Thus this phase could have been formed metastably in a very short period of time under shock compression in the parental bodies of these meteorites.

2.03.3.2.3 CAS phase

The ‘CAS phase’ was first described by Irifune et al. (1994) as a new Ca- and Al-rich high-pressure phase in a continental crust composition at pressures above $\sim$15 GPa, which was suggested to be a major host for aluminum and calcium in the subducted marine sediments in the mantle transition region. Subsequent experimental studies demonstrated that this phase has the ideal composition of CaAl$_2$Si$_2$O$_8$, possessing a hexagonal barium ferrite-type structure with space group $P6_3/mmc$ (Gautron et al., 1999). Moreover, this high-pressure phase with a composition of (Ca$_3$Na$_{1-x}$Al$_{1+x}$Si$_3$)$_{11}$O$_{11}$ was recently discovered in a shergottite shocked Martian meteorite in association with stishovite and/or K, Na-rich hollandite (Beck et al., 2004), both of which are known to be stable only at pressures above $\sim$9 GPa.

The CAS phase is suggested to have silicon in fivefold coordination in a trigonal bipyramid site at high pressure and high temperature, which is supposed to decompose into fourfold and sixfold coordinations upon quenching and subsequent release of pressure (Gautron et al., 1999). In situ Raman spectroscopy and X-ray diffraction measurements actually indicated the formation of fivefold coordinated silicon under pressure, which should play an important role in the transport properties of minerals through the formation of oxygen vacancies (Gautron et al., 2005).

2.03.3.2.4 Phase D, 8-AlOOH

Phase D was first noted by Liu (1986) as a new dense hydrous magnesium (DHMS) phase in serpentine, which was later confirmed by in situ X-ray diffraction (Irifune et al., 1996b). Both X-ray power diffraction profile and the chemical composition of this phase were also refined on the quenched sample (Irifune et al., 1996b; Kuroda and Irifune, 1998). Two groups subsequently succeeded in refining its crystal structure independently (Yang et al., 1997; Kudoh et al., 1997). The stability of phase D has since been studied experimentally using both KMA (Ohtani et al., 1997; Irifune et al., 1998b; Frost and Fei, 1998) and LHDAC (Shieh et al., 1998), which demonstrated that this phase has a wide stability field up to 40–50 GPa, at temperatures to $\sim$1800 K, whereas it dehydrates to form an assembly containing Mg-Pv and Mw at higher temperatures (Shieh et al., 1998).

Serpentine is the major hydrous mineral in the subducted slab, and phase D should be the only possible DHMS present in the upper part of the lower mantle transported via the subduction of slabs.
(Isshiki et al., 1998b; Shieh et al., 1998; Ohtani et al., 2004), although the newly found $\delta$-AlOOH (Suzuki et al., 2000) could be an alternative water reservoir in the lower mantle under very limited Al-rich circumstances. For both phase D and $\delta$-AlOOH, structural changes associated with hydrogen bond symmetrization are expected to occur on the basis of $ab$ initio calculations (Tsuchiya et al., 2002, 2005a), which should affect the compressional behavior and hence density changes of these hydrous phases in the lower mantle.

### 2.03.3.2.5 MgCO$_3$, CaCO$_3$

Carbonates are important constituents of pelagic sediments, parts of which are supposed to subduct into the mantle. It has been shown that MgCO$_3$ magnesite is the major carbonate in the mantle (e.g., Bielmann et al., 1993), whose stability under high pressure has been studied using LHDAC. Magnesite was reported to be stable at pressures up to 80 GPa, almost throughout the lower mantle (Gillet, 1993, Fiquet et al., 2002), but a recent in situ X-ray diffraction study demonstrated it transforms to an unknown phase (magnesite II) at pressures above $\sim$115 GPa, at 2000–3000 K (Isshiki et al., 2004). Although the dissociation of magnesite into assemblages of MgO + CO$_2$ (Fiquet et al., 2002) or MgO + C + O$_2$ (Liu, 1999) was suggested on the basis of thermodynamic considerations, such reactions are unlikely to occur along appropriate geotherms in the lower mantle (Isshiki et al., 2004).

In contrast, certain amounts of CaCO$_3$ could survive in the subducted slabs without decarbonation or reaction with surrounding minerals, due to low temperatures of the slabs, and thus are delivered into the lower mantle. CaCO$_3$ adopts the aragonite structure under $P,T$ conditions of the uppermost mantle, which was recently found to transform to a high-pressure form with an orthorhombic symmetry at pressures greater than $\sim$40 GPa and at temperatures 1500–2500 K using LHDAC (Ono et al., 2005c). Although the possibility of the transformation of CaCO$_3$ aragonite to a trigonal phase is suggested on the basis of DAC experiments at room temperature (Santillán and Williams, 2004), this phase could have been metastably formed, and the orthorhombic post-aragonite phase should be stable at least to depths of $\sim$2000 km in the lower mantle (Ono et al., 2005c). Thus, MgCO$_3$ and possibly CaCO$_3$ are the potential hosts of CO$_2$ throughout most parts of the lower mantle, except for the bottom parts of the D" layer (Isshiki et al., 2004).

### 2.03.4 Phase Transitions and Density Changes in Mantle and Slab Materials

#### 2.03.4.1 Chemical Compositions and Density Calculations

Subducting oceanic lithosphere is modeled by layers of basaltic oceanic crust of $\sim$6 km thickness, underlain by thicker layers ($\sim$50–100 km) of residual harzburgite and fertile lherzolite, which are covered with thin ($\sim$1 km) terrigenous and/or pelagic sediments. Typical chemical compositions of these lithologies are listed in Table 1. Most parts of the sedimentary materials are believed to be trapped to form accretion terrains underneath island arcs upon subduction of slabs at ocean trenches, although geochemical evidence suggests that certain parts of such materials may be subducted deeper into the mantle (e.g., Loubet et al., 1988). At least part of the bottom warmer lherzolite layer of a slab may also be assimilated to the surrounding mantle during subduction in the upper mantle and mantle transition region, and thus the slab approaching the 660 km seismic discontinuity can reasonably be modeled by a layered structure of basaltic and harzburgitic rocks (Ringwood and Irifune, 1988).

The chemical composition of the lower mantle has been a major controversial issue in the mineralogy of the Earth’s interior. Some (e.g., Ringwood, 1962) believe peridotitic or pyrolitic materials are dominant in the whole mantle, while others (e.g., Liu, 1982; Anderson, 1989; Hart and Zindler, 1986) claim that more Si-rich chondritic materials should be representative for the composition of the lower mantle (Table 1). The difference is based on rather philosophical arguments on the origin and subsequent differentiation processes of the Earth, which are critically dependent on the models of condensation/evaporation processes of elements and compounds in the primordial solar system and the possible formation of deep magma ocean in the early stage of the formation of the Earth. As the elastic properties, particularly those related to shear moduli, of high-pressure phases have not been well documented under the pressure and temperature conditions of the lower mantle, it is hard to unambiguously evaluate the feasibility of these two alternative composition models in the light of mineral physics and seismological observations (e.g., Bina, 2003; Mattern et al., 2005). Moreover, the knowledge of variation of temperature with depth is vital to address this issue, which also has not been well constrained in the lower mantle.
Here, we assume the whole mantle is of a pyrolitic composition to address the phase transitions and associated density changes in the lower mantle, as there are significant variations in the chondritic/cosmochemical models and also because high-pressure experimental data on the latter compositions have been scarce to date. We also assume the major lithologies transported into the lower mantle via subduction of slabs are of mid-ocean ridge basalt (MORB) and harzburgite compositions. Phase transitions in MORB have been extensively studied down to the depths near the mantle–core boundary. In contrast, although virtually no experimental data exist on harzburgite compositions in this depth region, they can be reasonably estimated from those available on the high-pressure phases with simple chemical compositions, as harzburgitic compositions have a minor amount of Fe and only very small amounts of Ca, and Al, and are well approximated by the MgO (FeO)–SiO$_2$ system.

We calculated the density changes in pyrolite, harzburgite, and MORB compositions using available experimental data as follows. The densities of the individual high-pressure phases that appeared in these lithologies were calculated at given pressures using the thermal EoS combining third-order Birch–Murnaghan EoS and Debye theory along an appropriate geotherm, using the PVT-EoS parameters given in Table 2. The resultant density changes of individual phases along the geotherm are depicted in Figure 9. The density changes in the bulk rocks were then calculated using the proportions of the individual phases with pressure along the geotherm.

### Table 1

Representative chemical compositions of lower mantle and those related to subducting slabs

<table>
<thead>
<tr>
<th>Lower mantle</th>
<th>Chondrite</th>
<th>Pyrolite</th>
<th>Harzburgite</th>
<th>MORB</th>
<th>Continental crust</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>53.8</td>
<td>44.5</td>
<td>43.6</td>
<td>50.4</td>
<td>66.0</td>
</tr>
<tr>
<td>TiO$_2$</td>
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<td>0.2</td>
<td></td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>3.8</td>
<td>4.3</td>
<td>0.7</td>
<td>16.1</td>
<td>15.2</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.4</td>
<td>0.4</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>3.5</td>
<td>8.6</td>
<td>7.8</td>
<td>7.7</td>
<td>4.5</td>
</tr>
<tr>
<td>MgO</td>
<td>35.1</td>
<td>38.0</td>
<td>46.4</td>
<td>10.5</td>
<td>2.2</td>
</tr>
<tr>
<td>CaO</td>
<td>2.8</td>
<td>3.5</td>
<td>0.5</td>
<td>13.1</td>
<td>4.2</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.3</td>
<td>0.4</td>
<td></td>
<td>1.9</td>
<td>3.9</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.1</td>
<td></td>
<td></td>
<td>0.1</td>
<td>3.4</td>
</tr>
</tbody>
</table>

MORB, mid-ocean ridge basalt.
Chondrite, Liu (1982); pyrolite, Sun (1982); harzburgite, Michael and Bonatti (1985); MORB, Green et al. (1979); continental crust, Taylor and McLennan (1985).

### Table 2

PVT-EoS parameters of lower-mantle phases determined from various experimental and theoretical data and their systematics

<table>
<thead>
<tr>
<th></th>
<th>Mg-Pv</th>
<th>Fe-Pv</th>
<th>Al$_2$O$_3$-Pv</th>
<th>Mg-PPv</th>
<th>Ca-Pv</th>
<th>MgO</th>
<th>FeO</th>
<th>SiO$_2$ (St)</th>
<th>SiO$_2$ (x-PbO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_0$ (cm$^3$ mol$^{-1}$)</td>
<td>24.45</td>
<td>25.48</td>
<td>24.77</td>
<td>24.6</td>
<td>27.45</td>
<td>11.36</td>
<td>12.06</td>
<td>14.02</td>
<td>13.81</td>
</tr>
<tr>
<td>$B_0$ (GPa)</td>
<td>257</td>
<td>281</td>
<td>232</td>
<td>226</td>
<td>236</td>
<td>158</td>
<td>152</td>
<td>314</td>
<td>325</td>
</tr>
<tr>
<td>$B_9$ (GPa)</td>
<td>4.02</td>
<td>4.02</td>
<td>4.3</td>
<td>4.41</td>
<td>3.9</td>
<td>4.4</td>
<td>4.9</td>
<td>4.4</td>
<td>4.2</td>
</tr>
<tr>
<td>$\Theta_0$ (K)</td>
<td>1054</td>
<td>854</td>
<td>1020</td>
<td>1040</td>
<td>984</td>
<td>725</td>
<td>455</td>
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<tr>
<td>$\gamma$</td>
<td>1.48</td>
<td>1.48</td>
<td>1.48</td>
<td>1.55</td>
<td>1.53</td>
<td>1.52</td>
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<td>$q$</td>
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<td>1.2</td>
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<td>1.2</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>2.4</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Mg-Pv (Shim and Duffy, 2000; Fiquet et al., 2000; Sinogeikin et al., 2004; Tsuchiya et al., 2004a, 2005b), Fe-Pv (Jeanloz and Thompson, 1983; Parise et al., 1990; Mao et al., 1991; Kiefer et al., 2002), Al$_2$O$_3$-Pv (Thomson et al., 1996; Tsuchiya et al., 2005c), Mg-PPv (Tsuchiya et al., 2004a, 2005b), Ca-Pv (Wang et al., 1996; Shim et al., 2000b; Karki and Crain, 1998), MgO (Fiquet et al., 1999; Sinogeikin and Bass, 2000), FeO (Jackson et al., 1990; Jacobsen et al., 2002; systematics), SiO$_2$ (Ross et al., 1990; Andrault et al., 2003; Karki et al., 1997a; Tsuchiya et al., 2004c).

High-$T$ Birch–Murnaghan equation was applied only for the hexagonal aluminous phase with parameters $V_0=110.07$ cm$^3$ mol$^{-1}$, $B_0=185.5$ GPa, $B_9=4$ (fix), $dB/dT=-0.016$ GPa K$^{-1}$ and $\alpha_0=3.44 \times 10^{-6}$ K$^{-1}$ (Sanehira et al., 2005).
Although some recent studies suggested that sub-adiabatic temperature gradients are required to match the observed and calculated density and bulk sound velocity for pyrolitic compositions (Bina, 2003; Mattern et al., 2005), we simply assumed adiabatic, while the calculated density changes of density changes in major minerals constituting structure in a peridotite composition are very close to but slightly lower than those of the corresponding phases in pyrolite, which are not shown in this figure. Dots represent the densities in PREM. Hex, hexagonal aluminous phase.

The mineral proportion changes in pyrolite, harzburgite, and MORB compositions are shown in Figure 10, while the calculated density changes of these lithologies are depicted in Figure 11. The density changes at pressures lower than 30 GPa are based on an earlier estimate of Irifune (1993), using the similar method and mineral physics parameters. Although the density change in pyrolite seems to agree well with that of PREM (Dziewonski and Anderson, 1981), the latter estimate inevitably has significant uncertainties, as this density profile is rather indirectly determined from seismic velocities with some assumptions. The calculated density values may also have significant errors mainly due to the uncertainty in the geotherm stated in the above. Nevertheless, mineral physics parameters to constrain the density have been reasonably well determined, mostly on the basis of in situ X-ray diffraction measurements, and the differences among these calculated density profiles are regarded as robust results.

2.03.4.2 Phase and Density Relations

2.03.4.2.1 Pyrolite

Figure 10(a) illustrates the phase transitions in pyrolite as a function of depth. Pyrolite transforms from an assemblage of ringwoodite (Rw) + majorite garnet (Mj) + Ca-Pv under the P,T conditions of the mantle transition region to that of Mg-Pv + Ca-Pv + Mj + Mw at depths near the 660 km seismic discontinuity. The spinel to post-spinel transition in this composition has actually been believed to occur at pressures near 23.5 GPa, at a temperature of \( \sim 2000 \) K, on the basis of quench experiments (e.g., Irifune, 1994). The slope of this phase transition boundary has also been determined by both quench experiments (Ito and Takahashi, 1989) and calorimetric measurements (Akaogi and Ito, 1993), yielding a value of \( c. -3 \) MPa K\(^{-1}\). Although some recent studies suggested somewhat lower transition pressures and larger Clapeyron slope, the spinel to post-spinel transition is generally believed to be the main cause of the 660 km discontinuity, which is followed by the smeared-out transition of majorite to Pv over a pressure interval of \( \sim 2 \) GPa (Irifune, 1994, Nishiyama et al., 2004).

Mg-Pv is stable throughout most regions of the lower mantle, but it is found to transform to the Mg-Ppv with the CaIrO\(_3\) structure in a peridotite composition at pressures close to those near the top of the D\(^*\) layer. A small density jump of about 1–1.5% is expected to occur associated with this transition in the lower mantle. Ca-Pv, on the other hand, is likely to remain in the Pv structure throughout the lower mantle. On the other hand, Mw remains in the rock salt (B1) structure at pressures to \( \sim 80 \) GPa, where it may transform to the NiAs (B8) structure if iron concentration is very high (Fei and Mao, 1994). An HS-to-LS transition has also been suggested to occur in this phase over the pressure range of the entire lower mantle, as shown in Figure 6, which may yield an additional gradual density increase over this interval and also affect partitioning of iron between this phase and the ferrosilicate Pv.
Although element partition data among the coexisting phases under the lower-mantle conditions have been limited to those below ~30 GPa in KMA for the pyrolite composition (e.g., Irifune, 1994; Wood, 2000), some results have also been obtained using LHDAC combined with ATEM at higher pressures (e.g., Murakami et al., 2005; Ono et al., 2005d). These studies demonstrated that the presence of a minor amount (~5 wt.%) of Al$_2$O$_3$ in Mg-Pv has dramatic effects on the partitioning of iron between Mg-Pv and Mw, in addition to those on the compressibility of Mg-Pv. Nevertheless, the variations in iron partitioning between the two phases would not cause any significant changes in the bulk density of the pyrolitic mantle (e.g., Bina, 2003). Some changes in the iron partitioning between Mg-Pv and Mw have also been suggested upon the Pv–PPv transition in a recent LHDAC study (Murakami et al., 2005), but it may also yield invisible effects on the density change in the pyrolitic bulk composition.

### Harzburgite

Harzburgite, with Mg# (= Mg/(Mg + Fe) × 100) = ~92 as listed in Table 1, crystallizes to form an assemblage of ~80% olivine and ~20% orthopyroxene at depths of the uppermost mantle, which transforms to Mg-Pv and Mw near the 660 km discontinuity via an assemblage of Rw + Mj + akimotoite (Akm, ilmenite form of MgSiO$_3$) as shown by Irifune.
and Ringwood (1987). Although no experimental data have been available at pressures higher than 26 GPa, the nature of the phase transition in this composition can be evaluated based on the changes in these two phases under the lower-mantle conditions. The result estimated along the adiabatic geotherm is shown in Figure 10(b), which shows that this lithology is less dense than pyrolite throughout the lower mantle except for a very limited region immediately below the 660 km discontinuity (Iriyune and Ringwood, 1987), where the density relation reverses due to the completion of the spinel to post-spinel transition at lower pressures in the harzburgite composition.

It is likely that Fe significantly lowers the Pv–PPv transition pressure (Mao et al., 2004, 2005), while the presence of Al seems to increase this transition pressure (Tsuchiya et al., 2005; Tateno et al., 2005), as shown in Figures 2–4. In harzburgite compositions, Mg-Pv should have less alumina and iron contents as compared with those of Mg-Pv in pyrolite under the lower-mantle conditions. Thus the pressures of the Pv–PPv transitions in these two compositions may be close to each other due to the opposite effects of Fe and Al, although further detailed experimental studies on these compositions are needed to resolve this issue.

2.03.4.2.3 MORB

Phase transitions in basaltic compositions, such as illustrated in Figure 10(c) for a MORB composition, are quite different from those expected in pyrolite and harzburgite compositions. Basaltic compositions are shown to crystallize to Mj + small amounts of stishovite (St) in the mantle transition region (Iriyune and Ringwood, 1987, 1993; Hirose et al., 1999; Ono et al., 2001), which progressively transform to an assemblage of Ca-Pv + Mg-Pv + St + Al-rich phase (hexagonal or CF/CT structures) over a wide pressure range of ~3 GPa (from ~24 to ~27 GPa). Although the garnetite facies of MORB, composed mainly of Mj, is substantially denser than pyrolite, a density crossover is expected to occur in a limited depth range (660 to ~720 km) at the uppermost lower mantle due to this smeared-out nature of the garnetite-to-Pv transition in MORB.

Once Ca-Pv and Mg-Pv are formed in basaltic compositions, it is shown that they become denser than pyrolite or peridotite throughout almost the entire region of the lower mantle (Iriyune and Ringwood, 1993; Hirose et al., 1999, 2005; Ono et al., 2001, 2005d). As St is highly incompressible (Figure 9), the density of the perovskite facies of basaltic compositions may approach that of the pyrolitic composition with increasing pressure. However, the transition of St to CaCl2 (CC) and α-PbO2 (AP) structures should keep this lithology denser than pyrolite throughout the lower mantle, as shown in Figure 11. In fact, most recent experimental studies using LHDAC (Ono et al., 2005d; Hirose et al., 2005) conclude that densities of basaltic compositions are higher than those in the representative model mantle compositions throughout the lower mantle by about 0.02–0.08 g cm−3, depending on the adopted pressure scale for gold.

2.03.5 Mineralogy of the Lower Mantle

2.03.5.1 The 660 km Discontinuity

The 660 km seismic discontinuity is a globally recognized feature, and is the sharpest among the proposed discontinuities throughout the whole mantle. The cause of this discontinuity, chemical or phase transition boundary, has been a major controversial issue in Earth sciences as stated earlier, but the detailed experimental study based on quench experiments using KMA strongly suggested that this is caused by the spinel to post-spinel transition in a pyrolite or peridotitic mantle (Ito and Takahashi, 1989; Iriyune, 1994). The experimental data on the sharpness, pressure, and Clapeyron slope of this phase transition all seemed to be consistent with those estimated from seismological observations.

However, some recent experimental, seismological, and geodynamics studies cast some doubt on the simple idea of the phase transition. Precise in situ X-ray diffraction measurements using KMA demonstrated that this transition occurs at pressures somewhat (~2.5–1 GPa) lower than that correspond to the 660 km discontinuity (Iriyune et al., 1998a; Matsui and Nishiyama, 2002; Nishiyama et al., 2004; Fei et al., 2004; Katsura et al., 2003), although some LHDAC experiments reported that the phase transition pressure is consistent with that of the discontinuity (Shim et al., 2001a; Chudinovskikh and Boehler, 2001). Seismological observations also suggest this discontinuity is divided into several discontinuities in some areas (Simmons and Gurrola, 2000), which cannot be explained by the spinel to post-spinel transition alone.

Moreover, recent in situ X-ray diffraction measurements have suggested that the Clapeyron slope of the spinel to post-spinel transition is significantly
larger ($-2$ to $-0.4$ MPa K$^{-1}$; Katsura et al., 2003; Fei et al., 2004; Litasov et al., 2005) than previously thought ($-3$ MPa K$^{-1}$; Ito and Takahashi, 1989; Akagi and Ito, 1993) and ab initio prediction ($-2$ MPa K$^{-1}$; Yu et al., 2006). If this is the case, it should be difficult to trap the subducted slabs underneath many subduction zones near this boundary, known as ‘stagnant slabs’ (e.g., Fukao et al., 1992, 2001; Zhao, 2004), in the light of geodynamics calculations (e.g., Davis, 1998). Moreover, the observed depth variations of the 660 km discontinuity sometimes reach $\sim$ 30–40 km (e.g., Flanagan and Shearer, 1998), which corresponds to a temperature difference of $\sim$ 1000 K if we adopt $dP/dT = -1$ MPa K$^{-1}$ for the spinel–post-spinel transition boundary. Such a temperature difference between subducting slabs and the surrounding mantle near the 660 km discontinuity should be too large to be accounted for by seismological tomographic observations and also by any reasonable models of thermal structures of the subducting slabs.

Nevertheless, considering the uncertainties in pressure and temperature measurements in the in situ X-ray observations in KMA due to unresolved problems on the pressure scales and temperature measurements at high pressure using thermocouple emf, it is generally accepted that the 660 km discontinuity can be explained by the spinel–post-spinel transition in a pyrolitic mantle. Recent studies also suggested possibilities of elucidating the multiple nature and the depth variation of the 660 km discontinuity by reactions involving akimotoite at relatively low temperatures (Weidner and Wang, 2000; Hirose, 2002). In this case, the high velocity/density gradients shown in some representative seismological models at depths of 660–750 km may be largely explained by the smeared-out transition of majorite to perovskite in pyrolite over this depth interval (Irfune, 1994).

Models with chemical composition changes may reconcile the contradictory experimental and seismological observations regarding the 660 km discontinuity. If the spinel–post-spinel transition does occur at pressures lower than that of 660 km ($\sim$ 2.35 GPa) by, for instance, 1 GPa, the phase discontinuity should locate at about 630 km in a pyrolite mantle. As the oceanic crust component of the subducted slab, modeled by the MORB composition, becomes less dense than the surrounding pyrolite mantle immediately below this depth as shown in Figure 11, it should have been buoyantly trapped on this primordial ‘630 km discontinuity’ at the initial stage of the onset of operation of plate tectonics.

The delamination and accumulation of the former oceanic crust, transformed to garnetite in the mantle transition region, can be enhanced by its plausible different viscosity relative to the surrounding mantle (Karato, 1997) and extremely slow reaction kinetics upon transition to the denser phase assemblage including Mg-Pv (Kubo et al., 2002). Continuation of this process of trapping basaltic crust over a couple of billion years should yield a thick (on average $\sim$ 50–100 km, depending on the production rates of oceanic crust and efficiency of the trapping) layer of garnetite near the 630 km discontinuity. The garnetite layer develops both upward and downward from this primordial discontinuity if it isostatically floats on this boundary. The bottom of this garnetite layer eventually reaches 660 km, under which the harzburgite portion of the subducted slab should be present. In fact, a recent mineral physics study suggests the uppermost lower mantle can be Mg rich as compared with the deeper regions (Bina, 2003).

Accumulation of oceanic crust above the 660 km seismic discontinuity was originally proposed by Anderson (1979) to form an eclogite layer in the lower half of the upper mantle and throughout the mantle transition region, who later confined it to the latter region and favored more mafic lithology named ‘piclogite’ (e.g., Anderson and Bass, 1986; Duffy and Anderson, 1989). Ringwood (1994) also proposed the presence of a thin (c. < 50 km) layer of former basaltic crust immediately above the lower mantle, as a result of accumulation of relatively young and warm slab materials at the 660 km discontinuity. The above model of thicker garnetite layer is thus in between those proposed by these authors. Precise measurements of elastic-wave velocities on these lithologies under the $P, T$ conditions of the mantle transition region are needed to further test these hypotheses.

### 2.03.5.2 Middle Parts of the Lower Mantle

The uppermost part of the lower mantle is believed to be structurally and chemically heterogeneous due to the presence of stagnant slabs (Fukao et al., 1992, 2001; Zhao, 2004) which were originally proposed as ‘megoliths’ on the basis of high-pressure experimental studies (Ringwood and Irfune, 1988; Ringwood, 1994). Moreover, there are some areas where slabs seem to penetrate deep into the lower mantle by tomographic images (e.g., van der Hilst et al., 1997; Fukao et al., 2001), which should contribute to the observed reflection,
refraction, or conversion of seismic waves at these depths. Thus, the presence of subducted slabs in the uppermost lower mantle may at least partly contribute to the transitional nature of the seismic velocities for a depth interval between 660 and ~750 km in some global models of the velocity profiles.

In the deeper parts of the lower mantle, discontinuous changes in seismic velocities have also been suggested to occur, particularly at depths 900–1200 km beneath some subduction areas (Kawakatsu and Niu, 1994; Niu and Kawakatsu, 1996; Kruger et al., 2001; Kaneshima, 2003). As there are no major phase transitions in the mantle material modeled by pyrolite as shown in Figure 10(a), such discontinuous changes are most likely to be related to the subducted slab materials. Both basaltic and underlain harzburgite layers of such slabs should yield locally high acoustic impedance to produce seismic discontinuities, because these are likely to be related to the subducted slab materials. Both basaltic and harzburgite materials seem to have seismic velocities higher than those of the mantle material (e.g., Bina, 2003), in addition to their lower temperatures compared to the surrounding mantle.

In further deeper parts of the lower mantle (~1200–1850 km in depth), the presence of seismic scattering bodies with a low-velocity signature was recognized (Kaneshima and Helffrich, 1999, 2003; Vinnik et al., 2001). As shown earlier, the most notable phase transition in major minerals in subducted slab and the surrounding mantle materials is the rutile to CaCl₂ transition of SiO₂ in subducted former oceanic crust under the P, T conditions of the middle part (~1600 km, corresponding to pressures of ~70 GPa; Tsuchiya et al., 2004c) of the lower mantle. A significant shear softening is expected to occur in stishovite associated with this phase transition (Karki et al., 1997b; Andraulr et al., 1998; Shieh et al., 2002). Thus, this transition in subducted basaltic material may explain the signatures of the scatterers observed in the middle part of the lower mantle.

In contrast, tomographic imaging and other seismological studies demonstrate that only little anomalous changes in seismic velocities exist in the middle to lower part of the lower mantle except for regions related to subducted slabs and rising plumes (e.g., Grand et al., 1997; Zhao, 2004; Mattern et al., 2005). As shown in the previous section, no major phase changes have been reported in Mg-Pv, Ca-Pv, and Mw at pressures up to ~120 GPa, except for the slight distortion of cubic Ca-Pv to a tetragonal structure and the possible HS-to-LS transition and the dissociation of Mw. It is expected that the transition in Ca-Pv may not occur at temperatures of the lower mantle, while the spin transition in Mw should occur continuously over a wide pressure range as shown in Figure 7 and Figure 6, respectively. Accordingly, both of these transitions would not cause any notable seismic velocity changes in this region, although further study is required to address the effects of the possible dissociation of Mw. Thus, the relatively homogeneous nature in seismic velocity distributions in the middle to lower part of the lower mantle is consistent with the absence of major phase transitions in the mantle material.

On the other hand, seismological, geochemical, and geodynamical studies suggest that there should be a chemically distinct region at depths below 1500–2000 km, presumably due to iron enrichment related to the primitive mantle materials or interaction with the rising hot plumes (e.g., Kellogg et al., 1999; Ishii and Tromp, 1999; Trampert et al., 2004). Attempts have been made to estimate the chemical composition of the lower mantle by mineral physics tests (e.g., Jackson and Rigden, 1998; Bina, 2003; Mattern et al., 2005), comparing calculated densities and bulk sound velocities of various compositions with those obtained seismologically. However, it is difficult to constrain the chemical composition of the lower mantle without reasonable estimations of thermal structures in this region and of shear properties of the relevant high-pressure phases. Actually, a wide range of chemical compositions from peridotite to chondrites can be accommodated for the acceptable geotherms, although anomalously high X₃₄ (Mg/(Mg + Fe)) and low X₃₄ (Si/(Mg + Fe)) and low X₄₈ and high X₅₄ are suggested in the uppermost and lowermost ~200 km of the lower mantle, respectively (Bina, 2003).

The possible iron and silica rich nature in the bottom part of the lower mantle may reflect the heterogeneous chemical composition and mineralogy of this region. These silicon-rich signatures can be explained by the presence of subducted oceanic crust materials in this layer, which is denser than the surrounding pyrolitic or harzburgitic lower-mantle materials, as shown in Figure 11. Actually, the CaCl₂→α-PhO₂ transition in SiO₂ is calculated to take place at 120–125 GPa and 2000–2500 K (Tsuchiya et al., 2004c), which should stabilize the SiO₂-bearing basaltic material in the D” layer. Moreover, SiO₂ is also expected to exist in this region as a product of the reaction between the solid silicate Pₐ (or PPₐ) of the mantle and the molten Fe of the outer core (Knittle and Jeanloz, 1991).
In contrast, the Mg-rich and Si-poor refractory nature of the uppermost part of the lower mantle suggested by Bina (2003) could be due to the presence of accumulated harzburgite-rich bodies of the stagnant slabs. This is mainly because harzburgite is less dense than pyrolite throughout the lower mantle, as is seen in Figure 11. Nevertheless, the density difference is not so large, and the thermal anomalies due to subduction of slabs or rising plumes may be more effective in circulation of the harzburgitic materials within the lower mantle.

2.03.5.3 Postperovskite Transition and the D″ Layer

The bottom ~200 km of the lower mantle is known as a highly heterogeneous region on the basis of seismological observations, named as the D″ layer to distinguish it from grossly homogeneous part of the lower mantle above (region D; Bullen, 1949). The horizontally and vertically heterogeneous nature of the D″ layer is primarily because this region is the chemical boundary layer between convective rocky mantle and molten iron core, which inevitably produces a large thermal boundary layer (ΔT > ~1000 K; e.g., Williams, 1998) and accordingly yields active reactions of mantle and core materials (e.g., Knittle and Jeanloz, 1991), partial melting of mantle and slab materials (Lay et al., 2004), generation of hot mantle plumes (Garnero et al., 1998), etc. Various models have been proposed to account for the observed complex seismological signatures of D″ as reviewed by Garnero et al. (2004).

The recent finding of the Pv–PPv transition in MgSiO₃ has dramatically affected the conventional interpretations of the complex and heterogeneous features of the D″ layer. Many researchers in different research fields of Earth sciences, including mineral physics, seismology, geochemistry, mantle dynamics, etc., have started studies relevant to these topics, and a number of papers have been published immediately after the appearance of the first report on this issue (Murakami et al., 2004a). As the rates of accumulating data are so fast and the relevant research fields so vast, we are unable to thoroughly evaluate all of these studies at this moment. So, instead of discussing the origin of the D″ layer based on rather immature knowledge in these broad research fields, we herein summarize and examine currently available phase relations and some physical properties of the PPv in terms of high-pressure experimental and theoretical points of view. We will make some discussion and speculations on the nature of the D″ layer within these mineral physics frameworks.

Now, what is most robust is that the Pv–PPv transition in MgSiO₃ does occur at pressures near the D″ layer on the basis of both high-pressure experiments and ab initio calculations. Also true is that the latter phase adopts the crystal structure of CaIrO₃ type, as evident from all of these studies. The density increase in Mg-Pv associated with this transition is most likely to be only 1.2–1.5% as constrained experimentally and predicted by ab initio calculations. The remarkable agreements among these independent studies on both experimental and theoretical bases strongly suggest that these should be regarded as facts beyond any doubts.

On the other hand, there are some uncertainties in the phase transition pressure and its temperature dependency. The pressures calculated with different scales in DAC experiments, even for those based on the EoS of gold, may differ by as much as 10–15 GPa at pressures of D″ layer (~120–136 GPa) due to the inaccuracy of the EoS’s of pressure reference materials as discussed earlier (see Figure 1), and accordingly this transition could be realized only at pressures of the outer core (Shim et al., 2004). Moreover, uncertainties in temperature measurements in LHDAC at these very high pressure regions are fairly large, and are generally ±10–20% of the nominal values. These yield additional uncertainties of greater than 2–5 GPa in pressure measurements in LHDAC. Thus the errors of the transition pressure can be ±20 GPa for the Pv–PPv transition in MgSiO₃ within the current state-of-the-art LHDAC technology. Moreover, it is fair to say the Clapeyron slope of this transition has been virtually unconstrained by LHDAC experiments.

In contrast, remarkably good agreement in phase transition pressures (~110 GPa, at 0 K) and the Clapeyron slopes (7–10 MPa K⁻¹) have been obtained in some independent ab initio calculations (Tsuiyama et al., 2004a; Oganov and Ono, 2004), which are consistent with the experimental results and also with what are expected by seismological observations (Sidorin et al., 1999). The mutual agreement among the results of the ab initio calculations, however, does not warrant the validity of these values, as these authors used basically the same technique with only some relatively minor difference in computational methods and techniques. Thus these results on the Pv–PPv phase boundary based on ab initio calculations should be further tested on the basis of experimental studies, before they are regarded as robust ones.

Nevertheless, there is no strong evidence against the occurrence of the Pv–PPv transition at pressures
about 120 GPa, with a Clapeyron slope of 7–10 MPa K$^{-1}$, and it is reasonable to tentatively take these values as realistic ones. It has been reported that such a large Clapeyron slope is expected to affect the thermal structure of the lower mantle and thus enhances the mantle convection and plume dynamics (Nakagawa and Tackley, 2004). For actual mantle compositions, effects of relatively minor elements such as Fe and Al should be taken into account, but, as we mentioned earlier, these may have opposite effects in modifying the transition pressure, which should be cancelling out each other. Actually, recent experimental results demonstrated that the Pv–PPv transition in peridotitic compositions occurs at pressures close to 120 GPa (Murakami et al., 2005; Ono et al., 2005d). Although a smeared-out transition is expected for this transition when some iron is incorporated in MgSiO$_3$ (Mao et al., 2004, 2005), these studies on the rock samples indicate that the pressure interval of the mixed phase region of Pv and PPv is not so large, suggesting the occurrence of a sharp boundary (Wyssession et al., 1998). It is also demonstrated that the PPv phase in the peridotite composition is highly magnesium rich relative to Mw (Murakami et al., 2005), whereas PPv is reported to favor iron compared with Pv in other experimental studies (Mao et al., 2004, 2005; cf. Kobayashi et al., 2005).

Another striking feature of PPv is its elasticity, as predicted by ab initio calculations (Tsuchiya et al., 2004b; Oganov and Ono, 2004; Iitaka et al., 2004). The predicted seismic wave speeds of PPv are slightly faster in $V_P$ and $V_S$ and slower in $V_{P\theta}$ than those of Pv at the transition $P, T$ condition as typically observed at the D$''$ discontinuity (Lay et al., 2004). These velocity changes across the transition boundary seem to explain the enigmatic anticorrelated anomaly between $V_S$ and $V_{P\theta}$ observed at the bottom of the mantle (Wookey et al., 2005; Wentzcovitch et al., 2006). Also, they can vary with changing the iron and aluminum contents in Pv and PPv (Tsuchiya and Tsuchiya, 2006).

Because of the peculiar crystal structure of PPv, which is highly compressible along the $b$-direction, this phase is suggested to be elastically quite anisotropic. The ab initio studies also reported that PPv polycrystalline aggregates with lattice-preferred orientation around some crystallographic directions produced by macroscopic stress appear to explain the observed anisotropic propagation of seismic waves in some regions of the D$''$ layer. In particular, some ab initio studies on high-temperature elasticity (Stackhouse et al., 2005a; Wentzcovitch et al., 2006) showed that the transversely isotropic aggregates of PPv can yield horizontally polarized S wave (SH) which travels faster than vertically polarized S wave (SV) at the lower-mantle $P, T$ conditions, as observed underneath Alaska and Central America (Lay et al., 2004). However, the peculiar nature of its shear elasticity suggests that the simple shear motion along the layered structure may not be applicable to the PPv phase at relevant pressures (Tsuchiya et al., 2004b).

Moreover, it was predicted that Mw would have substantially large elastic anisotropy under the lower-mantle conditions (Yamazaki and Karato, 2002), suggesting that the PPv phase may not be important in producing anisotropic nature in the D$''$ layer.

The most likely region, where the Pv–PPv transition plays important roles in the D$''$ layer, is probably underneath some of the subduction zones, where the temperatures are expected to be relatively lower than that of the surrounding mantle. In these relatively cold regions in the D$''$ layer, it is known that a sharp discontinuity exists on the top of this layer, under which the highly anisotropic nature of propagation of SV and SH has also been recognized. If this discontinuity corresponds to the Pv–PPv transition, then one of the most likely features of this transition, that is, its large Clapeyron slope of $\frac{dP}{dT} = 7–10$ MPa K$^{-1}$, suggests that such discontinuity may not exist in warmer regions. For instance, if the temperature in the warmer region is higher than the cold areas by several hundred degrees (such a lateral temperature variation is very likely to exist in the CMB region), this transition would occur in the middle of the D$''$ layer. However, as the temperature is expected to increase sharply toward the CMB within the D$''$ layer, the geotherm in the warmer region may not cross the Pv–PPv phase boundary as illustrated in Figure 12. In contrast, it is interesting to see that there is a possibility that the geotherm in the colder region might cross the boundary twice, as suggested by recent computational modeling (Hernlund et al., 2005; Wookey et al., 2005).

Thus, if the transition pressure and the Clapeyron slope of the Pv–PPv transition predicted by ab initio calculations are correct, many of the observed features in the CMB region can be explained. In warmer regions such as underneath Hawaii or South Africa, this transition would not have any significant roles in producing the peculiar features, such as the presence of ultra-low-velocity region or a large low-velocity structure in these regions, which should be attributed to other phenomena, such as partial melting of the D$''$ layer material or chemical changes (e.g., Lay et al.,
Reactions between Mg-Pv in the warm regions with liquid iron may produce an iron-rich PPv phase in these regions, which could also contribute to the observed low velocities in these regions, as suggested by Mao et al. (2005). Such reactions between Pv (or PPv) and molten iron should be further explored experimentally to address the nature of the (ultra-)low-velocity zones within the D″ layer.

2.03.6 Summary

Recent advances in both experimental and computational techniques have enabled the quantitative study of phase transitions and mineral physics properties under the lower-mantle $P,T$ conditions. Although uncertainties in pressure and temperature are of the order of ~10% of the nominal values in typical experiments of LHDAC, this apparatus can now produce pressures and temperatures equivalent to those of the entire mantle of the Earth. In contrast, pressures available in KMA have long been limited to ~30 GPa in spite of its superiority in the accuracy of $P,T$ measurements over LHDAC. However, recent developments in KMA using SD anvils doubled this pressure limit, allowing detailed mineral physics studies down to the middle part of the lower mantle.

The accuracy of the mineral physics studies based on ab initio calculations has also been dramatically improved in the last decade. A variety of methods and techniques have been developed for the practical applications of DFT to mineral physics studies at very high pressure and temperature. As a result, remarkable agreements among the results from different research groups have been obtained for the phase transition pressures, elastic properties, etc., of some high-pressure phases under the lower-mantle pressures. Thus, such mineral physics properties of high-pressure phases in the lower mantle can now be evaluated and cross-checked on the basis of ab initio calculations and the independent experimental studies using LHDAC and KMA.

Phase transitions in major and minor minerals relevant to the mantle and subducted slabs have been studied by using the above independent methods, which clarified structural phase transitions in most of these minerals at pressures and temperatures characteristic of the lower mantle, although there remain some controversial results on the phase transition pressures, their temperature dependencies, element partitioning among the coexisting phases, etc. Although the elastic properties of high-pressure phases, particularly shear properties, have not well documented under the lower-mantle conditions, EoS parameters of some of these phases have successfully been determined by a combination of synchrotron source and KMA-LHDAC or by ab initio methods. Thus the density changes in representative mantle and slab compositions can be reasonably evaluated on the basis of the thermoelastic data on individual high-pressure phases and mineral proportion changes in these compositions.

The 660 km discontinuity has conventionally been interpreted in terms of the spinel–post-spinel phase transition in Mg$_2$SiO$_4$. However, results of the recent experimental, seismological, and geodynamics studies do not seem to be totally consistent with this interpretation. The presence of a basaltic garnetite layer, as a result of accumulation of subducted oceanic crust materials, may explain such inconsistency and the complex structure near the 660 km discontinuity. The validity of this and other classes of mineralogical models relevant to the origin of the 660 km discontinuity can be evaluated on the basis of mineral physics tests, when accurate elastic-wave velocity data become available for the pyrolite and basaltic compositions under the $P,T$ conditions corresponding to these depths.

The middle part of the lower mantle is believed to be generally homogeneous in both mineralogy and chemistry, as compared with those in the uppermost and lowermost parts of the lower mantle. No major phase transitions are expected to occur in the subducted slab lithologies and the surrounding mantle under the $P,T$ conditions of this part of the lower
mantle, except for the rutile-to-CaCl\textsubscript{2} transition in SiO\textsubscript{2} and HS-to-LS transition in Mw (and perhaps Pv). The seismic scatterers of presumably flat bodies found in the middle part of the lower mantle should be related to this phase transition in the former subducted oceanic crust, which may subduct into the deep lower mantle once it passes the density crossover near the 660 km discontinuity. Thus, some parts of the basaltic component of the slab may ultimately reach the bottom of the lower mantle because of its higher density relative to the mantle materials throughout the lower mantle. In contrast, harzburgite-rich layer may be present in the upper part of the lower mantle as a result of accumulation of main bodies of stagnant slabs in this region. However, as the density difference between this layer and the surrounding mantle is not large, thermal effects should be predominant over the chemical effects in gravitational stability of such a layer in the upper part of the lower mantle.

The recently discovered Pv–PPv transition should have significant implications for the structure, properties, and dynamics of the D'' layer, although its actual presence in this region has not been fully proved. Nevertheless, some properties, such as Clapeyron slope, transition pressure, elastic anisotropy, and density increase, relevant to the PPv transition seem to be consistent with the seismologically observed signatures in some places of the D'' layer. Further detailed and more accurate experimental studies on this transition are required based on independent techniques using KMA, or LHDAC with improved accuracy, in addition to the theoretical studies and establishment of reliable pressure scales, to understand the nature of this region of the lower mantle.

References


Liu X (2006) Phase relations in the system KAlSi\textsubscript{2}O\textsubscript{6}–NaAlSi\textsubscript{2}O\textsubscript{6} at high-pressure-high temperature conditions and their implication for the petrogenesis of lингwite. Earth and Planetary Science Letters 246: 317–325.


Tsuchiya T and Tsuchiya J (2006) Effect of impurity on the elasticity of perovskite and postperovskite: Velocity contrast across the postperovskite transition in (Mg,Fe,Al) (Si,Al)O$_3$. 61
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