Mineral Physics Pertinent to the Constitution of the Mantle and Core

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Studies on the physical and chemical properties of materials of the earth's and planetary interiors have made remarkable progress in recent years. This paper reviews the important experimental and theoretical results obtained by the Japanese mineral physics community in the last decade. Phase equilibria of mantle minerals were determined in detail at pressure-temperature conditions corresponding to depths down to the lower mantle. Thermodynamic and elastic properties of high pressure silicates were also measured in recent years. These data enable us to calculate seismic velocity and density profiles in the deep mantle, which can be compared with those obtained by seismic studies. Such mineral physics studies demonstrated that pyrolite or peridotite are reasonable model compositions for the upper mantle and the transition zone. However, the lower mantle composition has only been loosely constrained. Melting behaviors of mantle peridotite and related rocks at high pressure were examined in the 1980s. These results suggested the occurrence of fractionation of majorite and perovskite in the magma ocean, when the earth was extensively melted in its accretional stage. Element partitioning experiments, however, concluded that the fractionation of these high pressure phases in the magma ocean is unlikely. Experimental studies on core materials were also made in 1980s. Oxygen and hydrogen were proposed as the light elements in the core on the basis of these experiments. Preliminary results on the reaction and partitioning of the elements between molten iron and silicates were also obtained. However, more extensive experimental studies are needed to constrain the composition of the core and processes at the mantle-core boundary.

1. Introduction

Mineral physics is a rapidly developing research field, which provides important constraints on models of the constitution and the evolution of the earth and planetary interiors. In 1980s, important progress in mineral physics has been made, especially in studies of the stability and properties of silicate perovskite, melting relations of the mantle and core materials, etc.

One of the most important technical developments in Japanese mineral physics laboratories is in high pressure experiments using large volume multianvil apparatus. Pressures above 25 GPa and temperatures in excess of 2,500°C have been generated

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with accurate pressure calibration and minimum temperature gradients in the samples. Precise phase equilibrium experiments and the synthesis of large volume of samples, both polycrystalline and single crystals, have been made using these high pressure techniques. In situ x-ray diffraction experiments were also carried out combining the multianvil apparatus with an intense x-ray source of synchrotron radiation. This experimental technique has made it possible to directly observe phase transitions and also to accurately determine the equations of state of high pressure phases.

Other important developments have been made in the elastic and calorimetric measurements on the high pressure phases. Minimization of single crystal size to several $10\text{ }\mu\text{m}$ in Brillouin scattering experiments has allowed us to measure the elastic constants of high pressure silicate phases. Calorimetric measurements of samples of only about 5 mg provided the transition enthalpies of high pressure silicates, which made it possible for us to accurately calculate the equilibrium phase relations. Although these experimental studies were made mainly in U.S. laboratories, most of the important high pressure samples used in these studies were synthesized in Japanese laboratories with the multianvil apparatus. It should be also noted that theoretical studies on high pressure silicates, which predict the phase transitions and the physical properties that are not accessible in the present state of the art, developed remarkably in the 1980s.

The contents of this paper can be divided into five parts: (1) phase transitions of mantle minerals, (2) physical properties of high pressure silicates, (3) compositional models of the mantle, (4) melting behavior of mantle silicates, and (5) core materials.

2. Phase Transitions of Mantle Minerals

Olivine, pyroxene, and garnet are widely accepted as the major constituent minerals of the upper mantle. High pressure transitions of these minerals have been studied extensively since the 1960s. Although most of the phase relations of these minerals were roughly determined by the 1970s, more detailed studies were made in the 1980s in order to determine accurate phase diagrams on the basis of high pressure experimental and thermochemical studies.

The olivine(α)-modified spinel(β)-spinel(γ) transitions in the system $\text{Mg}_2\text{SiO}_4(\text{Fo})$ – $\text{Fe}_2\text{SiO}_4(\text{Fa})$ have been studied since 1960s (see Akimoto, 1987). Recently the phase relations in the Mg_2SiO_4 -rich portion were extensively reinvestigated by Katsura and Ito (1989) using a multianvil apparatus. They determined the equilibrium boundaries of the α - β - γ transitions up to 21 GPa and 1,600°C, performing both normal and reverse experiments (Fig. 1). The chemical compositions of the coexisting phases were also determined in their study. Yagi *et al.* (1987) determined the α - γ transition boundary of Fe_2SiO_4 by in situ x-ray diffraction method using synchrotron radiation. On the other hand, calorimetric studies were made to obtain the enthalpies of the α - β - γ transitions in Mg_2SiO_4 (Akaogi *et al.*, 1984) and in the system Mg_2SiO_4 – Fe_2SiO_4 (Akaogi *et al.*, 1989) (Table 1). The calculated phase relations (Fig. 1) were consistent with Katsura and Ito's data and the equilibrium phase boundaries were further extrapolated beyond their experimental ranges. The experimentally determined and calculated widths of the α - β transition loop for the upper mantle olivine ($\text{Mg}/(\text{Mg} + \text{Fe}) = 0.89$) are consistent

Fig. 1. Phase relations in the system Mg_2SiO_4 - Fe_2SiO_4 . (a) Phase boundaries experimentally determined at 1,200 and 1,600°C (Katsura and Ito, 1989). (b) Calculated phase boundaries (solid curves, Akaogi *et al.*, 1989) and experimentally determined boundaries (dashed curves, Katsura and Ito, 1989) at 1,600°C. α , olivine; β , modified spinel; γ , spinel.

with that observed for the 400 km discontinuity (Katsura and Ito, 1989; Akaogi *et al.*, 1989).

Phase relations in the Mg-rich portion of the system MgO - FeO - SiO_2 above about 23 GPa are characterized by the formation of $(\text{Mg}, \text{Fe})\text{SiO}_3$ perovskite. Accurate determination of these stability relations is important to clarify the mineralogy of the lower mantle and the nature of the 670 km discontinuity. Ito and Yamada (1982) examined the phase relations in the system MgSiO_3 - FeSiO_3 and determined the stability fields of $(\text{Mg}, \text{Fe})\text{SiO}_3$ ilmenite and perovskite. Ito and Takahashi (1989) investigated the corresponding phase relations in the system Mg_2SiO_4 - Fe_2SiO_4 (Fig. 2). They obtained negative slopes for the ilmenite-perovskite transition in MgSiO_3 and for the dissociation of spinel to the assemblage of perovskite + periclase in Mg_2SiO_4 . They also found that the dissociation of the spinel solid solution into perovskite + magnesiowustite occurs in a very narrow pressure interval (<0.15 GPa) at 1,600°C. The observed transition pressure and the width of the spinel dissociation reaction supports a model in which the 670 km discontinuity is attributed to this reaction rather than a chemical

Fig. 2. Phase relations in the system $\text{Mg}_2\text{SiO}_4\text{--Fe}_2\text{SiO}_4$. Solid and dashed boundaries are at 1,100 and 1,600°C, respectively (Ito and Takahashi, 1989). Sp, spinel; Pv, perovskite; Mw, magnesiowustite; St, stishovite.

Table 1. Thermochemical data for transitions of high pressure silicates.

Transition	ΔH^* (kJ/mol)	ΔS^* (J/mol·K)	ΔV_{298}^* (cm^3/mol)
$\text{Mg}_2\text{SiO}_4^{\text{a,b}}$			
$\alpha \rightarrow \beta$	30.0 ± 2.8	-7.7 ± 1.9	-3.16
$\beta \rightarrow \gamma$	9.1 ± 2.1	-7.3 ± 1.4	-0.98
$\gamma \rightarrow \text{Pv} + \text{Per}$	96.8 ± 5.8	11.1 ± 3.7	-3.79
$\text{MgSiO}_3^{\text{b-c}}$			
$\text{Px} \rightarrow \text{Mj}$	30.8 ± 3.1	-4.2 ± 1.7	-2.74
$\text{Mj} \rightarrow \text{Il}$	25.0 ± 5.3	-6.8 ± 2.3	-2.23
$\beta + \text{St} \rightarrow \gamma + \text{St}$	4.5 ± 1.1	-3.5 ± 0.6	-0.49
$\gamma + \text{St} \rightarrow \text{Il}$	6.3 ± 4.8	-2.8 ± 2.5	-0.42
$\text{Il} \rightarrow \text{Pv}$	54.7 ± 6.6	12.8 ± 2.8	-1.91

^a Akaogi *et al.* (1984, 1989), ^b Ito *et al.* (1990), ^c Akaogi *et al.* (1987), ^d Ashida *et al.* (1988), ^e Yusa *et al.* (1993).

change. A calorimetric study of MgSiO_3 perovskite (Table 1) by Ito *et al.* (1990) confirmed the negative slopes for the ilmenite-perovskite transition in MgSiO_3 and for the spinel dissociation reaction in Mg_2SiO_4 . Although the negative slope of the spinel dissociation at the 670 km discontinuity tends to impede slab subduction, its magnitude may not be large enough to prevent slab penetration at a depth of 670 km.

High pressure transitions of pyroxene and garnet have been also extensively studied. Kato and Kumazawa (1985a) first reported the occurrence of MgSiO_3 tetragonal garnet (majorite). Sawamoto (1987) examined the phase relations among pyroxene, garnet, ilmenite, perovskite, and stishovite + β (or γ)- Mg_2SiO_4 in the MgSiO_3 composition. A calorimetric study of the high pressure phases of MgSiO_3 made it possible to calculate the equilibrium phase diagrams in MgSiO_3 up to 26 GPa and 2,300°C using an internally

Fig. 3. Phase relations in MgSiO_3 . Phase boundary curves are thermodynamically calculated (Yusa *et al.*, 1993). Experimental data points are from Ito and Navrotsky (1985) (triangles), Ito and Takahashi (1989) (circles), Sawamoto (1987) (squares), and Presnall and Gasparik (1990) (diamonds). Px, pyroxene; Gar, garnet; Il, ilmenite; Pv, perovskite; β , modified spinel; γ , spinel; St, stishovite.

consistent thermodynamic data set (Table 1), as shown in Fig. 3 (Yusa *et al.*, 1993).

The system $\text{Mg}_4\text{Si}_4\text{O}_{12}(\text{En})\text{--Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}(\text{Py})$ is an appropriate model for the pyroxene-garnet system in the deep mantle. Kanzaki (1987) determined the stability fields of majorite garnet and ilmenite in this system at pressures up to 22 GPa. Irifune and Ringwood (1987a) extended these experiments to 26 GPa and confirmed the partial solubility of the Py component in MgSiO_3 perovskite. Akaogi *et al.* (1987) calculated the stability field of majorite garnet in the En-Py system, using measured thermochemical data. Their results on the En-Py system are summarized in Fig. 4. The results indicate that, in contrast to the α - β and postspinel transitions in the Fo-Fa system, the pyroxene-garnet transition occurs gradually with increasing pressure and is unlikely to yield sharp velocity and density jumps in the mantle.

High pressure transitions of some other important minerals have been also reported. Phase transitions of $\text{CaMgSi}_2\text{O}_6$ diopside were examined by Irifune *et al.* (1989) using a multianvil apparatus and by Tamai and Yagi (1989) with a diamond anvil cell. Their results showed that at pressures above about 17 GPa diopside dissociates into CaSiO_3 perovskite and MgSiO_3 components, the latter being β - or γ - Mg_2SiO_4 + stishovite, ilmenite, and perovskite, depending on pressure. Yagi *et al.* (1989) confirmed that CaSiO_3 perovskite is stable in the whole range of lower mantle conditions. An MgAl_2O_4 phase with a calcium ferrite structure was synthesized by Irifune *et al.* (1991). Tsuchida and Yagi (1989) found that stishovite transforms to a CaCl_2 structure at about 90 GPa, which might be stable in the D'' layer of the lowermost mantle.

In addition to the phase transition experiments on the simple systems described above, the corresponding model mantle compositions have been examined experimentally. Akaogi and Akimoto (1979) examined phase equilibria of a peridotitic com-

Fig. 4. Phase relations in the system $\text{Mg}_4\text{Si}_4\text{O}_{12}$ – $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ at $1,500^\circ\text{C}$ (Irifune and Ringwood, 1987a; Akaogi *et al.*, 1987b). Px, pyroxene; Gar, garnet; Il, ilmenite; Pv, perovskite; β , modified spinel; γ , spinel; St, stishovite.

position close to pyrolite up to about 20 GPa. Takahashi and Ito (1987) extended these experiments to pressures over 25 GPa and $1,600^\circ\text{C}$. These studies confirmed that the major phase transitions observed in the simple systems occurred in a similar manner in the model mantle compositions, and also determined the partitioning of major elements among the coexisting phases. Phase equilibrium experiments up to about 27 GPa and $1,600^\circ\text{C}$ were made by Ito and Takahashi (1987a) in the system CaSiO_3 – MgSiO_3 – Al_2O_3 and by Irifune and Ringwood (1987b) in a pyrolitic composition. Their studies clarified the formation of majorite up to about 16 GPa and the dissociation of majorite garnet to MgSiO_3 -rich perovskite (or ilmenite) plus CaSiO_3 perovskite (and Al-rich unknown phase) above about 20–23 GPa. Figure 5 summarizes the change of mineral proportions in a pyrolite mantle at depths down to the lower mantle. Although the transitions in the Fo-Fa system have been examined in detail, the post-majorite transitions above about 20 GPa have been only poorly understood. Several possible post-majorite aluminous phases have been reported: perovskite s.s. in the En-Py system, MgAl_2O_4 calcium ferrite, ϵ - MgAl_2O_4 (Liu, 1978), and Ca, Mg-hollandite (Madon *et al.*, 1989). Phase transitions in eclogite and harzburgite compositions were also studied by Irifune and Ringwood (1987a, b), who discussed the effects of these phase transitions on the slab subduction in the deep mantle.

It is well known that small amounts of volatile components such as H_2O and CO_2 cause considerable effects on the melting behavior and the physical properties of silicates. However, hydrous silicates and carbonates stable in the transition zone and the lower mantle have remained unclarified. A hydrous silicate phase B in the system MgO – SiO_2 – H_2O was confirmed to have a high density and be stable at pressures 10–20 GPa

Fig. 5. Volumetric mineral constitution of pyrolite down to the uppermost lower mantle (Ito and Takahashi, 1987a; Irifune and Ringwood, 1987b). Ol, olivine; MS, modified spinel; Sp, spinel; Opx, Ca-poor pyroxene; Cpx, Ca-rich pyroxene; Gar, garnet; Mj, majorite garnet solid solution; Mg-Pv, MgSiO_3 -rich perovskite; Ca-Pv, CaSiO_3 -rich perovskite; Mw, magnesiowustite; X, Al-rich unknown phase.

(Akaogi and Akimoto, 1980, 1986; Kato and Kumazawa, 1985b). The crystal structure and the exact composition of phase B were determined later by Finger *et al.* (1989), who also found anhydrous phase B possessed the structure and composition relevant to the hydrous phase B. Kanzaki (1991) examined the phase relations in the $\text{MgO-SiO}_2\text{-H}_2\text{O}$ system and found two new phases, denoted E and F, which are stable at about 13–17 GPa. These phases, especially hydrous phase B, may be important hydrous silicates present in the transition zone in relatively low temperature regions, such as the subduction zone.

3. Physical Properties of High-Pressure Silicates

Elasticity data on mantle minerals are indispensable to evaluate mineralogical mantle models in the light of the observed seismic velocity profiles. The elastic properties of important high pressure silicates were determined under ambient conditions mostly by Brillouin scattering techniques. These include $\beta\text{-Mg}_2\text{SiO}_4$ (Sawamoto *et al.*, 1984), $\gamma\text{-Mg}_2\text{SiO}_4$ (Weidner *et al.*, 1984), MgSiO_3 ilmenite (Weidner and Ito, 1985), and MgSiO_3 perovskite (Yeganeh-Haeri *et al.*, 1989), which were synthesized as single crystals of several $10\text{ }\mu\text{m}$ in diameter using a multianvil apparatus (Ito and Weidner, 1986; Sawamoto, 1986). Bulk moduli of polycrystalline MgSiO_3 majorite and $\text{Mg}_4\text{Si}_4\text{O}_{12}\text{-Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ garnets were measured in compression experiments using synchrotron radiation x-ray diffraction (Yagi *et al.*, 1987, 1992). These elastic data are listed in Table 2.

The rectangular parallelepiped resonance (RPR) method has also been used to measure the elastic properties of mantle minerals. Although this technique has been applied only to minerals stable at 1 bar because relatively large crystals ($\geq 1\text{ mm}$ in

Table 2. Physical properties of high pressure silicates.

Phase	K_{0s} (GPa)	K'_{0s}	μ_0 (GPa)	μ'_0	α_0 ($\times 10^{-6} \text{ K}^{-1}$)	γ_0	δ_s
α - Mg_2SiO_4	129	5.1	82	1.8	26.2	1.25	4
β - Mg_2SiO_4	174 ^a	4.8 ^a	114 ^a	1.7 ^a	20.6 ^j	1.3	3
γ - Mg_2SiO_4	184 ^b	5.0 ^b	119 ^b	1.7 ^b	18.6 ^k	1.35	3
MgSiO_3 Px	108	5.0 ⁱ	77	2.0 ⁱ	27	1.1	6
MgSiO_3 Mj	161 ^c	4.9 ⁱ	90 ⁱ	1.4 ⁱ	18	1.1	6
MgSiO_3 Il	212 ^d	4.3 ⁱ	132 ^d	1.7 ⁱ	24 ^l	1.5 ^l	5 ^p
MgSiO_3 Pv	246 ^e	3.9 ⁱ	184 ^e	2.0 ⁱ	20 ^m	1.5 ^o	5 ^p
CaSiO_3 Pv	288 ^f	3.9 ⁱ	125 ⁱ	1.9 ⁱ	20 ⁿ	1.5 ⁿ	5 ^p

^a Sawamoto *et al.* (1984); ^b Weidner *et al.* (1984); ^c Yagi *et al.* (1992); ^d Weidner and Ito (1985); ^e Yeganeh-Haeri *et al.* (1989); ^f Yagi *et al.* (1989); ^g Gwanmesia *et al.* (1990); ^h Rigden *et al.* (1991); ⁱ estimated by Duffy and Anderson (1989); ^j Suzuki *et al.* (1980); ^k Suzuki *et al.* (1979); ^l Ashida *et al.* (1988); ^m Ross and Hazen (1989); ⁿ same as MgSiO_3 perovskite; ^o Akaogi and Ito (1993); ^p assumed; others: compiled by Jeanloz and Thompson (1983) and Irifune (1987).

edge length) are needed for the measurements, accurate measurements at room and high temperatures are possible in this method. The high temperature elastic properties of Mg_2SiO_4 and Fe_2SiO_4 olivines, MgO and pyrope garnet were measured by this method (Sumino, 1979; Sumino *et al.*, 1983; Suzuki and Anderson, 1983). Techniques for ultrasonic measurements at high pressure have also been developed, and the pressure derivatives of elastic constants of minerals including MgO and MgAl_2O_4 spinel were reported (Yoneda, 1990; Fujisawa and Ito, 1984).

Thermal expansion data are also important to constrain the mineralogy of the mantle. The thermal expansion of some high pressure silicates were measured at 1 bar: β - and γ - Mg_2SiO_4 (Suzuki *et al.*, 1979, 1980), Fe_2SiO_4 olivine and spinel (Suzuki *et al.*, 1981; Yamanaka, 1986), and MgSiO_3 ilmenite (Ashida *et al.*, 1988). The results are shown in Table 2. Although much effort has been directed to the experimental determination of the thermal expansion of Mg-rich perovskite because of its prime importance in the estimation of lower mantle mineralogy, the reliability of the obtained data is still controversial (see Wang *et al.*, 1991, and the references therein). Since the uncertainty of the thermal expansion of Mg-rich perovskite is probably caused by marginal metastability of perovskite at high temperature and 1 bar, thermal expansion measurements in its stability field are highly desirable.

The heat capacities of high pressure minerals are also important thermophysical data which are necessary to evaluate the Debye temperature and Gruneisen parameter. Watanabe (1982) and Ashida *et al.* (1987, 1988) measured the heat capacities of α - β - γ - Mg_2SiO_4 , and MgSiO_3 ilmenite, while Akaogi and Ito (1993) have reported the heat capacity of MgSiO_3 perovskite.

Theoretical studies of the crystal structure and the physical properties of high pressure silicates have also been made on the basis of molecular dynamics and first principle calculations (Matsui and Kawamura, 1987; Matsui *et al.*, 1987; Matsui, 1988; Park *et al.*, 1988). The results of these theoretical studies are generally in good agreement

with the experimentally determined physical properties and structures. This agreement gives credibility to the theoretically predicted structures and physical properties of high pressure silicates at very high pressure and high temperature which are still inaccessible to experimental studies.

We now discuss some theoretical results closely related to the constitution of the mantle. The transition of stishovite into a dense phase with the $\text{Pa}\bar{3}$ symmetry was predicted by theoretical calculations (Matsui and Matsui, 1988; Park *et al.*, 1988). Although Tsuchida and Yagi (1989) found experimentally that stishovite first undergoes a transition to the CaCl_2 structure at about 90 GPa, the decomposition of $(\text{Mg, Fe})\text{SiO}_3$ perovskite into $(\text{Mg, Fe})\text{O}$ plus $\text{Pa}\bar{3}$ -type SiO_2 might occur at higher pressures. A theoretical study by Wolf and Bukowinski (1987) showed ferroelastic behavior of silicate perovskite, which would cause successive transitions from orthorhombic to cubic via tetragonal symmetry under lower mantle conditions. Drastic changes in the physical properties might be present in association with these transitions. Matsui and Price (1991) showed a similar transition of MgSiO_3 perovskite from orthorhombic to cubic structure. The latter phase was predicted to have a high ionic conductivity at very high temperatures near the melting point at high pressure.

4. Compositional Models of the Mantle

Compositional and mineralogical models of the upper and lower mantle are the subject of vigorous debate. Possible compositional difference between the upper mantle (above 670 km in depth) and the lower mantle (below 670 km) has been discussed extensively from the viewpoints of geophysics, mineral physics, and geochemistry (e.g., Silver *et al.*, 1988). In a chemically homogeneous mantle model, the upper mantle and the lower mantle are assumed to have the same pyrolitic composition, and whole mantle convection is expected to occur. However, in a chemically stratified mantle model, the lower mantle is intrinsically denser (SiO_2 -rich or FeO -rich) than the upper mantle because of the compositional difference, and two-layer convection is likely to occur. A different stratified mantle model has also been proposed, where the transition zone has a picritic eclogite (piclogite) composition, with the peridotitic upper mantle above 400 km depth and the perovskite lower mantle (Anderson and Bass, 1986).

The phase relations and the physical properties of the high pressure minerals described in the previous sections provide constraints on mantle models from two directions. First, the phase relations established by high pressure experiments and thermodynamic calculations define the depths and the sharpness of the phase transitions which should occur in the mantle. Second, the measurements of the elastic moduli and their pressure and temperature dependences enable us to calculate the velocity and density profiles for given model mantle compositions, which are then compared with those obtained from seismic observations.

Seismological studies indicate that the 670 km discontinuity is very sharp (e.g., Nakanishi, 1988). Some earlier studies concluded that the 670 km discontinuity could not be attributed to the dissociation of $(\text{Mg, Fe})_2\text{SiO}_4$ spinel into $(\text{Mg, Fe})\text{SiO}_3$ perovskite and $(\text{Mg, Fe})\text{O}$, because this reaction was expected to be spread out over a depth range of more than 20–30 km (Jeanloz and Thompson, 1983; Lees *et al.*, 1983). However,

refinements of the phase relations demonstrated that this reaction occurs in a very narrow pressure interval corresponding to a depth range of at most 4 km (Ito and Takahashi, 1989), which is consistent with seismic observations of the 670 km discontinuity. Anderson and Bass (1986) argued that the observed velocity increase is rather abrupt at the 400 km discontinuity and therefore it could not correspond to the α - β transition in the system Mg_2SiO_4 - Fe_2SiO_4 . The phase relations established by subsequent high pressure experiments and thermodynamic studies, however, demonstrated that the α - β transition occurs in a depth interval of 10–20 km (Katsura and Ito, 1989; Akaogi *et al.*, 1989), which is in good agreement with the seismic observations.

The elastic constants of important high pressure silicates were measured under the ambient conditions, as discussed in the previous section. Using these elastic data, the velocity and density profiles were calculated and compared with the seismological models (Weidner and Ito, 1987; Akaogi *et al.*, 1987; Irifune, 1987; Duffy and Anderson, 1989). One of the results obtained by Weidner and Ito (1987) is shown in Fig. 6. The observed velocity jumps at the 400 km discontinuity are about 40% of the velocity changes for the α - β transition of mantle olivine under ambient conditions. However, this does not necessarily mean that the mantle is composed of only 40% olivine at the 400 km depth, because the velocity jump for the α - β transition is very sensitive to the pressure and temperature derivatives of the elastic constants of β -phase (Weidner and Ito, 1987). In fact, Gwanmesia *et al.* (1990) and Rigden *et al.* (1991) concluded that models with olivine content in a range from 45 to 65% are acceptable on the basis of their measurements of pressure derivatives of the elastic moduli of β - Mg_2SiO_4 .

The transition zone between 400 and 670 km is marked by high gradients of the seismic velocities (e.g., Dziewonski and Anderson, 1981). The steep gradients may be explained by the successive phase transitions in the pyrolite mantle: the β - γ transition in olivine, the pyroxene-garnet transition, and the post-majorite transition including the exsolution of CaSiO_3 perovskite. In the piclogitic model (Anderson and Bass, 1986),

Fig. 6. Comparison of observed and calculated P- and S-wave velocities in the mantle (Weidner and Ito, 1987). Dotted curves are from the seismic studies by Walck (1984) and Grand and Helmberger (1984). Solid curves are the calculated velocities from the elasticity data.

the steep velocity gradients were explained by the pyroxene-garnet transition, where a very high bulk modulus for majorite garnet was assumed on the basis of earlier experiments by Jeanloz (1981). However, Akaogi *et al.* (1987) showed that the piclogitic transition zone gives smaller velocity gradients, using the new bulk modulus data for majorite of Yagi *et al.* (1987), and is accordingly inconsistent with seismic observations.

The boundary region between the transition zone and the lower mantle is marked by the presence of a very sharp velocity jump at 670 km and also a high velocity gradient at depths of about 600–800 km (Fig. 6). These features are explained in the pyrolitic mantle model as follows. The former jump is due to the spinel dissociation into perovskite and magnesiowustite, while the latter represents the smeared out transition of majorite garnet to denser phases including CaSiO_3 - and MgSiO_3 -rich perovskites at depths of about 650–750 km (Ito and Takahashi, 1987a). The velocities in the lower mantle are consistent with those of the mixture of perovskite and magnesiowustite in the pyrolitic composition, as shown in Fig. 6. However, alternative compositional models with a SiO_2 -rich or FeO-rich lower mantle are still acceptable, when we consider uncertainties in the pressure and temperature derivatives of the elastic moduli of the relevant high pressure phases (Weidner and Ito, 1987; Duffy and Anderson, 1989). It has been pointed out that the thermal expansion of $(\text{Mg}, \text{Fe})\text{SiO}_3$ perovskite provides a very important constraint to test the compositional models of the lower mantle (Jackson, 1983; Jeanloz and Thompson, 1983). Recent analyses of thermal expansion show that the pyrolitic composition fits the seismic data better than the other compositional models (Chopelas and Boehler, 1989).

Fig. 7. Temperature distribution in the pyrolite mantle (Ito and Katsura, 1989; Akaogi *et al.*, 1989; Akaogi and Ito, 1993). Solidus of dry peridotite (I-T, Ito and Takahashi, 1987b) and melting curve of $(\text{Mg}_{0.9}, \text{Fe}_{0.1})\text{SiO}_3$ perovskite (K-J, Knittle and Jeanloz, 1989a) are also shown.

Temperatures in the transition zone have been often estimated using the phase diagrams of the Mg_2SiO_4 – Fe_2SiO_4 system. Recently Ito and Katsura (1989) and Akaogi *et al.* (1989) estimated the temperatures at the 400 and 670 km discontinuities as 1,400 and 1,600°C, respectively, from the locations of the α – β and postspinel transitions. Akaogi and Ito (1993) further calculated the adiabatic temperature profile in the lower mantle. Figure 7 illustrates the temperature profiles thus obtained for the upper and lower mantle. In a chemically stratified mantle model with layered convection, the temperature in the lower mantle is expected to be higher than that in a homogeneous mantle model with whole mantle convection. However, even in the former case, the temperature should be lower than the melting temperature of MgSiO_3 -rich perovskite. Figure 7 also shows the melting curve of perovskite by Knittle and Jeanloz (1989a) using diamond anvils, and that determined for peridotite by Ito and Takahashi (1987b) with a multianvil apparatus. The present geotherm is indeed far below these melting curves throughout the mantle.

5. Melting Behaviors of Mantle Silicates

Melting of silicates is an essential process of magma generation, and is thought to be one of the most important processes controlling the evolution of the earth's mantle. Until the 1970s the melting relations of silicate minerals were studied from a petrological point of view, mostly at pressures below 4 GPa. Development of multianvil techniques made it possible to investigate melting relations at pressure above 20 GPa and temperatures higher than 2,000°C. Using these techniques melting experiments were carried out in several simple silicate systems including Mg_2SiO_4 and Fe_2SiO_4 (Ohtani, 1979; Ohtani and Kumazawa, 1981).

Melting relations of mantle peridotites and related rocks were studied at pressures of 10–25 GPa using multianvil apparatus in the last decade. These studies were carried out on the assumption that global melting had occurred during the early stage of the earth's history (e.g., Abe and Matsui, 1985; Sasaki and Nakazawa, 1986). Takahashi and Scarfe (1985) and Takahashi (1986) investigated the melting relations of mantle peridotite at pressures up to 15 GPa, and found that the melting temperature interval between the solidus and liquidus of peridotite decreases significantly with increasing pressure, accompanied by a change of the liquid composition from basaltic to komatiitic. Ito and Takahashi (1987b) and Ohtani and Sawamoto (1987) extended the melting experiments of the peridotitic and chondritic compositions to 25 GPa (Fig. 8). They found that the liquidus phase is olivine at pressures below about 15 GPa, majorite garnet at 15–25 GPa, and Mg-perovskite above 25 GPa. These experimental results would have important implications for the evolution of the mantle, if the global melting more than several hundred km in depth (magma ocean) occurred in the accretional stage of the earth. The above experimental results suggest that fractionation of olivine, majorite, and MgSiO_3 -rich perovskite could occur at the corresponding depths in the deep mantle and that the primitive mantle should be chemically stratified.

Experiments on element partitioning between the high pressure silicates and the coexisting melts impose very important constraints on the above models of fractionation of high pressure phases in the deep mantle. Ohtani *et al.* (1989) and Yurimoto and

Fig. 8. Melting relations of peridotite (Ohtani and Sawamoto, 1987; Ito and Takahashi, 1987b). Dominant subsolidus phases are shown with symbols in boxes: Ol, olivine; MS, modified spinel; Sp, spinel; Pv, perovskite; Mw, magnesio-wüstite. Other phases are: Px, Ca-poor pyroxene; Mj, majorite; L, liquid. Shaded areas are transition intervals in the system $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$.

Ohtani (1992) investigated partitioning of minor and trace elements between majorite garnet and silicate melt at 16–20 GPa, and discussed possible fractionation of majorite together with the genesis of various types of komatiites. Ito and Takahashi (1987b) examined the partitioning of major elements at 25 GPa and concluded that MgSiO_3 - and CaSiO_3 -rich perovskites could be fractionated, if any, only in a small extent. Kato *et al.* (1988a, b) determined the partition coefficients of major and trace elements among the Mg- and Ca-perovskites, majorite, and melts. They concluded that there is no evidence of gross differentiation in a mantle controlled by majorite or Mg-perovskite fractionation. These results, however, do not rule out the possibility of fractionation in the primitive mantle, because the subsequent vigorous convection in the mantle could have obliterated the evidence of the stratification formed in the earlier stage.

The density and viscosity of silicate melts are very important properties in understanding magmatic processes. It has been suggested that, in some depth ranges of the mantle basaltic melts could be denser than the surrounding peridotitic mantle (Stolper *et al.*, 1981). This density-crossover at high pressure may have significant implications for the evolution of the mantle. However, only a few experiments have been carried out for measurements of the density and the viscosity of silicate melts at high pressures, because of experimental difficulties. At pressures up to 2 GPa, Taniguchi (1989) measured densities of the silicate melts in the system $\text{CaMgSi}_2\text{O}_6\text{-CaAl}_2\text{Si}_2\text{O}_8$ by the sinking/floating sphere method. A new technique to measure viscosity and density of silicate melts at high pressures was developed by Kanzaki *et al.* (1987), who directly observed sinking Pt (or Mo) spheres in $\text{NaAlSi}_3\text{O}_8$ and $\text{Na}_2\text{Si}_2\text{O}_5$ melts at 3 GPa with an x-ray shadowgraph using synchrotron radiation.

6. Core Materials

The earth's core consists of a liquid outer core and a solid inner core, which are made mostly of iron alloyed with small amounts of nickel. The phase relations of pure iron at high pressures and high temperatures are therefore of basic importance to understand the state of the core. The α - γ - ϵ transition boundaries of iron were recently reexamined by an x-ray diffraction study using synchrotron radiation (Akimoto *et al.*, 1987). It was found that the density of the outer core is about 10% lower than that of pure iron at the relevant P, T conditions. This implies that some light elements should also exist in the outer core. Until the 1970s silicon and sulfur were considered as the leading candidates for the light elements. Ringwood (1979) discussed the possibility that the oxygen solubility in molten iron increases with pressure, and proposed that oxygen is probably the principal light element in the outer core. Ohtani *et al.* (1984) and Kato and Ringwood (1989) experimentally confirmed the increase of oxygen solubility in molten iron with pressure, suggesting complete miscibility between Fe and FeO liquids at 25 GPa and 2,200°C. In experiments on the systems Fe-FeO-FeS and Fe-Ni-O-S, Urakawa *et al.* (1987) found that the eutectic temperatures decrease by several hundred degrees as compared with the melting temperature of pure iron at 15 GPa. They also found a much smaller pressure dependence for these eutectic temperatures. These results suggest that the melting point of iron decreases by more than one thousand degrees in the presence of oxygen and sulfur under the core's P,T conditions (Fig. 9).

Fig. 9. Melting curves of core materials at high pressures. Melting temperatures of Fe (Williams *et al.*, 1987), FeO (Knittle and Jeanloz, 1991), and FeS (Williams and Jeanloz, 1990) are shown. Eutectic temperatures are also shown in Fe-FeO system (Ohtani *et al.*, 1984; Kato and Ringwood, 1989), Fe-FeS system (Williams and Jeanloz, 1990), and Fe-FeO-FeS and Fe-Ni-O-S systems (Urakawa *et al.*, 1987). CMB represents the depth of the core-mantle boundary.

On the basis of the observation that solubility of hydrogen into iron increases drastically with pressure, Fukai (1984) and Fukai and Suzuki (1986) proposed that formation of iron hydride at high pressure may play an important role during the core formation processes. Suzuki *et al.* (1984, 1989) demonstrated that the formation of iron hydride occurred at pressures of about 5 GPa in the iron-silicate-water system, which was accompanied by a large decrease of melting temperature of the metallic phase by several hundred degrees. These experimental results imply that hydrogen is one of the most likely candidates for the light elements in the core, if water was effectively incorporated into the earth's interior in the accretional stage.

Very recently, partition experiments on transition metal elements among iron, silicates, and oxides were carried out at high pressure and high temperature. Urakawa (1991) examined partitioning of iron and nickel between magnesiowustite and the metallic phase, while Suzuki *et al.* (1992) determined the partition coefficients of iron, cobalt, and nickel between metal, olivine, and pyroxene. Ohtani *et al.* (1991) examined partitioning of several transition metal elements among Mg-perovskite, magnesiowustite, and metallic iron. Although the experiments were carried out in a limited pressure and temperature range, these partition data are useful to constrain the core segregation processes and to examine whether the core-mantle system is in equilibrium or not.

The nature of the core-mantle boundary and the D'' layer in the lowermost mantle have been recently discussed based on mineral physics approaches. A preliminary study using a diamond anvil cell by Knittle and Jeanloz (1989b) revealed the occurrence of complex reactions between perovskite and molten iron under the core's P, T conditions, and suggested that this reaction occurs in the D'' region. Ito and Katsura (1991) found similar reactions with considerable dissolution of Si and O into molten iron from silicate melt at 24 GPa and 2,550°C. The solubility of these elements in molten iron was suggested to be further enhanced at higher pressures. Accordingly, both Si and O may be important light elements in the core, which would reduce the SiO₂ content in the mantle from chondritic toward peridotitic compositions during the core-mantle separation.

7. Concluding Remarks

Using the multianvil techniques developed in 1980s, the phase relations of mantle minerals were accurately determined under P, T conditions corresponding to the uppermost lower mantle. Thermodynamic studies of the high pressure silicates provided detailed phase equilibrium diagrams which are in harmony with the experimental results. Physical properties, such as elastic moduli and thermal expansivities, of the high pressure silicates were also measured at the ambient pressure. Mineral physics tests based on these experimental results reveal that the upper mantle composition is consistent with pyrolite. Although the experimental data on the postspinel transition is consistent with the nature of the seismic 670 km discontinuity, the question of whether or not the lower mantle composition is the same as the upper mantle still remains to be solved in 1990s. Accurate determinations of the mineral physics parameters of lower mantle minerals are required to place tighter constraints on these issues. Possible transitions in silicate perovskite, predicted by the theoretical studies, should be investigated experimentally.

Melting experiments on model mantle rocks at 10–25 GPa have clarified that the

melting behavior of these materials at pressures corresponding to the transition zone and the lower mantle are very different from those under upper mantle conditions. These results strongly suggest that fractionation of majorite garnet and perovskite would have occurred and a stratified mantle would have been formed in the early stage of the formation of the earth, if the earth experienced extensive global melting. The formation and evolution processes of the magma ocean will be clarified in more detail by a combination of computer simulations and high pressure experimental studies in 1990s.

Some experiments on element partitioning and the reactions between core materials and silicates have been carried out in the 1980s. However, there is still active debate on the light elements in the core. These results are rather qualitative or preliminary; further studies are needed to clarify the present state and the formation processes of the core. Development of experimental and theoretical studies in mineral physics will help to clarify the composition of the core and the nature of the D" layer in 1990s.

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