Phase Transformations: Implications for Mantle Structure

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The role of phase transformations on radial and lateral velocity and density variations in the Earth's mantle is examined. Pyrolite is taken as a reference chemical composition. Specific attention is given to the chemical interaction among the multiple components in the entire system. In particular, aluminum influences the width and depth of the 410 km discontinuity. The velocities and density at the 410 km discontinuity are rather insensitive to lateral variations of the temperature aside from the change in the depth of the discontinuity. Formation of CaSiO$_3$ perovskite may be an important contributor to the 520 km discontinuity. Aluminum also plays a major role in defining the character of the 660 km discontinuity. Slight variations in Al content or temperature from the reference model changes the magnitude of the 660 velocity increase by a factor of two. Ilmenite forming phase transitions will introduce lateral velocity variations resulting from lowered temperatures that can be mistaken as a slab sitting on the 660 km discontinuity. These many different implications result from considering the whole chemical system.

INTRODUCTION

Mantle acoustic velocities and density reflect the properties of the constituent minerals. Changes in these properties result from changes in pressure, temperature, composition, and phase. Of these, changes in phase have the greatest capacity of creating the largest variations in the shortest distances.

Phase transitions have been implicated in the cause of the major seismic discontinuities in the mantle. The phase transitions occur as one crystal structure becomes more stable than another. These transitions take place in pressure-temperature-composition space and the effects of the transition on the physical properties of the mantle depend on the details of the interactions within this space. Transitions can be as sharp as the breakdown of ringwoodite to a perovskite bearing assemblage, possibly occurring over a depth range of less than a kilometer, to extended transformations, such as the pyroxene to garnet transformation that may be spread out over 100 km depth range. Lateral variations that affect the pressure of the transformation will cause a discontinuity to vary vertically in the former case, but will appear in the tomographic image in the latter case.

Phase transitions play an active role in convection, providing buoyancy forces as the temperature dependence of the depth of the transition varies. Honda and S. Balachandar [1993] and Tackley, et al. [1993] demonstrate that an endothermic phase transition can introduce episodic
Table 1. Composition of pyrolite model from *McDonough and Sun* [1995]. The last column indicates the cumulative cation percent including all cations that are more abundant.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Wt%</th>
<th>Cation %</th>
<th>Sum cation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>45</td>
<td>37.94</td>
<td>37.94</td>
</tr>
<tr>
<td>MgO</td>
<td>37.8</td>
<td>47.52</td>
<td>85.46</td>
</tr>
<tr>
<td>FeO</td>
<td>8.05</td>
<td>5.68</td>
<td>91.13</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.45</td>
<td>4.42</td>
<td>95.56</td>
</tr>
<tr>
<td>CaO</td>
<td>3.55</td>
<td>3.21</td>
<td>98.76</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.38</td>
<td>0.26</td>
<td>99.02</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.36</td>
<td>0.59</td>
<td>99.61</td>
</tr>
<tr>
<td>NiO</td>
<td>0.25</td>
<td>0.17</td>
<td>99.78</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.2</td>
<td>0.13</td>
<td>99.9</td>
</tr>
<tr>
<td>MnO</td>
<td>0.14</td>
<td>0.1</td>
<td>100</td>
</tr>
</tbody>
</table>

Convection through the 660 km discontinuity. Conversely, an exothermic transition will assist convection. *Weidner and Wang* [1998] point out that the phase transformations that likely contribute to the 660 km discontinuity can assume either endothermic or exothermic characteristics depending on the details of the phase relations and the composition of the Earth in this pressure-temperature-composition space. In fact, both at 410 km depth and at 660 km depth, phase transitions are occurring in different chemical components with opposite signs of their respective Clapeyron slopes. At 410, while the olivine transforms to wadsleyite with a positive slope, the pyroxene to garnet transformation is negative. At 660 km, the breakdown of ringwoodite has a negative slope in contrast to the probable positive slope of the garnet to perovskite transformation.

Not only do the subsystem transformations occur with different characteristics at these different depths, but they also interact chemically. The width of the 410 discontinuity depends on how complete the pyroxene to garnet transformation has progressed by 410 km depth. The magnitude of the 660 discontinuity can vary by as much as a factor of two owing to the control of Al on the perovskite forming transformations. The improved resolution of seismic data require that we treat the phase transformations with increasing care. No longer can we model the mantle as though it were dominated by olivine. A focus of this paper is to begin a realistic modeling of the phase transformations of the mantle.

Our goals are modest in this regard, we include in our discussion the five most abundant cations: Mg, Si, Al, Fe, and Ca. We use phase equilibria data to define the stable assemblages at relevant pressures and temperatures, and cation distribution data to define the chemical composition of each phase. This information, along with our current estimates of physical properties of these phases, provides a mineralogical model with volume percents of each phase along with the aggregate velocities and density. The absolute values of the results such as acoustic velocity at a particular depth, or the depth of a particular transformation have uncertainties that reflect the input data. However, such modeling enables us to identify the role of temperature and chemical variations that might be expected in the Earth. It also identifies areas where more precise laboratory data will help to define Earth characteristics.

We explore various chemical interactions between an olivine-normative component and a pyroxene-normative component. We find that all major velocity discontinuities have contributions from both systems, and that there must be considerable influence of both systems in these discontinuities. In the spirit of providing a reference model, we focus on a pyrolite composition [*McDonough and Sun*, 1995]. Table 1 summarizes the abundance of the principal cations in this model. The five cations that we include here represent nearly 99% of the cations in pyrolite. We demonstrate that within the framework of this model, the depth of the 660 km discontinuity is not monotonically tied to temperature. Rather, there exists a minimum depth and both higher and lower temperatures increase the depth of the discontinuity. Some such features may be generalizable to other model compositions, others not.

Table 2 helps to illustrate the importance of phase, or crystal structure, in defining sound velocities and density by comparing these properties for several materials related to MgSiO₃. The first four entries all have the same composition, but are progressively higher pressure phases. The last two, are for different compositions but share crystal structure (ferrosilite has the same structure as enstatite, and pyrope has the same structure as majorite). There is a several percent difference in each of these properties between any of the phases. The transition from one phase to another will be localized in the mantle to a relatively narrow region. Thus, in these regions, the phase transitions will dominate most other variation in state variables that are occurring.

A mantle rock is composed of several minerals and the physical properties are a weighted average of the properties of the individual phases. Acoustic velocities and density are well defined functions of the properties of the individual phases and depend on the volume percents of these phases. In cases where the elastic properties differ radically among the phases, such as a partial melt, and for diffusion controlled properties, such as electrical conductivity and
rheology, the geometry of aggregation can also become important.

Chemical composition influences the physical properties of the system by defining the proportions of the stable phases at a particular pressure and temperature and by the partitioning of elements between phases. Examples of the effects of composition on the seismic properties is illustrated in Table 2. By substituting all of the magnesium in orthoenstatite with iron (ferrosilite) the longitudinal and shear wave velocities decrease by 19% and 25%, while the density increases by 25%. Thus, a variation of 1% in these properties requires about 4% variation in iron content. In contrast, replacing 25% of the (Mg, Si) content in garnet with Al (forming pyrope) results in a 1% increase in each of these values. However, adding Al to the system may stabilize the garnet phase instead of the ilmenite phase, a change of over 10% in these properties.

While our goal is to review our understanding of several of the phase transitions that may shape the properties of the mantle, we do not try to be comprehensive. We focus on a narrow compositional range as defined by our reference model, pyrolite. We emphasize the phases that are volumetrically dominant, and those that control physical properties. We especially try to identify chemical interactions between the traditional systems of olivine and pyroxene-garnet to emphasize the importance of creating whole system models. These interactions indeed may dominate the character of the Earth in regions of phase transformations.

THE 410 KM DISCONTINUITY

The major seismic discontinuity at 410 km depth is widely accepted to result from a solid-solid phase transition in the Earth's upper mantle. Experimental observations indicate that olivine transforms to wadsleyite at the appropriate pressures and temperatures [Katsura and Ito, 1989]. To first order, the seismically modeled increases in density and elastic properties across 410 match those predicted for this transformation by plausible mantle compositions [e.g., Ito and Stixrude, 1992], while the amount of olivine required to match seismic models indicate a more silica rich region than olivine [Duffy, et al., 1995]. On the other hand, Gaherty, et al. [1998] demonstrate that if the velocity increase is parameterized consistent with the laboratory data, then pyrolite provides a correct match to the impedance contrast of the discontinuity for shear waves. In addition, seismically inferred topography on the boundary appears to be consistent with the predicted Clapeyron slope for the transition [e.g., Vidale and Benz, 1992]. However, in this region, there are phase transitions that involve the

### Table 2. Comparison of acoustic velocities for different phases and compositions in relation to MgSiO_3 in the orthopyroxene structure (enstatite).

<table>
<thead>
<tr>
<th>Phase</th>
<th>V_p, km/s</th>
<th>V_s, km/s</th>
<th>Density, gm/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enstatite (MgSiO_3)</td>
<td>8.048</td>
<td>4.856</td>
<td>3.210</td>
</tr>
<tr>
<td>Majorite (MgSiO_3)</td>
<td>8.972</td>
<td>5.062</td>
<td>3.513</td>
</tr>
<tr>
<td>Ilmenite (MgSiO_3)</td>
<td>10.065</td>
<td>5.886</td>
<td>3.810</td>
</tr>
<tr>
<td>Perovskite (MgSiO_3)</td>
<td>11.004</td>
<td>6.567</td>
<td>4.105</td>
</tr>
<tr>
<td>Ferrosilite (FeSiO_3)</td>
<td>6.53</td>
<td>3.62</td>
<td>4.002</td>
</tr>
<tr>
<td>Pyrope (MgAl_2SiO_6)</td>
<td>9.098</td>
<td>5.104</td>
<td>3.559</td>
</tr>
</tbody>
</table>

non-olivine component. Such reactions tend to be distributed over depth, contributing to velocity gradients as well as influencing lateral variations induced either by chemical or temperature variations. These reactions interact with the olivine transitions, affecting its width and depth as well.

Phase Relations and Element Partitioning

Several experimental investigations have been carried out to characterize the olivine-wadsleyite transition including the examination of samples quenched from high-pressure and temperature experiments on the (Mg,Fe)_2SiO_4 system [e.g. Katsura and Ito, 1989] as well as in-situ X-ray diffraction (such as by Morishima, et al., [1994] on the Mg_2SiO_4 system). Studies on this transition in more complex systems such as the CaO-MgO-Al_2O_3-SiO_2 (CMAS) system [Gasparik, 1990, 1996a, b], garnet-peridotite [Ito and Takahashi, 1987], garnet-lherzolite [Akaogi and Akimoto, 1979], and synthetic pyrolite [Irfune and Ringwood, 1987b] were carried out on quenched samples. In an Fe-containing system, the olivine-wadsleyite transition occurs in the order of olivine → olivine + wadsleyite → wadsleyite over certain pressure range which is determined by the Fe content of the system and temperature. Generally, higher temperature and lower Fe content result in higher transition pressure (and thus deeper discontinuity) and narrower pressure range (and thus sharper discontinuity).

Experimental data show that pyroxene component undergoes gradual changes across 410, involving enstatite, Ca-rich pyroxene, and garnet. The olivine-normative component interacts with the pyroxene-normative component via Fe partitioning: garnet tends to take Fe from olivine or wadsleyite whereas pyroxenes tend to give Fe to olivine
There appears to be certain temperature dependence also, with higher Al content at higher temperatures. We use linear pressure and temperature dependence to model these observations and the partitioning coefficients are in general agreement with experimental data within 0.05 (Figures 1 - 3).

**Factors Affecting 410 Discontinuity**

Both mantle temperature and composition have significant influence on the depth and shape of the 410 discontinuity. The positive slope of the olivine-wadsleyite boundary is reasonably well known and effects of mantle temperature have been discussed on this basis by many authors. The 410 discontinuity has been treated as the olivine-wadsleyite transition in the presence of a “silent” phase, which does not affect the phase transition in any way. This assumption is thermodynamically incorrect for (1) the olivine- and pyroxene-normative components interact with each other through Fe partitioning, and (2) the pyroxene-normative components can be dominated either by

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**Figure 1.** Ca content in diopсидic pyroxene as a function of pressure and temperature. Two dotted lines are fit to Fe-bearing data at 1473 K (upper dotted line) and 1873 K (lower dotted line).

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or wadsleyite. *Akaogi and Akimoto* [1979], *Irifune and Ringwood* [1987a, b], and *Takahashi and Ito* [1987] have studied this transition in complex systems such as peridotite and synthetic pyrolite.

In order to model the mineralogy as a function of depth, it is necessary to describe the elemental partitioning among equilibrated phases, especially as they control phase transitions. Figures 1 - 3 show the available experimental data on partitioning coefficients of Ca, Fe, and Al between the pyroxene-normative components and comparison with data on the CMAS system [Gasparik, 1989]. The Ca content in both diopсидic pyroxene and garnet increases rapidly with pressure and decreases with temperature. There appears to be a systematic difference in the systems containing Fe with that without Fe. For diopside, Ca content is lower than that in the Fe-free system, perhaps Fe preferentially occupies the large cation site, competing with Ca. Similar effects may exist for garnet, especially at high temperatures. For garnet, the Al content decreases rapidly with pressure due to the formation of majoritic garnet.

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**Figure 2.** Al content in garnet as a function of pressure and temperature. Two dotted lines are fit to the Fe-bearing data at 1473 K (upper) and 1873 K (lower), respectively.
pyroxenes or garnets, depending on total aluminum content in the system as well as temperature.

The phase relations and element partitioning data discussed in the previous section allow us to model details of the olivine-wadsleyite transition in complex systems to examine possible effects on the 410. We emphasize here that the olivine- and pyroxene-normative components cannot be treated separately in modeling the 410 discontinuity, because they interact with each other through Fe partitioning. This is also the case for the 660 discontinuity as discussed in a later section.

**Volume Fractions of Phases**

Figures 4 and 5 illustrate the effects of mantle temperature and aluminum content on the volume fractions of the thermodynamically stable phases through the 410 discontinuity for pyrolite. We compare various temperature profiles in the transition zone: (1) isothermal, (2) a uniform gradient of 0.7 K/km [Brown and Shankland, 1981; Ito and Katsura, 1989], and (3) a temperature gradient of 0.7 K/km plus an increase due to the exothermic transition from olivine to wadsleyite [Ito and Katsura, 1989]. The temperature gradient alone does not have significant effect on volume fractions which are indistinguishable from the isothermal case (Figure 4A). The latent heat, which will heat a pure olivine sample by 85 K on completion of the transition to wadsleyite, gives a 40 K increase across the phase transition in this system, for an adiabatic reaction zone. This increase makes pyroxenes transform into garnet at shallower depths (Figures 4B and C). Increasing the foot temperature from 1473 K (Figure 4B) to 1673 K (Figure 4C) further stabilizes garnet.

The temperature effects are small compared to those from varying aluminum content. Figure 5 shows the pyrolite mantle, with aluminum contents of 1, 3, and 5 cation percent, all along the same 1473 K geotherm, and

![Figure 3](image_url) Figure 3. Ca content in garnet. Again, two dotted lines are fit to Fe-bearing data at 1473 K (upper) and 1873 K (lower), respectively.

![Figure 4](image_url) Figure 4. Volume fractions of stable phases in pyrolite (Table 1) as a function of mantle temperature. A: along a 1473 K isotherm; B: along a geotherm with a gradient of 0.7 K/km and a foot temperature of 1473 K. Also included is the latent heat effect due to the olivine-wadsleyite transition; C: similar to B but with a foot temperature of 1673 K.
transition as a three parameter function of depth, \( z \), through the interval of the transition as:

\[
X(z) = X_0 + \left( \Delta X_1 - \frac{8\Delta X_2}{3}(z - z_0) / \Delta z + \left( \frac{8\Delta X_2}{3} \right) \right) \frac{[z - z_0]}{\Delta z}^3
\]

where the three parameters include \( \Delta X_1 \), the total increase in velocity or density over the transition interval; \( \Delta z \), the total width, in terms of depth, of the transition interval as defined by the width of the two phase region. \( \Delta X_2 \) is the deviation from linearity measured at the midpoint of the transition interval. \( \Delta X_2 / \Delta X_1 \) is well constrained by the experimental data to be about 0.13(1). The parameter, \( \Delta X_1 \), depends on the difference of the values of the velocity or density between olivine and wadsleyite along with the amount of olivine present at 410 km. \( \Delta z \) depends on the olivine phase diagram along with the interactions between the different chemical components. \( \Delta z \) should take into

Figure 5. Volume fractions of stable phases with varying Al contents as shown (ratio of all other cations remains constant). For the low Al (1 cation %) model, pyroxenes dominate the non-olivine component. Note that in this plot the higher pressure field for pyroxenes is not shown, which should include wadsleyite/ringwoodite plus stishovite. Note gradual increase in garnet as Al content increases.

with the same latent heat effects. As aluminum content increases, the garnet field expands at the cost of reducing pyroxenes in the system. This has an important influence on the detailed structure of the 410.

**Fine Structure of 410**

Using the thermoelasticity data consistent with *Duffy and Anderson* [1989], we calculate density and velocity profiles across 410 (Figure 6). *Weidner* [1986], *Stixrude* [1997], and *Gaherty, et al.* [1998] have discussed the non-linearity of the profiles across 410. *Gaherty, et al.* [1998] parameterized the dependence of velocity or density increase (expressed as \( X \)) due to the olivine-wadsleyite phase

Figure 6. Density (upper), Vs (middle), and Vp (lower) of pyrolite with various Al contents. All models follow a geotherm whose zero pressure temperature is 1473 K. Higher Al models have high density and velocities because garnets have higher shear and bulk moduli than pyroxenes.
account the fact that the iron content in the olivine-wadsleyite system will be buffered by the other minerals present thereby yielding a larger Fe content in the final wadsleyite than in the initial olivine as pointed out by Stixrude [1997]. Irfune and Isshiki (1998) demonstrated this effect experimentally in a peridotite system in which the iron content in the olivine-normative component also varied with the extent of the pyroxene to garnet transformation reflecting the differing partition coefficients of the different phases. These effects are incorporated into the calculations discussed here.

Iron: The iron content of the total system has a direct impact on the shape and width of the 410 discontinuity. Phase relations in the $\text{Mg}_2\text{SiO}_4 - \text{Fe}_2\text{SiO}_4$ system [Katsura and Ito, 1989] imply that in an Fe-rich mantle, the olivine-wadsleyite transition will result in a shallower and more spread-out discontinuity. Figure 7 to 9 show the effects of composition and temperature on the 410 discontinuity in two pyrolite mantle models, one with 5.7 cation percent Fe, the other 6.5%. This 14% increase in Fe content results in a 3 - 4 km change in 410 depth, and a similar change in the transition width.

Aluminum. The amount of Al in the total system affects the stability field of garnet, which, in turn, affects Fe content in olivine/wadsleyite and the amount of pyroxene in the system. Figure 5 shows this effect in pyrolite. Garnet is almost nonexistent in the system with 1% of Al, whereas it dominates the pyroxene-normative component in the system with 5% Al. Note that in the low Al case, pyroxene eventually transforms into wadsleyite plus stishovite close to 410 km resulting in a larger magnitude of the 410 discontinuity. In the case of higher Al, a gradual transformation of pyroxene to garnet

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**Figure 7.** Width of the olivine-wadsleyite two phase region at the 410 km discontinuity for pyrolite as a function of thermal models. (1) - constant mantle temperature; (2) - temperature gradient 0.7 K/km, no latent heat; (3) - latent heat 85 K for olivine-wadsleyite transition, no temperature gradient; (4) - combined effects of latent heat and temperature gradient.

**Figure 8.** Width of the olivine-wadsleyite two phase region at the 410 km discontinuity for pyrolite as a function of small variations in Al and Fe. (A) - $\text{Al}_2\text{O}_3$ = 5%, $\text{FeO} = 5.7$%; (B) - $\text{Al}_2\text{O}_3$ = 1%, $\text{FeO} = 5.7$%; (C) - $\text{Al}_2\text{O}_3$ = 5%, $\text{FeO} = 6.5$%.
Figure 9. Depth of the 410 km discontinuity (defined by the mid-point of the olivine - wadsleyite transformation) as a function of mantle composition. All models are based on pyrolite with slight variations in Al and Fe. (A) - Al₂O₃ =5%, FeO = 5.7%; (B) - Al₂O₃ = 1%, FeO = 5.7%; (C) - Al₂O₃ = 5%, FeO = 6.5%.

Figure 10. Change in acoustic velocities and density due to a 100K decrease in temperature for two mantle geotherms. Changes include the contributions of phase transformations and changes in properties of the different phases.

wadsleyite transition. Second, temperature affects stability field of pyroxenes and garnets, which then affects Fe content in the olivine-normative component. The effects come from (1) ambient mantle temperature, (2) temperature gradient, and (3) latent heat due to the exothermic olivine-wadsleyite phase transition. Figure 4 shows volume fractions of various phases along two geotherms. In a hotter mantle, Ca-poor pyroxene (labeled DPx) disappears and the garnet fraction increases. The largest effect on the depth and width of 410 among the three is the latent heat (Figure 7).

Lateral Variations

Lateral variations in temperature and composition will introduce lateral variations in the velocities and density. The total effect of lowering the temperature by 100K is illustrated in Figure 10 for two different foot temperatures. These curves include both the effects of changes in the phase boundaries and the inherent temperature dependencies of the mineral properties. The large positive property change near 410 km depth results from the shallowing of the olivine to wadsleyite transformation. The overall positive baseline is due to the increase in property with lowering of temperature. The negative Clapeyron slope of

takes place across 410 to about 520 km, resulting in higher gradients in density and velocities. Aluminum affects the overall magnitude of density and velocities throughout the region around the 410 discontinuity (Figure 6), as garnet has higher density and elastic moduli than those of the pyroxenes. Aluminum also affects the width and depth of the 410 discontinuity, as garnet tends to take Fe and make the olivine-normative component Fe poor, therefore making the discontinuity narrower (Figures 7 and 8) and deeper (Figure 9). A 2% increase (from 3 %) in Al has about the same effect as Fe content increase from 5.7 to 6.5 %.

Temperature. Mantle temperature also has a significant role in controlling the sharpness and depth of the 410 discontinuity, mainly through two routes. First, temperature affects the width and depth of the olivine-
the pyroxene to garnet transformation reduces the baseline offset since lower temperatures yield less garnet and thus lower aggregate properties. Thus, there are some depths where the changes in properties become very insensitive to temperature as these latter two effects cancel. The actual depth where these properties are insensitive to temperature variations depends on the details of the pyroxene to garnet transformation and the amount of Al in the system. Lowering the Al content or increasing temperature, moves this to shallower depths. These models suggest that this temperature-insensitive depth is very close to the 410 discontinuity.

Lateral variations in Al content will have a large effect on the velocities and density as illustrated in Figure 11. A reduction in the Al content by 2% is illustrated for two mantle temperatures. Since garnet is less stable, more pyroxene is present with reduced values for these properties. In addition the olivine to wadsleyite transformation occurs at shallower depth owing to the increase in iron content of this system.

THE 520 KM DISCONTINUITY

Bounded by two major seismic discontinuities at 410 and 660 km depths, the 250-km-thick transition zone is a region where changes in physical properties take place due both to the inherent effect of pressure and to a number of phase transformations that occur with increasing depth. In addition to the pyroxene to garnet transformation that began at depths shallower than 410, transformations include wadsleyite to ringwoodite as well as the formation of a Ca rich perovskite both of which may cause changes in density and velocities near 520 km depth. In recent years, laboratory high temperature equation-of-state data have grown rapidly, owing to major technical developments in large-volume apparatus and in the diamond anvil cell [Wang, et al., 1998]. These measurements were made either at the pressure and temperature conditions corresponding to those of the transition zone, or at slightly lower pressures and/or temperatures.

Phase Relations.

Following Gasparik's [1990, 1996a, b]; results on phase relations in the CMAS, we assume that Ca enters majorite-garnet solid solutions completely, until CaSiO₃ perovskite begins to exsolve (~17.5 GPa). The most noteworthy feature is that the garnet is characterized by a maximum solubility of Ca. For the pressure and temperature of interest here, the critical Ca content in garnet is roughly 10 mol%, all in the dodecahedral site. For Ca-rich systems where Ca content is greater than the maximum solubility, the reaction exhibits a first-order character, mimicking the behavior of a univariant boundary [see Figure 2 of Gasparik, 1996b].

Al and Ca do not enter the olivine system. Communication between the olivine and pyroxene components is only via partitioning of Fe on the Mg site in the phases involved. The Fe partitioning data of Akaogi and Akimoto [1977] are used in our modeling.

Mineral Physics Data

We use Duffy and Anderson [1989] for estimates of the thermoelastic properties of the mineral phases that are relevant to the 520 km region with minor modifications reflecting recent data. For example, the volume and density dependencies of majorite on the contents of Ca, Fe, as well as pyroxene (i.e., Al), are all based on available experimental data (Fe: Matsubara, et al. [1990]; Ca: Hazen, et al. [1994]; and Al: Yagi, et al., [1992]). Ca is assumed to be in the dodecahedral site only. As both Ca and Fe can also be present in non-majorite garnet components (e.g., as grossular and almandine, respectively), we assume that both Fe and Ca partition equally into the majorite- and non-majorite components for the garnet and the effects are expressed as an average of the two end-member cases. Data for CaSiO₃ perovskite are from Wang, et al. [1996].
Between 480 and 520 km is a fast changing region. Formation of CaSiO$_3$ perovskite results in a first-order density and bulk modulus jump, as the Ca content in the dodecahedral site of garnet exceeds 10 mol%. At ~510 km, volume fraction of CaSiO$_3$ perovskite jumps from zero to 4.5% for pyroilit leaving 10 mol% Ca in the dodecahedral site of garnet. Associated with this transition is a change in garnet composition: $\text{Mg}_3\text{Py}_{47} \rightarrow \text{Mg}_4\text{Py}_{56}$. Owing to the higher Fe partitioning coefficient of ringwoodite with garnet, the Fe content in garnet decreases. Deeper than 520 km, CaSiO$_3$ perovskite continues to exsolve from garnet until 570 km, with slight changes in composition in garnet. At the bottom of the transition zone the stable phases are ringwoodite, CaSiO$_3$ perovskite, and Ca-free garnet.

Formation of CaSiO$_3$ perovskite results in a significant increase in elasticity and density profiles for pyroilit close to 520 km. Table 3 lists density and sound velocity changes across 520 km depth due to both transformations from wadsleyite to ringwoodite and from garnet to CaSiO$_3$ perovskite. This result suggests that formation of CaSiO$_3$ perovskite is an important contributor to the 520-km discontinuity which will be characterized by a first order jump. The size of the jump due to formation of CaSiO$_3$ perovskite is comparable to the contribution of the wadsleyite - ringwoodite transition. While the wadsleyite to ringwoodite transition occurs over a pressure interval, the significant Fe enrichment in the olivine component should be taken into account in estimating depth range of the transition. If we were to use the Fe content in the wadsleyite only, a depth range of ~21 km depth would be required [Katsura and Ita, 1989], however, the wadsleyite-ringwoodite transition does not follow a constant Fe content line (ringwoodite is more Fe enriched in the presence of garnet) yielding a depth range for the wadsleyite to ringwoodite transformation to be ~12 km depth for pyroilit.

**660 KM DEPTH AND PEROVSKITE FORMING TRANSFORMATIONS**

Diamond anvil studies by Liu [1975] determined that MgSiO$_3$ in the perovskite crystal structure was likely the most abundant mineral within the Earth. Subsequently, there have been inumerable studies that focus on the physical and chemical properties of this important phase. Two things became clear: the acoustic velocities of a perovskite assemblage are significantly greater than those of lower pressure phases such as ringwoodite and majorite, and most minerar's ultimately transform to a perovskite bearing phase assemblage. Furthermore, both ringwoodite and majorite, the two most abundant minerals in a pyroilit
transition zone, undergo this transformation near the 660 seismic discontinuity. Indeed, a velocity jump due to the phase transition is inescapable, and will be much more significant than most proposed changes in major element chemistry that might occur at this depth. The seismic discontinuity has thus been interpreted as caused by the perovskite forming transformation.

Knittle and Jeanloz [1987] concluded that perovskite dominates the mineralogy to the core-mantle boundary by demonstrating the lack of evidence for a post-perovskite phase in this system within the P-T field of the Earth’s mantle. This conclusion has been recently brought into question by Saxena et al. [1996] who reported the breakdown of the perovskite phase at mid-mantle pressures. The lack of corroboration of Saxena’s results by other laboratories leaves this an open question at this time. Large-volume high pressure devices have been able to reach the pressure and temperature conditions into the lower mantle. Through many experiments, including multi component systems such as peridotites [Takahashi and Ito, 1987; Akaogi and Akimoto, 1979; Irfune and Ringwood, 1987a, b; O’Neill and Jeanloz, 1990] as well as chemically pure systems [Akaogi and Akimoto, 1977; Ito and Yamada, 1982; Sawamoto, 1987] stability boundaries have been delineated in the chemically complex system expected to make up the transition zone and lower mantle.

A synthesis of the CMAS system (Ca-Mg-Al-Si) that is relevant to the 660 km discontinuity [after Gasparik, 1990] is illustrated in Figure 13. This diagram includes phase relations in two rather independent systems: the olivine-normative component and the pyroxene-normative component. The olivine – normative phases have an (Mg + Fe + Ca)/Si ratio of 2, while the pyroxene-garnet system is characterized by an (Mg + Fe + Ca)/Si ratio of 1. The olivine – normative phases (olivine, wadsleyite, ringwoodite) are generally devoid of Ca and Al, while Ca and Al strongly affect the stability fields of the pyroxene-garnet component phases. At pressures comparable to the 660 km discontinuity, the olivine – normative component transforms from ringwoodite (gamma) to perovskite plus magnesiowustite. The pyroxene-garnet system will undergo transformations to garnet, possibly to ilmenite and finally to perovskite. The perovskite forming transition in the pyroxene–normative system also occurs at a depth near the 660 km discontinuity.

Table 3. Percent change in density and sound velocities across 520 km for a pyrolite model due to the wadsleyite → ringwoodite (β→γ) transformation and formation of CaSiO₃ perovskite from garnet (gt→pv). The amount of changes due to the formation of CaSiO₃ perovskite is at the critical depth where Ca content in garnet is reduced to 10%.

<table>
<thead>
<tr>
<th>Δ(%)</th>
<th>β→γ</th>
<th>gt→pv</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ</td>
<td>1.34</td>
<td>0.73</td>
</tr>
<tr>
<td>Vₚ</td>
<td>1.27</td>
<td>0.45</td>
</tr>
<tr>
<td>Vₛ</td>
<td>1.79</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Figure 13. Phase diagram of the CMAS system (CaO, MgO, Al₂O₃, SiO₂) from Weidner and Wang [1998] as modified after Gasparik [1996a, b]. Abbreviations are Gt-garnet, Sp-spinel or ringwoodite phase, CaPv-CaSiO₃, perovskite phase, Pv-MgSiO₃, perovskite phase, Mw-magnesiowustite, St-stishovite, Il-MgSiO₃, in the ilmenite phase. Solid lines indicate the phase boundaries of the olivine normative and the pyroxene normative systems. The numbers on the lightest lines indicate the pyrope content of the garnet in equilibrium with the other phases. Dashed lines indicate possible geotherms with labels that indicate the temperature at 660 km depth. The region between the two heavy lines indicates the possible garnet composition for pyrolite.

Clapeyron Slopes

The Clapeyron slope of this boundary in the olivine system has been recognized as having important implications for convection models [Christensen and Yuen, 1984]. Navrotsky [1980] pointed out that perovskite forming transitions may well have a negative slope. Ito and
Yamada [1982] confirmed this possibility while Ito and Takahashi [1989] made the most definitive study of the transition. Calorimetric data by Ito, et al. [1990] and more recently Akaogi and Ito [1993] combined with phase equilibria observations serve to estimate the P-T Clapeyron slope of the phase boundary for the breakdown of ringwoodite to perovskite plus magnesiowustite. They find that \( \partial P/\partial T \approx \) -3 MPa/K (the slope in Figure 13 is -2 MPa/K). Since this transition involves a density increase of about 6%, it provides a buoyancy force that opposes convection.

In contrast to the olivine component, the pyroxene-garnet system has the possibility for positive Clapeyron slopes for the perovskite forming phase transition. In particular the garnet to perovskite and the garnet to ilmenite transformations likely have positive slopes while the ilmenite to perovskite has a negative slope. While phase equilibria data are limited that define the slope for the Al rich system, Yusa, et al. [1993] combined phase equilibria data with calorimetric data for the end member MgSiO_3 system. They concluded that the garnet to perovskite transition is positive with a slope of about 5 MPa/K for a partially disordered tetragonal garnet. As disorder increases, they predict that the slope should increase. The addition of Al completely disorders the garnet causing the structure to be cubic. The phase diagram of Gasparik [1990] in Figure 13 supports a positive slope for this boundary, but with a slope of about 2.5 MPa/K. The density change for this boundary is extremely large, in excess of 12% at lower mantle conditions; more than twice the magnitude of that for the spinel to perovskite plus magnesiowustite.

If the Al content or the temperature is sufficiently low then the phase transition in the mantle may become garnet to ilmenite to perovskite. The first of these has a strong positive Clapeyron slope while the second is negative. Since the volume change from garnet to ilmenite is about the same as that from ilmenite to perovskite, the net effect on buoyancy of the double phase change is about the same as garnet transforming directly to perovskite. This is due to the fact that

\[ \partial P/\partial T = \Delta H/\Delta V \]

where \( \Delta H \) is the enthalpy change of the transition. Since enthalpy is a state variable,

\[ \Delta H_{\text{tot}} = \Delta H_1 + \Delta H_2 \]

where \( \Delta H_{\text{tot}} \) refers to the garnet to perovskite transformation, \( \Delta H_1 \) is for the garnet to ilmenite transformation and \( \Delta H_2 \) is for the ilmenite to perovskite transformation. Thus with similar volume changes:

\[ \Sigma(\Delta P_i)(\partial P/\partial T)_i = \Sigma(\Delta P_i) \Delta H/\Delta V_i \]

\[ = (\Delta P_{\text{tot}}) \Delta H_{\text{tot}}/\Delta V_{\text{tot}} \]

Thus, the presence or absence of the ilmenite phase does not affect the total buoyancy of the perovskite forming transformations but it will affect the depth dependence of the density distribution.

In order to assess the impact of the phase transitions on vertical and lateral variations of physical properties, it is essential to understand the role of the major element chemistry in defining the mineralogy and hence the physical properties in the perovskite forming phase transitions. We emphasize that the system must be viewed as a whole. Significant features are lost if we ignore the interaction between the olivine-normative components and the pyroxene-normative portion. We adopt the pyrolite composition of McDonough and Sun [1995] as the representative chemical composition of the mantle. The relative abundance of elements of this model are given in Table 1.

In the models discussed below, we include the cations: Mg, Fe, Si, Al, and Ca. While the importance of sodium has been discussed by Gasparik and Lithvin [1996], Gasparik [1997], its abundance is a factor of 5 lower than calcium and, hence, is not included in the current discussion.

Calcium, the least abundant cation considered here, plays a relatively passive role at 660 km depth. Calcium passes from pyroxene to garnet and finally to a perovskite phase. Irifune, et al. [1989] demonstrated that diopside (CaMgSi_2O_6) produces two distinct perovskite phases: CaSiO_3 and MgSiO_3. Thus, calcium is responsible for its own perovskite phase which accounts for about 7% of the volume of a pyrolite lower mantle. This phase is mostly formed at pressures around 500 km and may participate in the 520 discontinuity as discussed above. In the lower mantle, we expect that this Ca rich perovskite persists throughout. Thus, it serves to dilute the impact of the reactions of garnet and ringwoodite to perovskite at the 660 km discontinuity.

Mg/Si. The divalent to tetravalent ratio (dominated by Mg/Si) defines the ratio of the olivine-normative phases to pyroxene-normative phases. Pyrolite sets this ratio at about 1.5 yielding a transition zone with 54% (by volume) of ringwoodite. The calcium perovskite phase accounts for 7%, thus leaving 39% in the garnet phase.

Aluminum. Aluminum, the fourth most abundant cation, may be extremely significant in defining the fine structure of the 660 km discontinuity [Weidner and Wang, 1990].
Slight variations in aluminum content or temperature can change the magnitude of the 660 discontinuity by a factor of two or introduce multiple discontinuities over a small depth range, can cause the depth of the discontinuity to be either positively or negatively correlated with temperature variations, and can cause the buoyancy contribution of the perovskite forming transition to be either positive or negative. These features rely on the accuracy of the phase diagram of Figure 13. While the general form of this diagram is probably correct, we should recognize that there may be inaccuracies in the absolute pressure and temperature scale that may or may not support the wide range of possibilities described here. One important factor is that the data for this diagram were for an iron free system. The presence of iron may change the P-T scale and alter the possible implications. With this caveat, we explore here the rich range of models for the 660 km discontinuity and the implications for the lateral variations of this discontinuity.

The stability field of garnet for different pyrope contents (defining aluminum content) is indicated by the lighter lines in Figure 13. The growth of the garnet field to both lower and higher pressure as well as lower temperature indicates the degree to which Al stabilizes the garnet structure. Figure 14 [from Irfune, et al., 1996] illustrates the enstatite-pyrope join at 1773K and 2073K. There is a relatively wide two phase region of coexisting garnet and perovskite controlled by the Al content of the system. Irfune [1994] demonstrated that the Al content in a peridotite would entirely enter the perovskite phase in the vicinity of the 660 km discontinuity. Indeed, the pyrolite composition of Table 1 yields a perovskite composition with 6.3 mol % AlO₃ after all perovskite forming transitions have occurred. Higher Al contents (in excess of 12 mol% AlO₃ in Figure 14) will promote an Al rich phase (corundum) in equilibrium with the perovskite phase at 1770K and about 27 GPa, while higher temperatures will expand the pure perovskite phase field. Thus, our model Earth will consist of two perovskites, one Ca rich; the other Ca poor, once the perovskite forming transitions in majorite and ringwoodite have occurred.

The reactions that form perovskite are dependent on the Al content and temperature. This phase diagram implies that a pyrolite chemistry can reach the perovskite dominated assemblage with the ringwoodite component transforming directly to perovskite plus magnesiowustite or by ringwoodite first transforming to garnet plus magnesiowustite and then to perovskite plus magnesiowustite. In this latter pathway, the 660 discontinuity is governed by the breakdown of garnet to perovskite, including the magnitude of the jump and the sign of the Clapeyron slope. To illustrate these paths, note that the pyrolite model will yield three phases in a large portion of the transition zone: ringwoodite, Ca-perovskite and garnet. In this assemblage, the garnet will have a pyrope content of about 50%. If all of the ringwoodite would transform to garnet plus magnesiowustite, then the composition of the garnet would be about 25% pyrope. These two compositions are illustrated in Figure 13 by the two heavy lines in the garnet field. At higher pressures than where the 2100K geotherm crosses the ringwoodite breakdown curve ringwoodite is no longer stable (relative to perovskite plus magnesiowustite). However, at pressures just above the breakdown of ringwoodite, perovskite is not stable in the presence of garnet with such a high Al content as 25% pyrope. Thus, garnet plus magnesiowustite will be present with no perovskite. As pressure increases, the garnet will begin to transform to perovskite over the two phase region. Thus, the reaction at constant temperature will be from
ringwoodite to garnet plus magnesiowustite to perovskite plus magnesiowustite. The reaction of ringwoodite to garnet plus magnesiowustite must take place at lower pressure than would the breakdown to perovskite, but there is in fact, no data in this pressure-temperature-composition space that defines the breakdown of ringwoodite to garnet and magnesiowustite. Yet this reaction must occur according to this phase diagram.

A lower temperature geotherm that passes through the ringwoodite to perovskite curve between the two heavy lines of Figure 13 will experience a different series of phase transitions. The pyrope-50 composition of garnet will be stable at pressures lower than this curve, but when ringwoodite breaks down, equilibrium must be established between the garnet and the perovskite. The garnet cannot take on all of the MgSiO$_3$ that is provided by ringwoodite since it would create pyrope 25, which will no longer a stable composition, but it can take some. Thus, perovskite does form, with some Al as prescribed by the garnet-perovskite equilibrium curves. However, the garnet will be richer in majorite than pyrope-50. Thus even in this case the garnet grows in volume at the expense of ringwoodite, with some of the ringwoodite transforming to perovskite.

Below the bottom heavy line, garnet will have begun to transform to an aluminous perovskite by the point at which ringwoodite creates a massive amount of Al free perovskite. In order to maintain an equilibrium Al content in the perovskite phase, a considerable amount of the garnet must simultaneously transform to perovskite. The result is a large volume change to perovskite from both the ringwoodite phase and the garnet phase. It is also possible that the garnet partially transformed to ilmenite prior to the breakdown to perovskite. This will yield a precursory velocity increase to the main discontinuity.

As we demonstrate below, the perovskite forming transition can create a seismic discontinuity whether the reaction is dominated by the breakdown of ringwoodite or if it is due to the garnet transformation in the absence of ringwoodite. However, the temperature dependence of the reactions will be quite different. A ringwoodite dominated transformation will exhibit a negative correlation owing to the negative Clapeyron slope of this reaction. By these phase diagrams, this will occur for the lower temperature region. On the other hand, if ringwoodite has transformed to garnet, then the breakdown to perovskite will be controlled by the positive slope of this reaction. Thus, at higher temperatures, increasing temperature will increase the depth of the 660 discontinuity. The transition from negative to positive slope will occur in the region of intersection of the two heavy lines of Figure 13 and the breakdown curve of ringwoodite. Thus, the depth of the 660 discontinuity increases with either higher or lower temperatures with the minimum depth corresponding approximately to the 1900K geotherm illustrated in Figure 13.

In order to model this system in more detail, we must assume the details of the ringwoodite-garnet plus magnesiowustite reaction. Following our previous study [Weidner and Wang, 1998] we assume that the Al content of garnet in equilibrium with ringwoodite is independent of temperature. Table 1 and 2 of Weidner and Wang [1998] give assumed physical properties of the relevant phases that we use here. To illustrate the richness of possibilities, we provide the results for two models; one with an Al cation abundance of 5% (slightly greater than the reference pyroilite model) and the other at 3%. Figure 15 illustrates the volume percent of garnet and ringwoodite along the three model geotherms-the temperature is referenced to 660 km depth. These models cover the range that include garnet transforming partially to ilmenite, which transforms to perovskite and accompanied with the breakdown of ringwoodite to perovskite as well as models where ringwoodite completely transforms to garnet plus magnesiowustite and then to the perovskite assemblage. Based on the relevant physical properties, we illustrate models of velocity and density in Figure 16. For reference, PREM [Dziewonski and Anderson, 1981] is also illustrated. Discrepancies in depth between the models and PREM are completely within the uncertainties of the phase diagrams used in this study. The density models show little influence of the reaction between ringwoodite and garnet, while acoustic velocities are strongly affected. The magnitude of the velocity jump can vary by a factor of two with the garnet dominated transition yielding the greatest velocity increase. All transitions yield a relatively sharp discontinuity. The two-phase loop between garnet and perovskite produces a sharp onset of the transition followed by a steep gradient over about 50 km. This shape simply reflects the non-linear results of a two-phase region Stixrude [1997].

Irifune, et al. [1998] recently report new data on the breakdown of ringwoodite to perovskite using in situ x-rays to define the reversible reaction and the pressure. They report a breakdown pressure about 2 GPa lower than previous values such as the one used here. If this new curve is indeed correct, but the rest of the phase diagram does not change under similar scrutiny, then the effect is to move the intersection of the heavy lines and the ringwoodite to lower pressures and temperatures. This will probably move it out of the region of possible geotherms. As a result, ringwoodite would not transform to perovskite
Figure 15. Calculated volume per cent of garnet and ringwoodite as a function of depth along the three geotherms for a pyrolite-like composition [from Weidner and Wang, 1998]. A) is for a system with 5 cation % Al and B) represents the results for 3% Al. Calculations are based on the phase diagrams described in the text.

in a pyrolite Earth. Rather, it would breakdown to garnet plus magnesiowustite and the garnet would transform to perovskite at the appropriate pressure. In this case, the 660 discontinuity is caused by the garnet to perovskite transformation. As seen in Figure 16, this will still have the appropriate characteristics, except the depth of the transition will be positively correlated with temperature over most of the temperature range until ilmenite becomes stable.

The stability of Al and Fe rich garnets is important to determine the buoyancy of subducted oceanic crust. O'Neill and Jeanloz [1994] and Faust and Knittle [1996] report garnet persisting to pressures as high as 50 GPa, well into the lower mantle. The presence of these phases will resist convection owing to their low density relative to perovskite bearing assemblages. Kesson, et al. [1994; Kesson, et al. [1995] have not observed garnets to such high pressures. Conrad [1998], using a double sided laser heated diamond anvil cell, which provides a more uniform temperature environment than previous techniques, reports that the iron and aluminum rich end-member garnet (almandine) breaks down to high pressure phases at pressures comparable to its magnesium counterpart, at about the pressures of the 660 discontinuity. The reaction products are mixed oxides rather than perovskite, but with densities comparable to a perovskite assemblage. Irfune, et al. [1996] report the breakdown of pyrope to perovskite plus corundum at 1770K to be about 27 GPa using a multi-anvil high pressure system. It thus appears that subducting oceanic crust may well undergo the densifying reactions at only slightly higher pressure than does a pyrolitic composition. This is an area that is actively under investigation in many laboratories using both diamond anvil systems and multi-anvil apparatus.

Iron. The role of iron on the phase stability fields in the olivine system for the perovskite forming reactions were reported by Ito and Takahashi [1989]. While there is the thermodynamic possibility for a wide two phase
region, they found that this transition is extremely sharp, independent of the iron content of the system. Akaogi, et al. [1998] report calorimetric and phase equilibria studies for the ringwoodite to perovskite transition at varying iron contents. The resulting phase diagram at 1873K is given in Figure 17. They confirm the very narrow two phase field in the Mg rich end of the transition with a total pressure range of 0.01 to 0.18 GPa. The role of iron on the stability fields of the pyroxene-garnet component have been less well studied. It remains quite possible that iron will affect the P-T diagram of the CMAS system of Figure 13.

Iron is about an order of magnitude less abundant in a pyrolite model than magnesium and can substitute for magnesium in all of the mantle phases. The relative distribution of iron among the phases has the potential of changing the aggregate properties if this substitution has a marked effect on the properties of one phase relative to others. Currently, we have no data that this is in fact the case. All phases have relatively small volume changes associated with iron substitution, with approximately similar changes from phase to phase. Thus, density, which is simply the total mass to volume ratio, will be insensitive to the distribution of iron among the phases. On the other hand the total iron content will be important in setting the total density allowing density to be a diagnostic for the bulk composition. Similarly, bulk modulus is relatively insensitive to the iron to magnesium ratio in most phases. Shear modulus is less well characterized for the phases around the 660 discontinuity. Thus, we have little evidence that the iron distribution among phases will have a seismic signature. Other properties, such as electrical conductivity may well be affected by the iron distribution among the different phases.

Figure 16. Calculated density and acoustic velocities for different geotherms for a pyrolite-like composition [from Weidner and Wang, 1998]. A) indicates these properties for a model with 5% Al and B) indicates the results for 3% Al. The properties were calculated using the parameters of Weidner and Wang [1998] and the phase diagrams described in the text. Temperature refers to the temperature at 660 km depth with an adiabatic gradient. The values for PREM are included for reference.
Measurements of iron partitioning among the phases in a perovskite bearing assemblage has received considerable attention [e.g. Ito, et al. [1984]; Katsura and Ito [1996]; Guyot, et al. [1988]; Kesson and Fitzgerald [1991]; Mao, et al., 1997]. The general conclusion is that iron enters the magnesiowustite phase in preference to perovskite in the Mg-Fe-Si system. Regardless of the iron content of the system, the Fe/(Fe+Mg) ratio for the perovskite is generally less than 0.1. Details of the different studies indicate some differences as to the exact magnitude of the partitioning as well as the pressure dependence. Wood and Rubie [1996] find that the presence of Al in the system can increase the amount of iron in the perovskite to be equal to that of the magnesiowustite phase. McCammon [1997] conducted a Mossbauer study of Al bearing perovskites and concluded that approximately 50% of the iron was ferric. Mao, et al. [1997] demonstrated that ferric iron preferentially partitions into the perovskite phase rather than the magnesiowustite phase. The perovskite structure has two distinct cation sites. The composition of perovskites include a cation pair either with charges of 4 and 2 (such as Si and Mg) or 3 and 3 (such as ferric Fe and Al). Thus, it is quite feasible that ferric iron coupled with aluminum substitutes for Mg and Si. Ferrous iron can also substitute for Mg. The real question that needs to be understood is what control does the oxygen fugacity exert over these possibilities. As a material that contains only ferrous iron sinks into the Earth through the perovskite forming transition, then in order for ferric iron to form, there must be accompanying metallic iron. A reaction such as:

$$3\text{FeO} = \text{Fe}_{2}\text{O}_3 + \text{Fe}$$

must occur. The $\text{Fe}_2\text{O}_3$ has the correct stoichiometry to enter the perovskite structure. Table 4 illustrates the volumetric consequences of this reaction. Two cases are given, one is for all of the iron to transform from ferrous, the other for none of the iron to transform.

The volume per cents are based on densities referenced to ambient conditions and will differ slightly as a function of pressure and temperature. The impact of all ferrous iron converting to ferric iron and metallic iron is concentrated in 6-7% of the mineralogy. If less than half of the iron undergoes this transformation [consistent with McCammon, 1997], then the transformation involves about 3% of the total. Thus, even if the physical properties of the two sides of the above equation are significantly different, it will have only a minor affect on bulk properties such as elastic modulus or density, that are volume driven. Significant differences may occur in properties such as electrical conductivity, that depend strongly on the electronic structure of the material. Wood and Rubie [1996] further point out that this may affect the character of the perovskite forming transition.

An interesting issue to consider is the possible chemical processing that may occur in such a system. As ferrous iron sinks through the perovskite forming transition.
transition with the formation of metallic iron, can this iron separate from the silicate ultimately reaching the core. This would reduce the density of the residual silicate. Such iron depleted portions would tend to rise, and if they cross the perovskite forming transition from below, would contain a large amount of ferric iron, with no metallic iron to reduce it to its former state. Thus, the apparent oxidation state of the mantle could evolve with time.

**Lateral Variations**

These phase transformations contribute to lateral variations in velocities as well as defining the details of the 660 discontinuity. Figure 18 illustrates the velocity perturbations, for this reference model, of reducing the temperature by 100K. Included here are only the effects of the temperature dependence of the phase diagrams and not the temperature dependence of the acoustic velocities of the individual phases. If these were included, the base line would shift up by less than 0.5%. Since the phase transitions depend on the reference temperature, three sets of curves are given that reflect three different reference temperatures. Diagram A illustrates the effect of the coldest geotherm considered here. The velocity increase at about 620 km results from the garnet to ilmenite transition. A larger temperature difference will both broaden and heighten this high velocity region. The large negative perturbation reflects the deepening of the ringwoodite breakdown boundary to deeper depths with a reduction in temperature. Curves in B are dominated by the assumed breakdown of ringwoodite to garnet. Since this reaction is not well constrained by data, the form of this velocity increase must be taken with reservations. This also relates to curves in C for depths shallower than 660 km. The increase deeper than the discontinuity reflect the positive Clapeyron curve of the garnet to perovskite transition.

Thus, the complexity of the perovskite forming transition can create significant velocity perturbations in the vicinity of the 660 discontinuity. In particular, the shallow high velocity region for the coldest geotherm (diagram A) could be mistaken for a slab that rests on the 660 discontinuity. The magnitude of the velocity increase in this region resulting from the formation of ilmenite for our calculations is less than that reported by Van der Hilst, et al. [1991] for the northern Philippine Sea Plate and the Sea of Japan. However, our model may underestimate the increase if the assumed unknown properties of the ilmenite phase are incorrect or if the amount of garnet that transforms to ilmenite is underestimated. The similarity of shape of the observed and calculated velocity anomalies suggests that such phase transformations must be considered in making conclusions with dynamic implications. Furthermore, these calculations indicate that the ratio of relative changes in S velocity to P velocity associated with phase transformations is close to two.

**CONCLUSION**

Phase transformations play a vital role in shaping the radial and lateral variations in seismic velocities and density within the mantle. Their effects can be predicted from the results of phase equilibria experiments used in concert with data of physical properties for the relevant phases. Aluminum and iron couple the phase transitions in the olivine- and pyroxene-normative systems requiring a whole-system analysis to define the details of the reactions. For example, the width of the olivine-wadsleyite phase
boundary is affected by the degree of completion of the pyroxene to garnet transformation. While the data base is still incomplete, it is now possible to predict features of the seismic model. Observations of these features in the Earth can then feed back to define more clearly where the mantle is with respect to the chemical-pressure-temperature-phase parameter space. For example, the model predicts that, in the vicinity of the 410 km discontinuity, the acoustic velocities are insensitive to temperature. This results from the competition between inherent temperature dependence of the velocities and the pyroxene to garnet transformation. The exact depth at which the temperature dependence is zero depends on ambient temperature as well as Al content, and of course, an accurate modeling of the phase diagram. Indeed, this region could be either shallower or deeper than the discontinuity.

A second example concerns the magnitude of the 660 km discontinuity, which may vary by a factor of two with a temperature change of 100-200K if the 660 discontinuity is located at the transition between garnet control and ringwoodite control of the perovskite forming reaction. If this is the case, then we might not expect the depth of the 660 to be directly related to temperature.

A third example relates to tomographic images of 'slabs sitting on the 660 discontinuity'. It is quite possible that the ilmenite forming transition could produce such a feature in a cold mantle. The observations should be evaluated with this possibility considered.

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