that at temperatures of about 1500°C, a possible temperature in the upper half of the mantle transition zone, the pressure range at which the olivine solid solution coexists with the Fe-rich spinel solid solution is extremely narrow, less than 3 kbar, and the total transformation width from α to β requires a pressure range of approximately 10 kbar.

All these implications are consistent with recent seismic models for the mantle transition zone shown as Figure 3, which were constructed from the models proposed by *Kanamori* [1967*b*], *Archambeau et al.* [1969], *Whitcomb and Anderson* [1970], and *Helmberger and Wiggins* [1971]. Figure 3 indicates that the first step of the sharp velocity increase occurs at depths between 380 to 430 km, and that a relative increase in *P*-wave velocity of 7 to 11% is involved. Recent laboratory measurement of the ultrasonic wave velocities for the high-pressure polymorphs of Mn_2GeO_4 reveals that the jump in *P*-wave velocity across the α-β transformation actually amounts to 5 to 18% [*Liebermann,* 1973*a, b;* H. Mizutani, personal communication, 1971]. From this observational and experimental background, it is quite natural

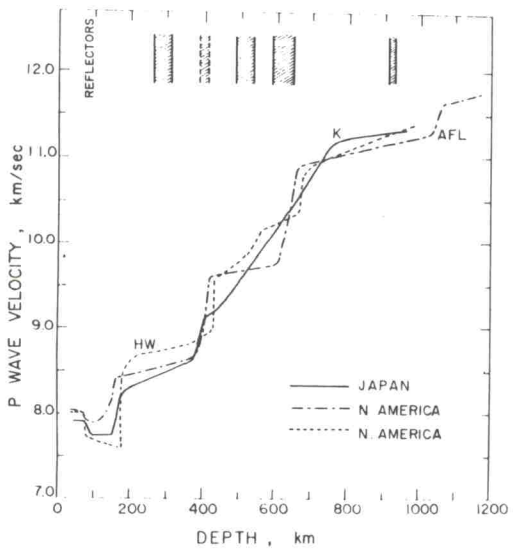


Fig. 3. Distribution of *P*-wave velocities in the outer 1200 km of the mantle. Curves designated by K, AFL, and HW represent the models proposed by *Kanamori* [1967*b*] for the Japanese islands, *Archambeau et al.* [1969] for the western continental United States, and *Helmberger and Wiggins* [1971] for the midwestern United States, respectively. Reflecting zones proposed by *Whitcomb and Anderson* [1970] are also indicated in the upper part of the figure.

to conclude that the olivine-modified spinel transformation is responsible for the seismic discontinuity between 380 and 430 km.

Helmberger and Wiggins [1971] reported that an abrupt change in the slope of their seismic model occurred between approximately 500 and 550 km (Figure 3). Relative increase in *P*-wave velocity associated with this inflection amounts to about 3%. *Whitcomb and Anderson* [1970] also obtained evidence for the presence of seismic reflectors at depths around 520 km. The phase diagram shown in Figure 2 suggests that this minor discontinuity is attributable to the β-γ transformation in the Mg_2SiO_4-Fe_2SiO_4 system. It should be remembered that the density increase in the β-γ transformation is generally 2–3%.

Thus, the mineralogy of the pyrolite composition for the region between 430 and 650 km would be represented in conformity with *Ringwood* [1970] as follows:

	wt %
Modified spinel phase and/or true spinel phase	
$\beta(Mg,Fe)_2SiO_4$ and/or $\gamma(Mg,Fe)_2SiO_4$	57
Complex garnet solid solution $M_3(Al,Cr,Fe^{3+})_2Si_3O_{12}$-$M_3(MSi)Si_3O_{12}$ where M = Mg, Fe^{2+}, Ca	39
Jadeite $NaAlSi_2O_6$	4

Modified spinel phase $\beta(Mg,Fe)_2SiO_4$ predominates in the region between 430 and 500 km. The region between 500 and 550 km is the β-γ transformation zone, where $\beta(Mg,Fe)_2SiO_4$ coexists with $\gamma(Mg,Fe)_2SiO_4$. This model also leads to the conclusion that $\gamma(Mg,Fe)_2SiO_4$ exists as a single phase in the rather limited depth interval of approximately 550 to 650 km, if the major seismic discontinuity occurring around 650 km is assumed to result from the transformation of $\gamma(Mg,Fe)_2SiO_4$ to more closely packed 'post-spinel' crystal structures.

Very recently, *Liu* [1974] reported that silicate garnet with $(Mg,Fe)_3Al_2Si_3O_{12}$ composition displays successive phase transformations at increasing high pressures. Although the structures of the intermediate high-pressure phase are as yet undetermined, the ultimate phase synthesized at pressures above 300 kbar and at temperatures of 1400°–1800°C was successfully identified as

perovskite-like structure. These recent experimental results imply that the complex garnet solid solution in the pyrolite mantle transforms to denser phases such as perovskite at pressures above 300 kbar. However, phase transformations accompanying the large density increase would not occur in the complex garnet solid solution at depths shallower than 650 km (≃230 kbar).

Mg^{2+}–Fe^{2+} PARTITION IN THE UPPER HALF OF THE TRANSITION ZONE

In a previous paper, *Nishizawa and Akimoto* [1973] estimated the chemical composition of $(Mg,Fe)_2SiO_4$ spinel in equilibrium with $(Mg,Fe)SiO_3$ pyroxene in the transition zone. They concluded that the partition reaction results in an increase in the iron content of the $(Mg,Fe)_2SiO_4$ solid solution of 1–2% through the olivine–spinel transformation. If we recall the pyroxene–garnet transformation described in a previous section, however, we know that the chemical equilibrium between $(Mg,Fe)_2SiO_4$ spinel and $(Mg,Fe)SiO_3$ pyroxene is meaningless in the actual transition zone.

In the present study we have obtained the thermochemical data necessary to calculate the distribution of Fe^{2+} and Mg^{2+} for the most probable minerals in the upper half of the transition zone. The following calculation is generally based on the mineralogic model just described for the mantle.

First we assume that the Fe:(Fe+Mg) ratio of total mantle material is 0.106 according to *Ringwood* [1966]. We also assume that the upper half of the mantle transition zone between 430 and 650 km consists of 60 wt % β and/or $\gamma(Mg,Fe)_2SiO_4$ and 40 wt % complex garnet solid solution, ignoring the small quantity of jadeite component. This model corresponds to the mineral assembly of 80 mole % β and/or $\gamma(Mg,Fe)_2SiO_4$ and 20 mole % complex garnet solid solution.

Further, it is assumed that the Mg^{2+}–Fe^{2+} partition relation between the β or γ phases and the complex garnet can be approximated by the simple $(Mg,Fe)_2SiO_4$ spinel–$(Mg,Fe)_3Al_2Si_3O_{12}$ garnet system. Then, we can calculate the chemical composition of the modified spinel or the true spinel solid solution in the mantle using the following two equations:

$$\{X_{Fe}^{Sp}/(1 - X_{Fe}^{Sp})\}/\{X_{Fe}^{Ga}/(1 - X_{Fe}^{Ga})\} = K'$$

$$(16/22)X_{Fe}^{Sp} + (6/22)X_{Fe}^{Ga} = X_{Fe}^{Total}$$

where X_{Fe}^{Sp} and X_{Fe}^{Ga} represent the mole fraction of Fe_2SiO_4 in $(Mg,Fe)_2SiO_4$ spinel and the mole fraction of $Fe_3Al_2Si_3O_{12}$ in $(Mg,Fe)_3Al_2Si_3O_{12}$ garnet, respectively. Conservation of Fe and Mg is involved in the second equation, where X_{Fe}^{Total} is the Fe:(Fe+Mg) ratio of total mantle material. In the present calculation we considered no discrimination in the partition behavior between the β and γ phases based on the similarity of divalent cation sites in both structures.

Figure 1 indicates that the apparent partition coefficient K' varies within a rather narrow range of 2.7 to 3.1 in the present experimental condition. This permits us to estimate tentatively the value of K' for the magnesium-rich side as 3. Substituting the value of 0.106 for X_{Fe}^{Total}, we finally obtained the value of $X_{Fe}^{Sp} = 0.13$. Thus the chemical composition of the modified spinel or true spinel phase in the transition zone was estimated to be $(Mg_{0.87}Fe_{0.13})_2SiO_4$.

Chemical composition of the upper mantle olivine was taken as $(Mg_{0.89}Fe_{0.11})_2SiO_4$ in Ringwood's pyrolite model. Accordingly, it is concluded that a 2% increase in Fe_2SiO_4 component in $(Mg,Fe)_2SiO_4$ solid solution is expected as a coupling effect of the olivine–modified spinel–true spinel transformation and the pyroxene–garnet transformation.

Stability relations of the Mg_2SiO_4–Fe_2SiO_4 system (Figure 2) indicate that the transformation pressure from $(\alpha + \gamma)$ to $(\alpha + \beta)$ is scarcely affected by such a small compositional change in $(Mg,Fe)_2SiO_4$. Figure 2 also suggests, however, that compositional effect on the transformation pressure from β to $(\beta + \gamma)$ and $(\beta + \gamma)$ to γ is extremely large. About 2% increase in Fe_2SiO_4 component results in the decrease of the transformation pressure from β to $(\beta + \gamma)$ by approximately 10 kbar at around 1500°C. These conclusions derived from the partition reaction are of great importance for refining the structure model of the mantle transition zone.

TEMPERATURE GRADIENT IN THE TRANSITION ZONE

Previously, *Akimoto and Fujisawa* [1968] and *Fujisawa* [1968] obtained a temperature estimate of 1150°–1530°C at a depth of 370 km based on their preliminary phase diagram for the olivine–spinel transformation in the Mg_2SiO_4–Fe_2SiO_4 system. In the present paper, we assigned seismic discontinuities at 380–430 km and 500–550 km to the olivine–modified spinel and modified spinel–true spinel transformations, respectively. We now