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Recent advances in the study of mantle phase transitions

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ABSTRACT

We review recent advances in the study of phase transitions of minerals in the Earth's mantle, including unsolved problems regarding these processes. The phase boundaries of $(Mg,Fe)_2SiO_4$ in the mantle transition zone are modified under the wet conditions by changes in thermodynamic properties of its polymorphs because of differences in the water solubilities of these minerals. The shift of phase boundaries has significant implications for the topography of the 410 km and 660 km seismic discontinuities. The post-perovskite phase with $CaIrO_3$ structure exists at pressures above 110 GPa and at high temperature. The effects of Al and Fe on phase transition are under debate. Several post-stishovite phases have been reported but equilibrium boundaries and existence in the real lower mantle are also still debatable. Spin transition occurs in magnesiowustite, perovskite, and post-perovskite phases at high pressures of the lower mantle and core. The pressure interval in the spin transition can be large at high temperature and so the transition might not cause a discrete change in physical properties under real Earth conditions.

1. Introduction

Studies of phase transitions in the mantle have significantly advanced, with several important discoveries made in the last decade. The pressure scale at high pressure and temperature has also been a matter of great debate since the earliest *in situ* X-ray diffraction studies (e.g., Irifune et al., 1998) suggested inconsistency between pressure in $(Mg,Fe)_2SiO_4$ at the 660 km seismic discontinuity and the post-spinel phase transition boundary. One of the most important discoveries in mantle mineral physics is that of the existence of hydrous wadsleyite and hydrous ringwoodite, which have a very high water solubility in their respective phases (e.g., Inoue et al., 1995; Kohlstedt et al., 1996). These major constituents in the mantle transition zone can accommodate water more than 2 wt.%, suggesting that the mantle transition zone is the most important water reservoir on Earth. The phase boundaries of minerals in the mantle transition zone are modified by a change in thermodynamic properties of their polymorphs because of differences of water solubility in these minerals. This shift in phase boundaries has significant implications for the topography of the 410 km and 660 km seismic discontinuities (e.g., Litasov et al., 2006).

The synthesis of the post-perovskite phase with the $CaIrO_3$ structure at pressures above 110 GPa and with high temperature (Murakami et al., 2004; Oganov and Ono, 2004) is also one of the most important discoveries in high pressure mineral physics. It is currently a matter of great debate whether the D″ layer at the bottom of the lower mantle is explained by this new high pressure phase.

The third important discovery concerns spin transitions in magnesiowustite and perovskite in the lower mantle (e.g., Badro et al., 2003). The spin transition in the lower mantle minerals can change several important physical properties of the deep lower mantle regions, such as the thermal conductivity of and partitioning behavior between Mg and Fe (Badro et al., 2004); further careful studies are needed to discern the full effect of spin transitions on the physical properties of minerals in real lower mantle conditions.

The most significant characteristics of the recent advance in mineral physics summarized briefly above are based on the two major researches such as the experimental works and theoretical works. The development of experimental works has been achieved by sophisticated techniques for high pressure and temperature generation by diamond anvil cell and large volume multianvil press combined with third generation synchrotron X-ray sources such as those at APS, ESRF and SPring-8. The details of the technical developments are reviewed recently (e.g., Ito, 2007; Weidner and Li, 2007; Mao and Mao, 2007). The molecular dynamics simulation in the early stage and now *ab-initio* calculations provided significant guiding principles for experimental scientists to synthesize the high pressure phases and interpretations of the various *in situ* X-ray observations made by high pressure and high temperature experiments. Many important contributions of *ab-initio* calculations to

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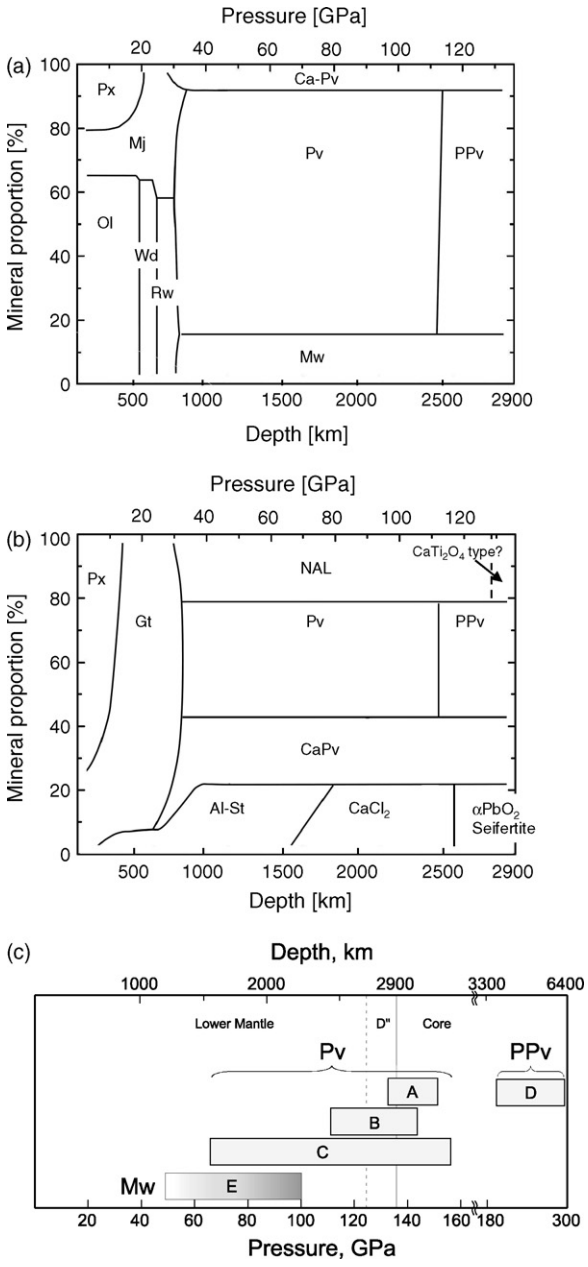

Fig. 1. (a) Phase relations of peridotite (Oganov and Ono, 2004; Murakami et al., 2004, 2005; Badro et al., 2004; Lin et al., 2007; Ohtani, 2005; Litasov et al., 2005a) and (b) those of MORB (Hirose et al., 2005; Ono et al., 2005; Litasov and Ohtani, 2005) to the base of the lower mantle. (c) The spin transition pressures in magnesiowustite, perovskite, and post-perovskite. (A) The spin transition pressure of ferrous iron in perovskite; (B) that of ferric iron in aluminous perovskite; (C) ferric iron in aluminum-free perovskite; (D) ferrous iron in post-perovskite at 2500 K calculated by Stackhouse et al. (2007); (E) that for ferrous iron in magnesiowustite at high temperature (Sturhahn et al., 2005; Tsuchiya et al., 2006a,b; Lin et al., 2007). Ol, olivine; Px, pyroxene; Mj, majorite; Wd, wadsleyite; Rw, ringwoodite; Pv, perovskite; Ca-Pv, $CaSiO_3$ perovskite; Mw, magnesiowustite; PPv, post-perovskite; NAL, NAL phase; $CaCl_2$, $CaCl_2$ type SiO_2; Seifertite, α-PbO_2 type SiO_2.

spin-transitions and post-perovskite transitions are conducted to date. We will also see briefly these important contributions in this manuscript.

Fig. 1(a) and (b) summarizes the phase transition sequences for mantle peridotite and MORB compositions up to the base of the lower mantle. There are currently several uncertainties and strong debate related to these phase transitions. In this paper, we review the recent advances in the study of phase transitions of mantle minerals, including discussion of unsolved problems.

2. Phase transformations in the mantle transition zone

The phase boundaries in the minerals composing the mantle transition zone have been studied extensively in this decade both by the quenching method and the *in-situ* X-ray diffraction method. The technical advances for in situ X-ray diffraction experiments at high pressure made it possible to make precise determination of the phase transition boundaries. The advance was achieved by combination of the third generation intense synchrotron X-ray source and large volume presses in beamlines such as SPring-8 and APS. In order to ascertain a precise determination of the phase boundary, the reliability and uncertainty of pressure scales at high temperature must be calibrated. The pressure scales at 10–15 GPa are generally consistent among several pressure scales, and the depth of the 410 km discontinuity can be explained by the olivine–wadsleyite phase transition. However, the inconsistency between the post-spinel phase boundary determined by the experiments (e.g., Irifune et al., 1998) and the 660 km seismic discontinuity observed in seismology provides a topic for intensive debate on pressure scale reliability in the pressure range at the base of the transition zone.

2.1. Phase transitions and phase boundaries in Mg_2SiO_4

The phase boundaries between olivine and wadsleyite under dry and wet conditions are shown in Fig. 2. Several experimental and theoretical studies on the effect of water on the olivine–wadsleyite phase transformation and the water partitioning between olivine and wadsleyite have been carried out.

Wood (1995) argued that hydrogen expands the stability field of wadsleyite to lower pressures because hydrogen is more soluble than olivine in wadsleyite. Smyth and Frost (2002) reported a shift of the olivine–wadsleyite phase boundary by about 1 GPa to lower pressure in olivine and peridotite compositions, both containing 3 wt.% H_2O, as determined by quenching experiments. Litasov et

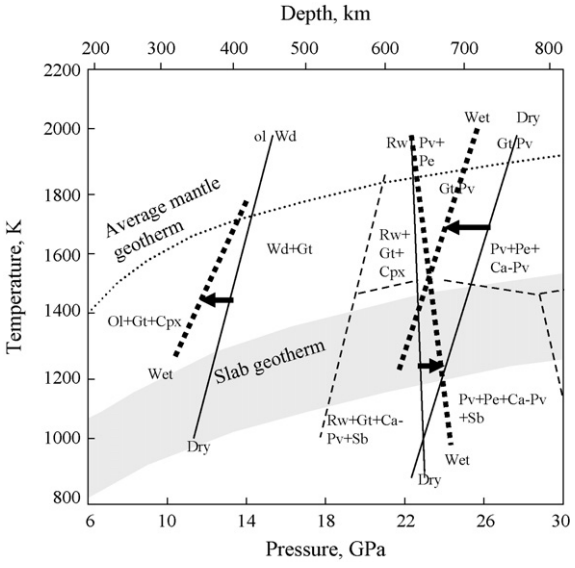

Fig. 2. The phase boundaries of the olivine–wadsleyite transition, the ringwoodite decomposition, and the garnet–post-garnet transition under dry and wet conditions (Litasov et al., 2005a,b; Sano et al., 2006). Cpx, clinopyroxene; Gt, garnet; Sb, superhydrous phase B; Pe, periclase; the other abbreviations are the same as those given in Fig. 1.

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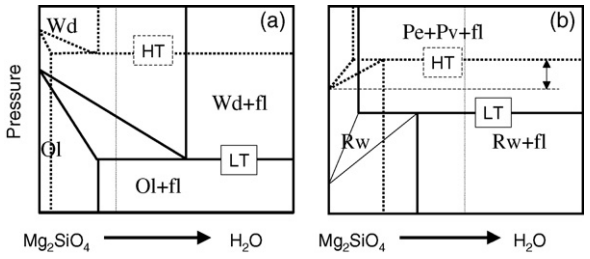

Fig. 3. Schematic phase diagrams of the Mg_2SiO_4 system at high pressure. (a) The effect of water on the olivine–wadsleyite transition (Wood, 1995; Smyth and Frost, 2002; Litasov et al., 2006), (b) the effect of water on the decomposition reaction of ringwoodite (Inoue et al., 1995; Kohlstedt et al., 1996; Ohtani et al., 2000). Ol, olivine; Wd, wadsleyite; fl, fluid; Rw, ringwoodite; Pe, periclase; Pv, perovskite.

al. (2006) determined the phase boundary by high pressure and temperature *in situ* X-ray diffraction experiments, and obtained a consistent shift of the phase boundary to a lower pressure (Fig. 2). The schematic phase diagrams of the Mg_2SiO_4–H_2O system, as given in Fig. 3(a), show a shift of the phase boundary by addition of water. The higher water solubility in wadsleyite at low temperature produces a large reduction of transition pressure, as shown in this figure.

Pressure scale is essential to compare the pressure of the phase boundaries with the discontinuities in the mantle observed in seismology. The pressure scale at high temperatures was a matter of great debate, since the discrepancy between the pressure of the dry post-spinel phase boundary and the 660 km discontinuity observed in seismology might introduce chemical heterogeneities in the transition zone and the lower mantle. The ambiguity of the pressure scale was initially identified by the report of determination of the post-spinel phase boundary by Irifune et al. (1998) based on the Au pressure scale by Anderson et al. (1989), i.e., they claimed that the phase boundary occurs at a pressure about 2 GPa lower than that expected by the pressure of the 660 km discontinuity. They suggested a possibility of the compositional change at the base of the transition zone as was initially proposed by Ringwood (1994). After the report of inconsistency of the phase boundary with the 660 km discontinuity, various attempts have been made to evaluate the pressure scales and to improve the scales at high pressure and temperature (e.g., Fei et al., 2004). In order to determine the phase boundaries at high pressures precisely, it is essential to establish the pressure scale based on a reliable equation of state (EOS).

Au, Pt, and MgO have been often used as the pressure marker for *in situ* X-ray diffraction studies at high-pressure and temperature by multianvil apparatus and diamond anvil cell (e.g., Fei et al., 2004). It has been reported that the pressure scale of Au proposed by Anderson et al. (1989) has a strong stress effect at low temperature, whereas it underestimates the pressure at high temperature due to incorrect evaluation of the thermal pressure (e.g., Matsui and Shima, 2003). Although the pressure scale is essential to determine the phase transformation boundaries and their Clapeyron slopes, there was no consistency among the different pressure scales especially at pressures above 20 GPa at high temperature. For instance, the pressure differences among different EOS of Au, Pt, and MgO (e.g., Jamieson et al., 1982; Anderson et al., 1989; Shim et al., 2001; Tsuchiya, 2003; Fei et al., 2004) may be as large as 2.5 GPa at 25 GPa and 2000 K. Fei et al. (2004) made comprehensive review of different pressure scales and calibrated Au and Pt scales based on the MgO standard (Speziale et al., 2001).

The post-spinel phase boundary of Mg_2SiO_4 determined by Fei et al. (2004) using Shim's Au pressure scale (Shim et al., 2002) is consistent with the 660 km discontinuity, i.e., the pressure difference between the phase boundary and the 660 discontinuity is about 0.6 GPa, assuming the temperature of the discontinuity is 1850 K.

The most remarkable of the results produced in recent *in situ* X-ray diffraction experiments is the gentle slope of the phase boundary. Previous results for the Clapeyron slope, dP/dT, were relatively large, around −2 MPa/K (Ito and Takahashi, 1989; Irifune et al., 1998), whereas the recent careful examinations of the phase boundary by Katsura et al. (2003), Fei et al. (2004) and Litasov et al. (2005a,b) indicated that the slope is smaller, around −0.4 to −1 MPa/K. The improvement of determination of the equilibrium boundary, especially at low temperatures below 1500 K, has been made by a recent *in situ* X-ray diffraction study, showing that there is a possibility that the old data overestimated the pressure of the phase transition due to slow transformation kinetics at low temperature (e.g., Kubo et al., 2002). The small Clapeyron slope of the post-spinel transition has important implications for the topography of the 660 km discontinuity, but the dry Clapeyron slope cannot explain the topography of this discontinuity within a reasonable local temperature variation at the bottom of the transition zone. Litasov et al. (2005a) determined the post-spinel phase boundary by using *in situ* X-ray diffraction study, as: P(GPa) = −0.0005T(K) + 23.54 using the Au pressure scale of Tsuchiya (2003) and P(GPa) = −0.0008T(K) + 24.42 using the MgO pressure scale of Speziale et al. (2001). Litasov et al. (2005a) also determined the phase boundary under wet conditions as P(GPa) = −0.002T(K) + 26.3, based on the Au pressure scale of Tsuchiya (2003). However, a recent theoretical calculation of the dry decomposition boundary of Mg_2SiO_4 ringwoodite by Yu et al. (2007) showed that the Clapeyron slope of the boundary is about −3 MPa/K, suggesting the observed topography of 660 km discontinuity may be explained by a reasonable temperature variation. In order to solve the pressure calibration issue, it is essential to improve the pressure scale at high temperature by introduction of the new procedures such as the absolute pressure scale by simultaneous measurements of equation of state and sound velocity of NaCl and MgO (e.g., Zha et al., 2000).

The dry and wet phase boundaries for the decomposition of ringwoodite (post-spinel transition) are shown in Fig. 2. It is important to note that the stability field of ringwoodite expands under wet conditions. The shift of the boundaries is greater at low temperatures whereas it is smaller at higher temperatures because of the differences in water solubility of the minerals with temperature. The effect of water on the post-spinel phase transition in the Mg_2SiO_4–H_2O system is shown schematically in Fig. 3(b). The maximum solubility of water in ringwoodite is as great as around 2 wt.% (e.g., Inoue et al., 1995; Kohlstedt et al., 1996) at ∼1300 K, whereas it is less than 0.5 wt.% (e.g., Ohtani et al., 2000) at around 1870 K. The change in maximum water solubility with temperature causes the change in the pressure shift of the decomposition boundary. The present experimental results suggest that the topography of the 660 km discontinuity may be caused at least partly by the existence of water in the transition zone, although we need further works to clarify the cause of the discrepancy between the recent experimental works and theoretical calculations.

The amount of water in the mantle transition zone may also be evaluated by the electrical conductivity observations. Huang et al. (2005) made the electrical conductivity measurement of hydrous wadsleyite and deduced experimentally the relation between the water content and the electrical conductivity. They argued existence of water up to 0.1–1 wt.% water in the mantle transition zone, and estimated the heterogeneity in water contents in the mantle transition zone. Koyama et al. (2006) also made analysis of the heterogeneity in water contents in the mantle transition zone based on combination of the electrical conductivity tomography and seismic tomography. They also clarified a localized water up to about

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0.5 wt.% in the mantle transition zone beneath subduction zones. Yoshino et al. (2008) recently measured the electrical conductivity of the dry and hydrous wadsleyites. They argued that the conductivity of the dry wadsleyite is consistent with the mean electrical conductivity value of the transition zone. However, since the electrical conductivity is also sensitive to the temperature, there is a weak constraint on the water content from the electrical conductivity due to the ambiguity of the geotherm in the transition zone. The observed electrical conductivity in the transition zone may be consistent with the water contents less than 0.5 wt.% instead of the dry condition which was stressed by Yoshino et al. (2008), if we take into account of the temperature ambiguity of the transition zone about 200 K and the experimental uncertainties.

2.2. Post-garnet transition and the effect of water on the transition boundary

The post-garnet transition has a positive Clapeyron slope and occurs at higher pressure than the decomposition reaction of ringwoodite under dry conditions (Hirose et al., 2000). Litasov et al. (2005b) made an *in situ* X-ray diffraction study of the phase transformation in MORB under dry conditions, and revealed that the post-garnet phase boundary is expressed as P(GPa) = 0.0046T(K) + 18.40, using the Au pressure scale of Tsuchiya (2003) as shown in Fig. 2. This phase boundary has a steeper slope compared to that reported by the quenching experiment (Hirose et al., 2000). The pressure interval of coexistence of garnet and Mg-perovskite is very narrow, less than 0.5 GPa.

Litasov and Ohtani (2005) and Sano et al. (2006) observed a shift in the post-garnet transition boundary by 1–2 GPa to lower pressure under wet conditions based on both quenching and *in situ* X-ray diffraction studies. The resulting equation for the post-garnet transition in hydrous MORB can be expressed as P(GPa) = 0.0049T(K) + 15.94 using the Au pressure scale of Tsuchiya (Sano et al., 2006).

3. Phase transitions of minerals under lower mantle conditions

Recent development of high pressure and temperature techniques made it possible to clarify various transitions in the lower mantle, such as the spin transitions in magnesiowustite and Mg-perovskite, and the several polymorphic phase transitions of the constituent minerals in the mantle. The phase transitions occurring in the lower mantle for mantle peridotite and MORB are shown in Fig. 1(a) and (b). Here we review these recently discovered phase transitions in the lower mantle.

3.1. Post-perovskite phase and phase transitions in Mg- and Ca-perovskite

Murakami et al. (2004) and Oganov and Ono (2004) reported the existence of a $CaIrO_3$ structured phase in $MgSiO_3$, which might account for the D″ layer at the base of the lower mantle. The characterization of the post-perovskite phase is one of the most important current issues for understanding core–mantle boundary regions. The effects of composition, such as iron and aluminum contents, on the post-perovskite phase boundary are controversial and currently much debated, as shown below.

The effects of iron on the post-perovskite transition boundary and Mg-Fe partitioning between perovskite and post-perovskite phases are important issues for debate. Tateno et al. (2007) showed that the transition pressure from the perovskite to post-perovskite phase in the $MgSiO_3$–$FeSiO_3$ system increases with increasing FeO content in the system, suggesting an enrichment of MgO in the post-perovskite phase compared to perovskite. Murakami et al. (2005) reported that the exchange partition coefficient of MgO and FeO between magnesiowustite and perovskite/post-perovskite, $K_D = (FeO/MgO)_{pv,ppv}/(FeO/MgO)_{mw}$, decreases associated with the post-perovskite transition at 2000 K, suggesting that there is MgO enrichment in post-perovskite compared to perovskite. The partitioning behavior is consistent with the phase relations reported by Tateno et al. (2007).

Mao et al. (2004), on the other hand, reported that the transition pressure decreases with an increase in $FeSiO_3$ content in the post-perovskite phase, which is the opposite relationship noted in the above works. Kobayashi et al. (2005) reported that the exchange partition coefficient of MgO and FeO between magnesiowustite and perovskite/post-perovskite, K_D, increases from perovskite to post-perovskite, suggesting that there is FeO enrichment in the post-perovskite phase, which is consistent with the result of Mao et al. (2004). The possible phase relations in the $MgSiO_3$–$FeSiO_3$ system are summarized in Fig. 4(a).

Murakami et al. (2005) reported that the post-perovskite transition boundary in natural peridotite with a KLB1 composition locates at a pressure close to the boundary in pure $MgSiO_3$ composition, whereas the post-perovskite phase boundary in the MORB composition occurs at lower pressures compared to that in the peridotite composition (Hirose et al., 2005; Ono et al., 2005; Ohta et al., 2008). Since the perovskite phase in MORB composition contains large amounts of aluminum, ferric iron, and ferrous iron, the results might indicate that aluminum and iron can lower the pressure of the post-perovskite phase boundary. Alternatively, some minor elements, such as Na_2O in post-perovskite in MORB, might lower the stability pressure of the phase.

The incorporation of aluminum in the post-perovskite phase could move the boundary toward higher pressure, and the post-perovskite phase transition in pyrope occurs at around 140–150 GPa (Tateno et al., 2005), which is higher than that of the post-perovskite transition pressure in $MgSiO_3$ around 120 GPa. Al_2O_3 transforms to Rh_2O_3-type at 96 GPa (Lin et al., 2004). Theoretical calculations for Al_2O_3 confirmed the transition of Rh_2O_3-type phase to $CaIrO_3$-type phase (Caracas and Cohen, 2005; Umemoto and Wentzcovitch, 2008). Ono et al. (2006) reported that the post-perovskite phase transition in Al_2O_3 occurs at around 130 GPa. The phase relation in $MgSiO_3$–Al_2O_3 system is shown in Fig. 4(b).

Currently, there is no consensus on the effects of iron and aluminum on the post-perovskite phase transition as shown in Fig. 4(a) and (b). This might be because of the structural and compositional complexities in perovskite and post-perovskite phases with different ferric and ferrous iron contents associated with Al_2O_3 substitution in their structures, large uncertainties in pressure and temperature determination, and the large pressure and temperature gradients in DAC under such extreme conditions. Slow reaction kinetics might also cause the apparent inconsistencies seen in recent reports. Further careful examination using well-characterized starting materials on ferric and ferrous iron, aluminum, and minor element contents will be indispensable in solving this important problem.

The slope of the post-perovskite phase boundary has been calculated theoretically by the *ab-initio* calculation. The Clapeyron slope of the post-perovskite phase transition boundary was first demonstrated by theory (Tsuchiya et al., 2004b), which suggested a large positive Clapeyron slope consistent with that of the analogous compound such as observed in $CaIrO_3$.

$CaSiO_3$ cubic perovskite is stable under the transition zone and lower mantle conditions, and some amount of aluminum can be dissolved under lower mantle conditions (see Fig. 1). Kurashina et al. (2004) and Komabayashi et al. (2007) reported that the $CaSiO_3$ perovskite phase has an orthorhombic symmetry at low tempera-

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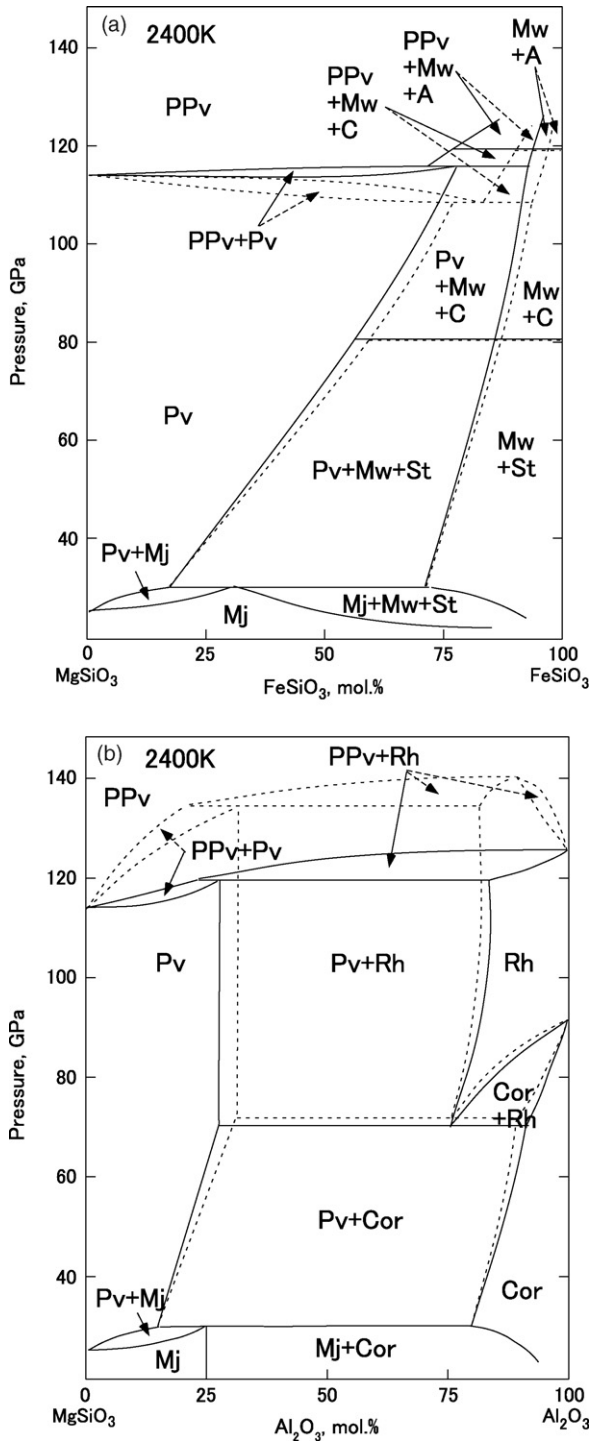

Fig. 4. (a) The phase relation of the $MgSiO_3$–$FeSiO_3$ system at 2400 K (Ohtani et al., 1991; Tateno et al., 2007; Mao et al., 2004). (b) The phase relation of the $MgSiO_3$–Al_2O_3 system at high pressure and 2400 K (Tateno et al., 2005; Lin et al., 2004; Oganov and Ono, 2005; Ono et al., 2006). Mj, majorite; Pv, perovskite; Mw, magnesiowustite; St, stishovite; C, $CaCl_2$ type SiO_2; A, α-PbO_2 type SiO_2; PPv, post-perovskite; Cor, corundum; Rh, Rh_2O_3 type Al_2O_3. The phase relations of the post-spinel phase transitions are still ambiguous, and possible phase relations are given as solid and broken curves.

tures, whereas it is cubic at higher temperature under lower mantle conditions. The temperature of the transition from the orthorhombic to the cubic phase depends on the Al_2O_3 content in this phase (Komabayashi et al., 2007), and the transition boundary intersects to the geotherm in the upper part of the lower mantle. Since acoustic velocity in some perovskites drops remarkably across the structural transition to high symmetry phases (e.g., Kurashina et al., 2004), it might account for the seismic reflectors observed in the upper part of the lower mantle (e.g., Niu et al., 2003; Kaneshima and Helfrich, 2003).

3.2. Post-stishovite phases and phase transitions of NAL phase under lower mantle conditions

Several post-stishovite phases have been discovered recently by *in situ* X-ray diffraction studies using a laser-heated diamond anvil cell (LHDAC) as was used for the post-perovskite phase transition. A $CaCl_2$ structured phase of SiO_2 has been reported previously at pressures around 50 GPa (Kingma et al., 1995) and the phase boundary from stishovite to the $CaCl_2$-type SiO_2 was determined by Ono et al. (2002). The $CaCl_2$ structure is very close to the rutile structure, i.e., a deformed stishovite-like structure, and there is no discontinuous volume change associated with the phase transition (e.g., Andrault et al., 1998). The transition from stishovite to the $CaCl_2$-type phase might be a second-order phase transition, and an anomalous change in elastic constants occurs associated with this transition (e.g., Carpenter et al., 2000; Karki et al., 1997; Shieh et al., 2002). Seismic reflectors have been reported in the lower mantle beneath subduction zones (e.g., Niu et al., 2003; Kaneshima and Helfrich, 2003); an anomalous Vs decrease associated with a reflector might be explained by this transition (e.g., Hirose et al., 2005; Ohtani, 2005). Recently, Lakshtanov et al. (2007) reported that the phase transition pressure decreases to around 30 GPa at room temperature in Al_2O_3 and water-bearing stishovite. It is an open question as to how much water can be accommodated in the $CaCl_2$-type SiO_2. Further studies are necessary to determine the solubility of Al_2O_3 and water in the $CaCl_2$-type SiO_2, and the effect of these components on the phase transition boundary.

The phase transition from $CaCl_2$-type to α-PbO_2-type structure has predicted by theoretical studies (e.g., Karki et al., 1997). Transformation of stishovite to α-PbO_2 phase was experimentally reported at pressures above 64 GPa with a negative Clapeyron slope by Dubrovinsky et al. (2001). Whereas, Murakami et al. (2003) reported that the transformation occurs at 121 GPa and 2400 K corresponding to the base of the lower mantle. This discrepancy might be due to the pressure and temperature uncertainties in LH-DAC, and kinetic problem associated with this transformation, and the difference in the starting materials. Tsuchiya et al. (2004a) estimated the phase boundary between $CaCl_2$ and α-PbO_2 as P(GPa) = 106.3 + 0.00579T(K) based on *ab-initio* calculations. This phase boundary is consistent with the results by Murakami et al. (2003).

Shieh et al. (2005) observed α-PbO_2-type phase using cristobalite. Back transformation from α-PbO_2-type to $CaCl_2$-type occurred only below 113 GPa. α-PbO_2-type was observed in MORB in the lower mantle conditions by Ono et al. (2005), Hirose et al. (2005), and Ohta et al. (2008). The α-PbO_2-type SiO_2 phase containing some amount of Al_2O_3 in a MORB composition is stable at relatively low pressures, well within the lower mantle pressure range. This phase was discovered in a Martian meteorite and named Seifertite (El Goresy et al., 2000). Since stishovite exists in the oceanic crust descending into the lower mantle, α-PbO_2-type SiO_2 is expected to exist in the oceanic crust descending into the base of the lower mantle. This phase further transforms to pyrite-type SiO_2 at pressures above 270 GPa at 2000 K, the conditions which exceed pressures of the base of the lower mantle (Kuwayama et al., 2005). The stability fields of the post-stishovite phases reported to date are summarized in Fig. 5.

The NAL phase, which is an alkali aluminum oxide phase, is one of the important high pressure minerals in the basaltic (MORB)

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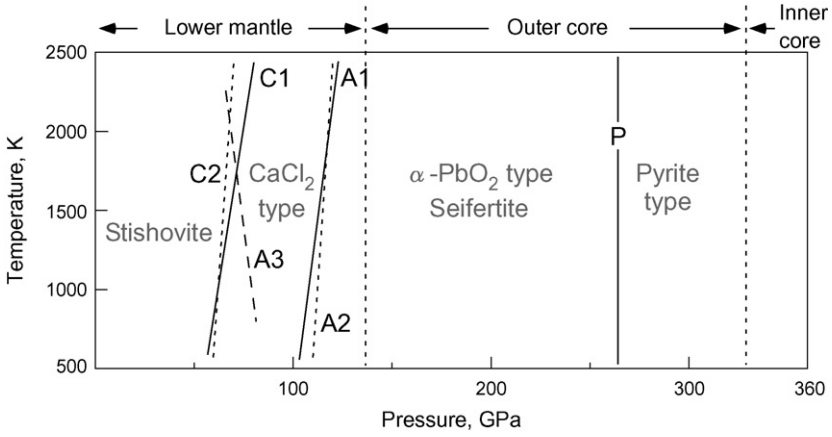

Fig. 5. Phase transitions of SiO_2 to the center of the Earth. C1 and C2 are the stishovite-$CaCl_2$ phase boundary by Ono et al. (2002) and Tsuchiya et al. (2004a,b), respectively; A1, A2, and A3 are that of the $CaCl_2$–α-PbO_2 transition by Murakami et al. (2003), Tsuchiya et al. (2004a,b), and Dubrovinsky et al. (2001), respectively; P is that of $CaCl_2$-pyrite phase boundary by Kuwayama et al. (2005).

composition. The phase transition sequence of the NAL phase in MORB composition is summarized in Fig. 1(b). Ono et al. (2005) reported that the NAL phase transforms to a $CaTi_2O_4$ structure at 142.5 GPa, and suggested that it might be stable at the base of the lower mantle. However, other studies indicate that the NAL phase is stable throughout the lower mantle (e.g., Hirose et al., 2005). We need further studies to clarify the phase transition in the NAL phase.

3.3. Spin transitions in lower mantle minerals

Spin transitions in the lower mantle minerals have been theoretically suggested by some authors (e.g., Burns, 1993; Ohnishi, 1978; Cohen et al., 1997). Recently, the existence of spin transitions has been confirmed experimentally in magnesiowustite and perovskite. The spin transition of iron in magnesiowustite was reported by Badro et al. (2003) and Lin et al. (2005) by using X-ray emission spectroscopy at 40–50 GPa at room temperature. After the discovery of the spin transition in magnesiowustite (Badro et al., 2003), various theoretical studies were made extensively to clarify the effect of pressure and ferric or ferrous iron content on the spin transition (e.g., Persson et al., 2006; Tsuchiya et al., 2006a,b). The effect of the spin transition of iron in compression was also studied experimentally by Lin et al. (2005), suggesting the existence of a kink in the compression curve in magnesiowustite at around 50 GPa. The broadening of the pressure interval of the spin transition in magnesiowustitie at high temperature has been suggested theoretically by Sturhahn et al. (2005) and Tsuchiya et al. (2006a,b). They suggested that spin transition occurs gradually along a wide range of pressure intervals in the lower mantle at high temperature. Lin et al. (2007) confirmed experimentally the broadening of the spin transition of magnesiowustite by using *in situ* X-ray emission spectroscopy (XES) at high pressure and temperature.

The spin transition in perovskite has also been reported by experimental and theoretical works. According to the theoretical works (Li et al., 2005; Zhang and Oganov, 2006; Stackhouse et al., 2007), the spin transition pressures in perovskite varies for ferric and ferrous irons; ferric iron shows a wide pressure interval of spin transition between about 60–160 GPa, whereas ferrous iron is in a high spin state at all mantle pressures and it transforms to the low spin state at pressures about 130–145 GPa. These theoretical results are consistent with the recent experimental works (Li et al., 2004, 2006); the recent XES and SMS (synchrotron Mössbauer spectroscopy) studies revealed a pressure-induced gradual loss of magnetic moment in an aluminum bearing perovskite sample between 20 and 100 GPa, indicating possible occurrence of mixed spin state and intermediate-spin state under high pressures to 100 GPa in aluminum bearing perovskite. Badro et al. (2004) reported that the transition in aluminum-free perovskite occurs in two steps, at around 70 and 120 GPa, whereas Li et al. (2004) suggested that the transition occurs gradually with increasing pressures in aluminum bearing perovskite.

The theoretical studies revealed that ferric iron on the Mg-site in post-perovskite is in the high-spin state at all mantle pressures (Zhang and Oganov, 2006), and ferrous iron also remains in a high-spin state in post-perovskite below 180 GPa (Stackhouse et al., 2006). Further studies of the spin transitions in perovskite and post-perovskite phases are needed by using well-characterized starting materials of ferric and ferrous ratios and their site occupancies. Schematic spin transition conditions of iron in magnesiowustite, perovskite, and post-perovskite at high pressure and temperature are also given in Fig. 1(c) based on the recent experimental and theoretical studies. These results suggest that the spin transition in both magnesiowustite and perovskite occurs in a wide pressure interval throughout the lower mantle, and it may not be detected as a sharp discontinuity in density, Vp and Vs, in the lower mantle (e.g., Crowhurst et al., 2008).

4. Summary and future studies

We have summarized the phase transitions occurring in the mantle transition zones and the lower mantle for mantle peridotite and the basaltic component (MORB) in slabs. Fig. 1(a) and (b) illustrate the phase assemblage and the phase transitions observed in these components. The phase boundaries in the mantle transition zone are modified by small amount of water suggesting existence of water in the mantle transition zone. The phase transitions in the lower mantle such as spin transitions, post-perovskite phase transition, and post-stishovite transition might explain some seismic velocity anomalies in the lower mantle and the D″ layer and some reflectors of the seismic velocity in the lower mantle.

There are several inconsistencies among recent reports on the phase transitions in the lower mantle, such as the effect of Al and Fe in the post-perovskite transitions; the existence of $CaTi_2O_4$ phase in the MORB component at the base of the lower mantle; the pressure interval of the spin transitions in magnesiowustite, perovskite, and post-perovskite phases in peridotite and MORB components in the lower mantle. We need further studies to clarify these unresolved issues to better understand the nature of the lower mantle.

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References

Anderson, O.L., Isaak, D.G., Yamamoto, S., 1989. Anharmonicity and the equation of state for gold. J. Appl. Phys. 65, 1534–1543.

Andrault, D., Fiquet, G., Guyot, F., Hanifland, M., 1998. Pressure-induced Landau-type transition in stishovite. Science 282, 720–724.

Badro, J., Fiquet, G., Guyot, F., Rueff, J.-P., Struzhkin, V.V., Vankó, G., Monaco, G., 2003. Iron partitioning in Earth's mantle: toward a deep lower mantle discontinuity. Science 300, 789–791.

Badro, J., Rueff, J.-P., Vankó, G., Monaco, G., Fiquet, G., Guyot, F., 2004. Electronic transitions in perovskite: possible nonconvecting layers in the lower mantle. Science 305, 383–386.

Burns, R.G., 1993. Mineralogical Application of Crystal Field Theory. Cambridge University Press.

Caracas, R., Cohen, R.E., 2005. Prediction of a new phase transition in Al_2O_3 at high pressures. Geophys. Res. Lett. 32, doi:10.1029/2004GL022204.

Carpenter, M.A., Hemley, R.J., Mao, H.K., 2000. High-pressure elasticity of stishovite and the P4(2)/mnm reversible arrow Pnnm phase transition. J. Geophys. Res. 105, 10807–10816.

Cohen, R.E., Mazin, I.I., Isaak, D.G., 1997. Magnetic collapse in transition metaloxides at high pressure: implications for the Earth. Science 275, 654–657.

Crowhurst, J.C., Brown, J.M., Goncharov, A.F., Jacobsen, S.D., 2008. Elasticity of (Mg,Fe)O through the spin transition of iron in the lower mantle. Science 319, 451–453.

Dubrovinsky, L.S., Dubrovinskaia, N.A., Saxena, S.K., Tutti, F., Rekhi, S., Le Bihan, T., Shen, G., Hu, J., 2001. Pressure-induced transformations of cristobalite. Chem. Phys. Lett. 333, 264–270.

El Goresy, A., Dubrovinsky, L., Sharp, T.G., Saxena, S.K., Chen, M., 2000. A monoclinic post-stishovite polymorph of silica in the Shergotty meteorite. Science 288, 1632–1634.

Fei, Y., Van Orman, J., Li, J., van Westrenen, W., Sanloup, C., Minarik, W., Hirose, K., Komabayashi, T., Walter, M., Funakoshi, K., 2004. Experimentally determined postspinel transformation boundary in Mg_2SiO_4 using MgO as an internal pressure standard and its geophysical implications. J. Geophys. Res. 109, doi:10.1029/2003JB002562.

Hirose, K., Fei, Y., Ono, S., Yagi, T., Funakoshi, K., 2000. In situ measurements of the phase transition boundary in $Mg_3Al_2Si_3O_{12}$: implications for the nature of the seismic discontinuities in the Earth's mantle. Earth Planet. Sci. Int. 184, 567–573.

Hirose, K., Takafuji, N., Sata, N., Ohishi, Y., 2005. Phase transition and density of subducted MORB crust in the lower mantle. Earth Planet. Sci. Lett. 237, 239–251.

Huang, X., Xu, Y., Karato, S., 2005. Water content in the transition zone from electrical conductivity of wadsleyite and ringwoodite. Nature 434, 746–749.

Inoue, T., Yurimoto, H., Kudoh, Y., 1995. Hydrous modified spinel, $Mg_{1.75}SiH_{0.5}O_4$: a new water reservoir in the mantle transition region. Geophys. Res. Let. 22 (2), 117–120.

Irifune, T., Nishiyama, N., Kuroda, K., Inoue, T., Isshiki, M., Utsumi, W., Funakoshi, K., Urakawa, S., Uchida, T., Katsura, T., Ohtaka, O., 1998. The postspinel phase boundary in Mg_2SiO_4 determined by in situ X-ray diffraction. Science 279, 1698–1700.

Ito, E., 2007. 2.08 Theory and practice-multianvil cells and high-pressure experimental method. Mineral physics. In: Price, G.D. (Ed.), Treatise on Geophysics, vol. 2., pp. 197–230.

Ito, E., Takahashi, E., 1989. Post-spinel transformations in the system Mg_2SiO_4-Fe_2SiO_4 and some geophysical implications. J. Geophys. Res. 94, 10637–10646.

Jamieson, J.C., Fritz, J.N., Manghnani, M.H., 1982. Pressure measurement at high temperature in X-ray diffraction studies: gold as a primary standard. In: Akimoto, S., Manghnani, M.H. (Eds.), High Pressure Research in Geophysics. Center for Academic Publications, Tokyo, pp. 27–47.

Kaneshima, S., Helfrich, G., 2003. Subparallel dipping heterogeneities in the mid lower mantle, J. Geophys. Res. 108, doi:10.1029/2001jb001596.

Karki, B.B., Stixrude, L., Crain, J., 1997. Ab initio elasticity of three high-pressure polymorphs of silica. Geophys. Res. Lett. 24, 3269–3272.

Katsura, T., Yamada, H., Shinmei, T., Kubo, A., Ono, S., Kanzaki, M., Yoneda, A., Walter, M.J., Ito, E., Urakawa, S., Funakoshi, K., Utsumi, W., 2003. $MgSiO_3$ phase boundaries measured in the laser-heated diamond cell. Phys. Earth Planet Inter. 136, 11–24.

Kingma, K.J., Cohen, R.E., Hemley, R.J., Mao, H.K., 1995. Transformation of stishovite to a denser phase at lower-mantle pressures. Nature 374, 243–245.

Kobayashi, Y., Kondo, T., Ohtani, E., Hirao, N., Miyajima, N., Yagi, T., Nagase, T., Kikegawea, T., 2005. Fe-Mg partitioning between (Mg,Fe)SiO_3 post-perovskite, perovskite, and magnesiowü stite in the Earth's lower mantle, Geophys. Res. Lett. 32, doi:10.1029/2005GL023257.

Kohlstedt, D.L., Keppler, H., Rubie, D.C., 1996. Solubility of water in the α, β and γ phases of $(Mg,Fe)_2SiO_4$. Contrib. Mineral Petrol. 123, 345–357.

Komabayashi, T., Hirose, K., Sata, N., Ohishi, Y., Dubrovinsky, R.S., 2007. Phase transition in $CaSiO_3$ perovskite. Earth Planet. Sci. Lett. 260, 564–569.

Koyama, T., Shimizu, H., Utada, H., Ichiki, M., Ohtani, E., Hae, R., 2006. Water Content in the Mantle Transition Zone Beneath the North Pacific Derived From the Electrical Conductivity Anomaly. In: Jacobsen, S.D., van der Lee, S. (Eds.), Earth's Deep Water Cycle, vol. 168. American Geophysical Union Monograph, Geophysical Monograph, pp. 171–179.

Kubo, T., Ohtani, E., Kondo, T., Kato, T., Toma, M., Hosoya, T., Samo, A., Kikegawa, T., Nagase, T., 2002. Metastable garnet in oceanic crust at the top of the lower mantle. Nature 420, 803–806.

Kurashina, T., Hirose, K., Ono, S., Sata, N., Ohishi, Y., 2004. Phase transition in Al-bearing $CaSiO_3$ perovskite: implications for seismic discontinuities in the lower mantle. Phys. Earth Planet Inter. 145, 67–74.

Kuwayama, Y., Hirose, K., Sata, N., Ohishi, Y., 2005. The pyrite-type high-pressure form of silica. Science 309, 923–925.

Lakshtanov, L.D., Sinogeikin, V.S., Litasov, D.K., Prakapenka, B.V., Hellwig, H., Wang, J., Sanches-Valle, C., Perrillat, J., Chen, B., Somayazulu, M., Li, J., Hotani, E., Bass, J., 2007. The post-stishovite phase transition in hydrous alumina-bearing SiO_2 in the lower mantle of the earth. Proc. Natl. Acad. Sci. USA 104, 13588–13590.

Li, J., Struzhkin, V.V., Mao, H.K., Shu, J., Hemley, R.J., Fei, Y., Mysen, B., Dera, P., Prakapenka, V., Shen, G., 2004. Electronic spin state of iron in lower mantle perovskite. Proc. Natl. Acad. Sci. USA 101 (39), 14027–14030.

Li, J., Sturhahn, W., Jackson, J.M., Struzhkin, V.V., Lin, J.F., Zhao, J., Mao, H.K., Shen, G., 2006. Pressure effect on the electronic structure of iron in (Mg,Fe)(Si,Al)O_3 perovskite: a combined synchrotron Mössbauer and X-ray emission spectroscopy study up to 100 GPa. Phys. Chem. Minerals 33, 575–585, doi:10.1007/s00269-006-0105-y.

Li, L., Brodholt, J.P., Stackhouse, S., Weidner, D.J., Alfredsson, M., Price, G.D., 2005. Electronic spin state of ferric iron in Al bearing perovskite in the lower mantle. Geophys. Res. Lett. 32 (L17307), doi:10.1029/2005/GL023045.

Lin, J.F., Struzhkin, V.V., Jacobsen, S.D., Hu, M.Y., Chow, P., Kung, J., Liu, H., Mao, H.K., Hemley, R.J., 2005. Spin transition of iron in magnesiowüstite in Earth's lower mantle. Nature 436, 377–380.

Lin, J.F., Degtyareva, O., Prewitt, C.T., Dera, P., Sata, N., Gregoryanz, E., Mao, H.K., Hemley, R.J., 2004. Crystal structure of a high-pressure/high temperature phase of alumina by *in situ* X-ray diffraction. Proc. Natl. Acad. Sci. USA, doi:10.1038/nmat1121.

Lin, J.F., Vankó, G., Jacobsen, S.D., Iota, V., Struzhkin, V.V., Prakapenka, V.B., Kuznetsov, A., Yoo, C.S., 2007. Spin transition zone in the Earth's lower mantle. Science 317, 1740–1742.

Litasov, K.D., Ohtani, E., 2005. Phase relations in hydrous MORB at 18–28 GPa: implications for heterogeneity of the lower mantle. Phys. Earth Planet. Inter. 150, 239–263.

Litasov, K.D., Ohtani, E., Sano, A., Suzuki, A., Funakoshi, K., 2005a. In situ X-ray diffraction study of post-spinel transformation in a peridotite mantle: implication for the 660-km discontinuity. Earth Planet Sci. Lett 238, 311–328.

Litasov, K.D., Ohtani, E., Sano, A., Suzuki, A., Funakoshi, K., 2005b. Wet subduction versus cold subduction. Geophys. Res. Lett., 32, L13312, doi:10.1029/2005GL022921.

Litasov, K.D., Ohtani, E., Sano, A., 2006. Influence of water on major phase transitions in the earth's mantle, Monograph, Earth's Deep Water Cycle. Geophys. Monogr. Ser. 168, 95–112, doi:10.1029/168GM08, AGU.

Mao, H.K., Mao, W.L., 2007. 2.09 Theory and practice-Diamond anvil cells and Probes for high P-T mineral physics studies, Mineral physics. In: Price, G.D. (Ed.), Treatise on Geophysics, vol. 2., pp. 231–268.

Mao, W.L., Shen, G., Prakapenka, V.B., Meng, Y., Campbell, A.J., Heinz, D.L., Shu, J., Hemley, R.J., Mao, H.K., 2004. Ferromagnesian postperovskite silicates in the D" layer of the Earth. Proc. Natl. Acad. Sci. USA 101, 15867–15869.

Matsui, M., Shima, N., 2003. Electronic thermal pressure and equation of state of gold at high temperature and high pressure. J. Appl. Phys. 93, 9679–9682.

Murakami, M., Hirose, K., Ono, S., Ohishi, Y., 2003. Stability of $CaCl_2$-type and PbO_2-type SiO_2 at high pressure and temperature determined by in-situ X-ray measurement. Geophys. Res. Lett. 30, 1207, doi:10.1029/2002GL016722.

Murakami, M., Hirose, K., Kawamura, K., Sata, N., Ohishi, Y., 2004. Post-perovskite phase transition in $MgSiO_3$. Science 304, 855–858.

Murakami, M., Hirose, K., Sata, N., Ohishi, Y., 2005. Post-perovskite phase transition and mineral chemistry in the pyrolitic lowermost mantle. Geophys. Res. Lett. 32, L03304, doi:10.1029/2004GL021956.

Niu, F., Kawakatsu, H., Fukao, Y., 2003. Seismic evidence for a chemical heterogeneity in the midmantle: a strong and slightly dipping seismic reflector beneath the Mariana subduction zone. J. Geophys. Res. 108, NO. B9, 2419, doi:10.1029/2002JB002384.

Oganov, A.R., Ono, S., 2004. Theoretical and experimental evidence for a post-perovskite phase of $MgSiO_3$ in Earth's D" layer. Nature 430, 445–448.

Oganov, A.R., Ono, S., 2005. The high-pressure phase of alumina and implications for Earth's D" layer. Proc. Natl. Acad. Sci. USA 102, 10828–10831.

Ohnishi, S., 1978. A theory of the pressure-induced high-spin-low-spin transition of transition metal oxides. Phys. Earth Planet. Inter. 17, 13–139.

Ohta, K., Hirose, K., Lay, T., Sata, N., Ohishi, Y., 2008. Phase transitions in pyrolite and MORB at lowermost mantle conditions: Implications for a

MORB-rich pile above the core–mantle boundary. Earth Planet. Sci. Lett. 267, 107–117.
Ohtani, E., Mizobata, H., Yurimoto, H., 2000. Stability of dense hydrous magnesium silicate phases in the systems Mg_2SiO_4-H_2O and $MgSiO_3$-H_2O at pressures up to 27 GPa. Phys. Chem. Minerals 27, 533–544.
Ohtani, E., 2005. Recent progress in experimental mineral physics: Role of water in mantle dynamics. In: van der Hilst, R.D., Bass, J., Matas, J., Trampert, J. (Eds.), Earth's Deep Mantle: Structure, Composition, and Evolution (Eds.), American Geophysical Union Monograph, Geophysical Monograph, vol. 160, pp. 321–334.
Ohtani, E., Kagawa, N., Fujino, K., 1991. Stability of majorite (Mg,Fe)SiO_3 at high pressures and 1800oC. Earth Planet Sci. Lett. 102, 158–166.
Ono, S., Hirose, K., Murakami, M., Isshiki, M., 2002. Post-stishovite phase boundary in SiO_2 determined by in situ X-ray observations. Earth and Planet. Sci. Lett. 197, 187–192.
Ono, S., Ohishi, Y., Isshiki, M., Watanuki, T., 2005. In situ X-ray observations of phase assemblages in peridotite and basalt compositions at lower mantle conditions: implications for density of subducted oceanic plate. J. Geophys. Res. 110, B02208, doi:10.1029/2004JB003196.
Ono, S., Oganov, A.R., Koyama, T., Shimizu, H., 2006. Stability and compressibility of the high pressure-phases of Al_2O_3 up to 200 GPa: Implications for the electrical conductivity of the base of the lower mantle. Earth Planet. Sci. Lett. 246, 326–335.
Persson, K., Bengtson, A., Ceder, G., Morgan, D., 2006. *Ab initio* study of the composition dependence of the pressure-induced spin transition in the (Mg1-x,Fex)O system. Geophys. Res. Lett. 33, L16306, doi:10.1029/2006GL026621.
Ringwood, A.E., 1994. Role of the transition zone and 660 km discontinuity in mantle dynamics. Phys. Earth Planet. Int. 86, 5–24.
Sano, A., Ohtani, E., Litasov, K.D., Kubo, T., Hosoya, T., Funakoshi, K., Kikegawa, T., 2006. In situ X-ray diffraction study of the effect of water on the garnet–perovskite transformation in MORB and implications for the penetration of oceanic crust into the lower mantle. Phys. Earth Planet. Inter. 159, 118–126.
Shieh, S.R., Duffy, T.S., Li, B., 2002. Strength and elasticity of SiO_2 across the stishovite-$CaCl_2$-type structural phase boundary. Phys. Rev. Lett. 89, 255507.
Shieh, R.S., Duffy, T.S., Shen, G., 2005. X-ray diffraction study of phase stability in SiO_2 at deep mantle conditions. Earth Planet. Sci. Lett. 235, 273–282.
Shim, S.-H., Duffy, T.S., Shen, G., 2001. The post-spinel transformation in Mg_2SiO_4 and its relation to the 660-km seismic discontinuity. Nature 411, 571–574.
Shim, S.-H., Duffy, T.S., Kenichi, T., 2002. Equation of state of gold and its application to the phase boundaries near 660 km depth in Earth's mantle. Earth Planet. Sci. Lett. 203, 729–739.
Smyth, J., Frost, D., 2002. The effect of water on the 410-km discontinuity: an experimental study. Geophys. Res. Lett. 29, doi:10.1029/2001GL014418.
Speziale, S., Zha, C.-S., Duffy, T.S., Hemley, R.J., Mao, H.K., 2001. Quasi-hydrostatic compression of magnesium oxide to 52 GPa: implications for the pressure–volume–temperature equation of state. J. Geophys. Res. 106, 515–528.
Stackhouse, S., Brodholt, J.P., Dobson, D.P., Price, G.D., 2006. Electronic spin transitions and the seismic properties of ferrous iron bearing $MgSiO_3$ post-perovskite. Geophys. Res. Lett. 33, L12S03, doi:10.1029/2005, GL025589.
Stackhouse, S., Brodholt, J.P., Price, G.D., 2007. Electronic spin transitions in iron bearing $MgSiO_3$ perovskite. Earth Planet. Sci. Lett. 253, 282–290.
Sturhahn, W., Jackson, J.M., Lin, J.F., 2005. The spin state of iron in Earth's lower mantle minerals. Geophys. Res. Lett. 32, L12307, doi:10.1029/2005GL022802.
Tateno, S., Hirose, K., Sata, N., Ohishi, Y., 2005. Phase relations in $Mg_3Al_2Si_3O_{12}$ to 180 GPa: Effect of Al on post-perovskite phase transition, Geo. Res. Lett. 32, L15306, doi:10.1029/2005GL023309.
Tateno, S., Hirose, K., Sata, N., Ohishi, Y., 2007. Solubility of FeO in (Mg,Fe)SiO_3 perovskite and post-perovskite phase transition. Phys. Earth Planet. Inter. 160 (3), 319–325.
Tsuchiya, T., 2003. First-principles prediction of the P-V-T equation of state of gold and the 660-km discontinuity in Earth's mantle. J. Geophys. Res. 108, doi:10.1029/2003JB002446.
Tsuchiya, T., Caracas, R., Tsuchiya, J., 2004a. First principles determination of the phase boundaries of high-pressure polymorphs of silica. Geophys. Res. Lett. 31, L11610, doi:10.1029/2004GL019649.
Tsuchiya, T., Tsuchiya, J., Umemoto, K., Wentzcovitch, R.M., 2004b. Phase transition in $MgSiO_3$ perovskite in the Earth's lower mantle. Earth Planet. Sci. Lett. 224, 241–248.
Tsuchiya, T., Wentzcovitch, R.M., da Silva, C.R.S., de Gironcoli, S., 2006a. Spin transition in magnesiowüstite in Earth's lower mantle. Phys. Rev. Lett. 96, 198501.
Tsuchiya, T., Wentzcovitch, R.M., da Silva, C.R., de Gironcoli, S., Tsuchiya, J., 2006b. Pressure induced high spin to low spin transition in magnesiowüstite. Phys. Stat. Sol. (b) 243, 2111–2116.
Umemoto, K., Wentzcovitch, R., 2008. Prediction of an U_2S_3-type polymorph of Al_2O_3 at 3.7 Mbar. Proc. Natl. Acad. Sci. USA 105, 6526–6530.
Weidner, D.J., Li, L., 2007. 2.12 Methods for the study of high P/T deformation and rheology. Mineral physics. In: Price, G.D. (Ed.), Treatise on Geophysics, vol. 2, pp. 339–358.
Wood, B.J., 1995. The effect of H_2O on the 410-kilometer seismic discontinuity. Science 268, 74–76.
Yoshino, T., Manthilake, G., Matsuzaki, T., Katsura, T., 2008. Dry mantle transition zone inferred from the conductivity of wadsleyite and ringwoodite. Nature 451, 326–329.
Yu, Y.G., Wentzcovitch, R.M., Tsuchiya, T., Umemoto, K., Weidner, D.J., 2007. First principles investigation of the postspinel transition in Mg_2SiO_4, Geophys. Res. Lett. 34, doi:10.1029/2007GL029462.
Zha, C., Mao, H.K., Hemley, R.J., 2000. Elasticity of MaO and a primary pressure scale to 55 GPa. Proc. Natl. Acad. Sci. 97, 13494–13499.
Zhang, F., Oganov, A.R., 2006. Valence state and spin transitions of iron in Earth's mantle silicates. Earth Planet. Sci. Lett. 249, 436–443.

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