

## Temperature and Discontinuities in the Transition Layer within the Earth's Mantle: Geophysical Application of the Olivine-Spinel Transition in the $Mg_2SiO_4$ - $Fe_2SiO_4$ System

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The nature of the transition layer (the C layer) is considered with the homogeneous chemical composition model. The physical properties of the transition layer are determined essentially by the mineral assemblage and the Fe/Mg ratio of mantle materials. The upper mantle is believed to be composed mainly of olivine and pyroxene, and the content of olivine possibly amounts to about 80% of the whole. The plausible values for the Fe/Mg ratio of mantle minerals lie between 1:9 and 2:8, and from the petrological evidences the magnesium-rich side in this range seems more probable. The olivine-spinel transition accounts for the sharp discontinuity that starts at the depth of about 370 km in the mantle and whose thickness is of the order of several tens of kilometers, according to the latest velocity models. The temperature at this depth is estimated to lie in the range between 1150° and 1530°C, using the Fe/Mg ratio of 1:9. The thickness of the transition region is directly related to the temperature distribution in it. The 50-km thickness requires a constant temperature distribution, but, to spread the thickness over a 70-km interval, the temperature must be raised by 100°C within this region, for a Fe/Mg ratio of 1:9. The location and the sharpness of discontinuities in the transition layer expected from the recent progress of high-pressure mineralogy show a substantial agreement with the latest seismological evidences. Contrary to the traditional interpretation, the actual transition region might not spread over the entire C layer, and there is a growing possibility that there exist several discontinuities in the transition layer that arise from successive polymorphic transitions in mantle minerals. The mode of sequence of seismic discontinuities in the transition layer varies with the ratio of olivine to pyroxene. If the content of coexisting pyroxene in the upper mantle increases, another seismic discontinuity corresponding to the pyroxene breakdown may become observable at the depth between olivine-spinel and post-spinel transitions.

### INTRODUCTION

The transition layer (C layer) in the earth's mantle extends from about 300 to 900 km and is characterized by a rapid rise of seismic velocity with depth. In a series of classical investigations on the origin of this region, it was strongly suggested that the ferromagnesian silicates, of which the upper mantle is supposed to be composed, would gradually transform to high-pressure modifications, probably close-packed oxides, in the transition layer [e.g., Birch, 1952]. Recent progress in high-pressure mineralogy strongly supports this hypothesis.

In the early stages of the investigation, it was widely thought, on the basis of the continuous velocity-depth curve, that the C region was a region of gradually transitional spreading over the depth interval from about 300 to 1000 km.

Various attempts have been made to explain this wide spreading of the transitional region. In the light of the recent experiments on the phase change in mantle minerals, it has become clear that an actual transition region should not spread over such a wide thickness. It is highly probable that there would exist several discontinuities in the transition layer that arise from successive phase changes in mantle minerals. Consequently, the discontinuous velocity-depth curve could possibly be obtained when the observation would become more accurate. Recently, this kind of velocity-depth curves has been obtained [e.g., Anderson and Toksöz, 1963; Johnson, 1967; Kanamori, 1967]. The sharpness and the locations of these discontinuities are controlled by the mineral composition, the ratio of Fe to Mg in the mantle materials, and the temperature distribution in the transition layer.

In the first two sections of this paper, the

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mineral composition and the Fe/Mg ratio in mantle materials will be determined from considerations of the elasticity, the density, and the petrological observations in the mantle. Then by comparing directly the experimental phase diagrams of the probable mantle minerals with the observed seismic velocity-depth curve, the locations and the sharpness of discontinuities in the transition layer will be discussed. In this discussion, if a close correlation can be established between a given seismic discontinuity and a given phase transition, the temperature at the depth of discontinuity can be determined with the aid of the knowledge of the phase relation considered. Now making use of the phase diagrams of the olivine-spinel transition in the  $Mg_2SiO_4$ - $Fe_2SiO_4$  system just obtained [Akimoto and Fujisawa, 1967] (see Figure 1), we will try to estimate the temperature at the top of the transition layer in the mantle, since it appears likely that the olivine-spinel transition occurs at the top of the transition layer. In this procedure the knowledge of mineral composition and the Fe/Mg ratio previously determined are essential.

The temperature distribution within the earth is one of the main unsolved problems in solid earth science. There have been many attempts to estimate the temperature distribution within

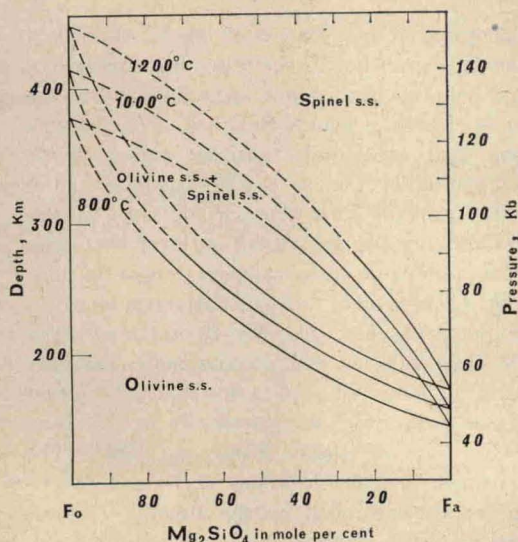


Fig. 1. Stability relation of olivine-spinel transition in the  $Mg_2SiO_4$ - $Fe_2SiO_4$  system at 800°, 1000°, and 1200°C [after Akimoto and Fujisawa, 1967].

the earth, but in all procedures used to make these estimates many grave assumptions have been introduced [e.g. Miki, 1954; Verhoogen, 1954]; therefore, the results are not necessarily convincing. Present estimations of temperatures in the mantle might, therefore, contribute to the study of the thermal state of the earth's interior.

#### MINERALOGICAL COMPOSITION ABOVE TRANSITION LAYER

In the present discussion the following assumption is essential: The chemical composition of mantle materials does not change throughout the mantle, but the component minerals transform and break down to denser structures. Therefore, the knowledge of materials in the upper mantle helps us to consider the mineral assemblage and the chemical composition in the whole mantle.

There are two main hypotheses on the mineralogical composition of the upper mantle: the peridotitic and the eclogitic hypotheses.

At first we assume the peridotitic mantle, based on the thorough petrological discussion of Ringwood [1966, pp. 298-307]. In the following discussions, however, we neglect, as a first approximation, a basaltic material that is important in a 'pyrolite' model [Ringwood, 1966, pp. 306-307]. For the upper mantle a pyrolite model might be better than a model in which the basaltic matter is neglected, but this would not necessarily be true for the lower mantle. Since the mineralogical composition of the lower mantle is directly correlated with that of the upper mantle in the present model, we must take account of the lower mantle. For this reason the basaltic material is neglected. This kind of consideration in petrology can, however, give only qualitative information about the mineralogical constitution of the upper mantle.

For quantitative arguments of the mineralogical composition of the upper mantle, the most convincing method is a direct comparison of the observed elastic properties of the upper mantle and elastic properties of various rocks determined experimentally under high pressures. By this method Kanamori and Mizutani [1965] obtained clear-cut results for upper mantle materials. Two of their results are as follows:

1. *P-wave velocity.* Among common rocks only peridotite, dunite, and eclogite have veloci-

ties that satisfy the observed values in the upper mantle. As for dunite and peridotite, the ratio in volume of olivine to pyroxene of 8:2 to 9:1 may give the most probable value of velocity and density for the upper mantle.

2. *Poisson's ratio.* From the seismological observations, the Poisson's ratio of the upper mantle above the depth of 400 km should be about 0.275 and should not exceed 0.30 [see, Bullen, 1963, p. 233]. Under a pressure of about 10 kb the Poisson's ratio of eclogite is determined to be about 0.31. Only fresh dunite having more than 80% olivine has a Poisson's ratio of about 0.27, and the pressure dependence of this ratio is very small. Therefore, eclogite could not be the main constituent of the upper mantle.

Putting all this information together, we may suppose that the constituents of the upper mantle are olivine, pyroxene, and garnet and that the upper mantle material contains 80% (in mole, approximately the same as in volume) of olivine, 20% of pyroxene (mainly *enstatite*), and negligibly small amounts of garnet.

Even if the amount of the basaltic material, which will transform to 'eclogite' below a depth of about 30 km in the mantle, reaches one-fourth the composition of the whole upper mantle (the amount in the pyrolite model), it would not have any noticeable effect in the following calculation, because the elastic wave velocity of eclogite is nearly the same as that of peridotite and the differences in the Poisson's ratio and density between peridotite and eclogite are not so large.

#### Fe/Mg RATIO IN THE MANTLE

The density and seismic wave velocity of olivine and pyroxene are strongly controlled by the Fe/Mg ratio in the solid solution. The relation between velocity and the Fe/Mg ratio of minerals has not been established, however. On the other hand, compressibilities of most of the common rock-forming minerals have been determined in the wide range that covers the pressures of the lower mantle, and it is possible to estimate the density of the mixture of these minerals under the conditions in the mantle. Now we will try to determine the Fe/Mg ratio in the mantle materials from the viewpoint of density.

*Fe/Mg ratio and density in the lower mantle.*

The essential assumptions made in this density calculation are as follows: (1) The chemical composition does not change throughout the mantle. (2) Olivine and pyroxene in the upper mantle break down into oxides and there exists only a mixture of MgO, FeO, and stishovite or the most dense form of SiO<sub>2</sub>. (Until recently it was widely believed that stishovite was the most dense form of SiO<sub>2</sub>. *Ida et al.* [1967] have measured by X-ray experiment the compressibility of stishovite under high pressures and have discovered that the compressibility of stishovite shows an abnormal behavior similar to the behavior of MnO<sub>2</sub> and SnO<sub>2</sub>, which crystallize in the same crystal structure as stishovite does (tetragonal). The most striking feature is that the *c* axis of these crystals actually increases with increasing pressure in the low-pressure region and has a maximum. The compressibility is very low at low pressure and then increases at pressures beyond the maximum in *c*. Another interesting fact is that in MnO<sub>2</sub> and SnO<sub>2</sub> an apparent first-order phase transition is observed in the higher-pressure range, though the high-pressure phase has not yet been investigated [*Clendenen and Drickemar*, 1966]. *Syono and Akimoto* [1968] investigated the polymorphic transition of PbO<sub>2</sub> (tetragonal at 1 atm) under high pressures and temperatures, and they found that PbO<sub>2</sub>, which once crystallizes in an orthorhombic structure under high pressures, transforms to the cubic calcium fluoride CaF<sub>2</sub> structure in the higher-pressure region. They also found that the associated density increase through these transitions reaches about 8.2%. From these facts they suggested the possibility that the rutile-type of SiO<sub>2</sub>, stishovite, transforms to the fluorite structure in the higher-pressure region.) (3) The Fe/Mg ratio is approximately the same in olivine and in pyroxene.

The densities of component minerals under high pressures were determined in the following ways:

1. *MgO and the most dense form of SiO<sub>2</sub>.* From the many available data on the density at pressures, which have been deduced from the high-pressure X-ray measurements (MgO) and the shock compression experiments (MgO, SiO<sub>2</sub>), we directly used the values for which the temperature effect had been considered; these are

the 4000°K isotherms obtained from the shock compression experiment of MgO and SiO<sub>2</sub> [Altshuler *et al.*, 1965]. Though the shock data of the matter in which the polymorphic transitions take place, such as SiO<sub>2</sub>, are relatively less reliable, we had no alternative but to use this kind of results.

2. *FeO*. There exists only the static-pressure X-ray measurement, in which the maximum experimental pressure is 276 kb [Cleneden and Drickamer, 1966]. In this case a wide range of extrapolation is necessary, and the Murnaghan-Birch equation of state was used. The best fit is obtained between the experimental results and the equation of state when a value of 1.49 mb is chosen for  $K_0$  (bulk modulus at 1 atm).

Though there is a possibility that a solid solution between MgO and FeO is formed, the density is calculated as a simple mixture of MgO, FeO, and SiO<sub>2</sub>. The density distributions were calculated for the following four cases of the Fe/Mg ratio:

- Case 1. Fe:Mg = 0:10.
- Case 2. Fe:Mg = 1:9.
- Case 3. Fe:Mg = 2:8.
- Case 4. Fe:Mg = 3:7.

The calculated density distributions are shown in Table 1 and Figure 2, with the density distri-

bution of the Bullen model A-i [see Bullen, 1963] and the Birch models I and II [Birch, 1964].

In cases 1 and 4, the densities calculated are greatly different from the value given by Bullen and Birch for the lower mantle. If we adopt the density value of case 1 as the density of the lower mantle, yielded moment of inertia of core becomes

$$I_{\text{core}} = 0.449 M_{\text{core}} R_{\text{core}}^2$$

where  $I$ ,  $M$ , and  $R$  are the moment of inertia, the mass, and the radius, respectively. This relation is of course impossible from stability considerations because the coefficient 0.449 exceeds the value 0.40 which applies to a sphere of constant density. In the case 4 the yielded moment of inertia of the core results in the relation

$$I_{\text{core}} = 0.354 M_{\text{core}} R_{\text{core}}^2$$

With this value we can estimate the ratio of the density at the core-mantle boundary to the density at the center of the core, if we suppose that density in the core increases linearly with the depth. From the simple consideration we obtain the relation

$$\begin{aligned} [(4/9) - 0.354] \rho_{\text{core boundary}} \\ = [(0.354/3) - 4/45] \rho_{\text{center}} \end{aligned}$$

TABLE 1. Density Distributions (grams per cubic centimeter)

Depth, km	This Paper				Bullen Model A-i	Birch Model	
	Case 1	Case 2	Case 3	Case 4		I	II
<i>Upper Mantle (olivine + pyroxene)</i>							
0		3.34	3.46				
33					3.32	3.43	3.32
100		3.42	3.53		3.38	3.43	3.32
200		3.49	3.62		3.47	3.45	3.35
300		3.56	3.69		3.55	3.53	3.44
400		3.63	3.77		3.63	3.68	3.62
<i>Lower Mantle (MgO + FeO + SiO<sub>2</sub>)</i>							
0	3.90	4.04	4.19	4.33			
1000	4.34	4.52	4.69	4.87	4.65	4.52	4.58
1400	4.54	4.73	4.92	5.10	4.88	4.74	4.81
1800	4.75	4.94	5.14	5.32	5.10	4.95	5.02
2200	4.96	5.16	5.36	5.55	5.31	5.16	5.22
2600	5.13	5.34	5.55	5.75	5.51	5.36	5.42
2800	5.22	5.43	5.64	5.85		5.46	5.52
2898					5.66		

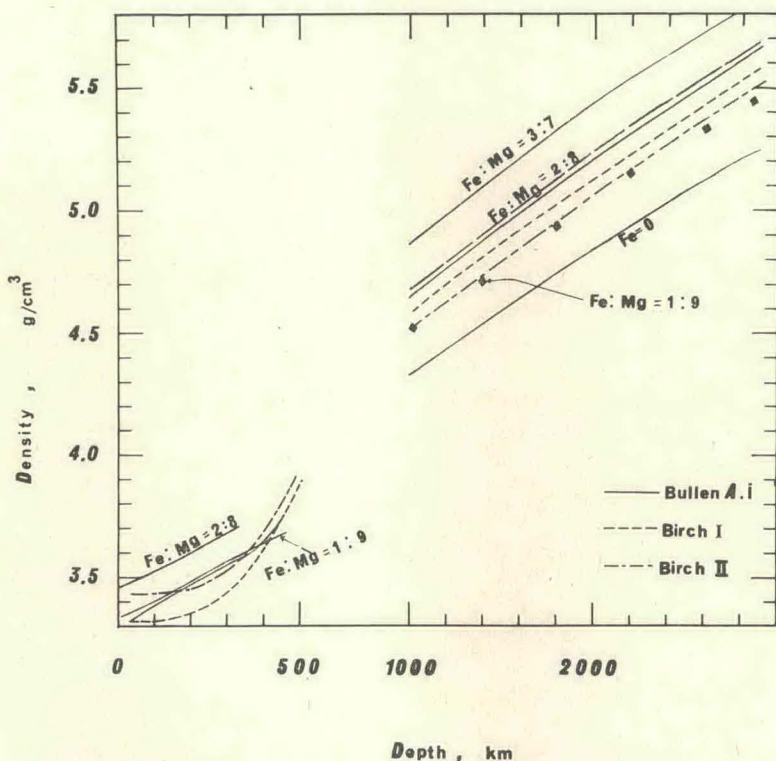


Fig. 2. Comparison of the density distributions based on four cases of the hypothetical mineral assemblages, together with the Bullen mode A-i, the Birch models I and II.

and so

$$\rho_{\text{center}}/\rho_{\text{core boundary}} = 3.11$$

where  $\rho$  denotes density. This value seems too high in view of recent results from shock experiments. Even under the pressures existing in the core none of the solid substances that are thought to be main constituents of the earth could be so compressible. For example, the ratios of zero-pressure density to density under pressures of the order of megabars in an element, an alloy, and two compounds are shown below.

Fe [Al'tshuler *et al.*, 1960]:

$$\rho_{(3.560 \text{ Mb})}/\rho_0 = 1.664$$

Fe<sub>80.2</sub>Si<sub>19.8</sub> alloy [Balchan and Cowan, 1966]:

$$\rho_{(3.6 \text{ Mb})}/\rho_0 = 1.77$$

Dunite (R. G. McQueen and S. P. Marsh, unpublished; see Birch [1966]):

$$\rho_{(1.123 \text{ Mb})}/\rho_0 = 1.56$$

Periclase (R. G. McQueen and S. P. Marsh, unpublished; see Birch [1966]):

$$\rho_{(1.258 \text{ Mb})}/\rho_0 = 1.41$$

In these calculations, the Bullen model A was used for the upper part of the mantle, and its use does not have any significant effect on the conclusions obtained above.

*Fe/Mg ratio and density in the upper mantle.* From the above discussion, we need only to treat values of the Fe/Mg ratios in the range between Case 2 and Case 3. Shock compression data are available for both olivine-rich (dunite: 92% olivine, Fe/Mg = 12/88) and pyroxene-rich (two bronzites: 92 and 94% pyroxene (90% enstatite)) rocks [McQueen *et al.*, 1967]; the Fe/Mg ratios of these are similar to the values for olivines and pyroxenes discussed below. In the following calculation we will assume the compressibility values of the above rocks, as deduced from the shock compression data, as the values for olivine and pyroxene having an Fe/Mg ratio of 1:9 or 2:8. When the com-

pressibility is reduced from the shock compression data, the results of static experiments [see *Birch*, 1966] are also taken into account in the low-pressure region.

Results are shown in Table 1 and Figure 2 together with the density distributions of the Bullen model A and the Birch models I and II. As is seen from this figure, the calculated density of the mineral assemblage of case 3 is higher than any of those distributions, whereas for the case 2 density is approximately consistent with the value estimated from the seismic observation.

However, the Fe/Mg ratio in the mantle may not as yet have been strictly determined, because the effect of temperature is neglected in this calculation and the density distribution in the mantle itself is now in dispute. Therefore, we also consider the petrological evidences for determining the Fe/Mg ratio in the upper mantle.

*Petrological evidences for the Fe/Mg ratio of olivine in the upper mantle.* Mafic and ultramafic inclusions in basaltic rocks and the kimberlite may be regarded as *cores of deep drilling* carried out by nature, and some kinds of peridotite inclusions may quite possibly be the slightly altered fragments of the upper mantle [e.g., *Ross et al.*, 1954; *O'Hara and Mercy*, 1963; *White*, 1966; *Kuno*, 1968]. The Fe/Mg ratio of olivine in the peridotite inclusion may provide useful information on the Fe/Mg ratio of olivine in the upper mantle.

Some kinds of peridotite inclusions are believed to represent the upper mantle materials for the following reasons: (1) The localities of the inclusion-bearing basalts are distributed throughout the world; nearly 200 localities are known throughout the oceanic, the orogenic, and the non-orogenic regions of the world [*Forbes and Kuno*, 1965]. (2) Peridotite is the commonest rock type as inclusion [*Kuno*, 1968]. (3) The close correlation that exists between suites of peridotite inclusions and types of host rocks implies a genetic relation between the two. Consequently, an origin as *accidental* fragments of crustal or mantle materials can be discounted for most of peridotite inclusions [e.g., *White*, 1966; *Kuno*, 1968]. (4) Striking systematic differences are found in the mineral composition, the bulk chemical composition, and other physical appearances

of these suites of peridotite inclusions, and we can presume the origin mechanism of each suite of them. Accordingly, most of the suites can be divided into two categories on the basis of their origin mechanisms: (a) peridotite inclusions that are non-altered or slightly altered fragments of the upper mantle material, and (b) the peridotite inclusions that originated by accumulation of crystals from host basaltic magma at its fractionation process. Garnet-peridotite inclusions in the kimberlite and garnet-peridotite of Norway and Switzerland [*O'Hara and Mercy*, 1963] and the lherzolite inclusions [*White*, 1966; *Kuno*, 1968] are believed to belong to the first category. (5) The peridotite inclusions in kimberlite, which is surely a mantle origin, shows close correlations to other peridotite inclusions which are believed to be fragments of mantle materials. (This is a strong support for the above discussions.)

The most interesting feature of the Fe/Mg ratio of olivine in peridotite inclusions is that this ratio increases in proportion to the stage of fractionation of the host rocks and gradually goes away from the primary ratio of the mantle material. Consequently, the values of the Fe/Mg ratio of these inclusions vary over a wide range according to the stage of differentiation of host rocks. In the case of olivines that are thought to be fragments of the upper mantle materials, however, the values are strongly concentrated

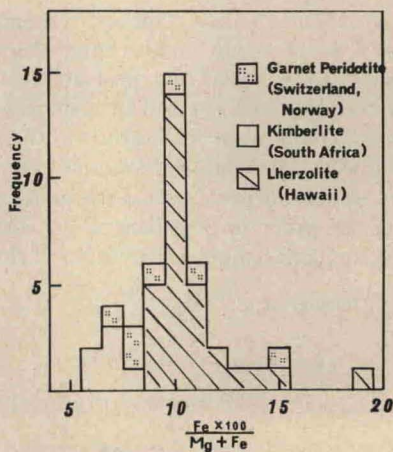


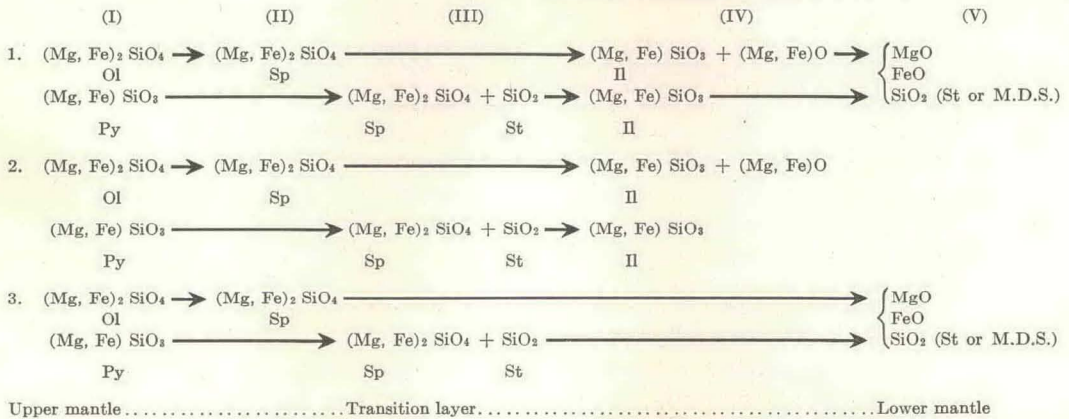
Fig. 3. Histogram of the Fe/Mg ratio of olivines in some peridotite inclusions. Garnet peridotite of Switzerland, Norway, the kimberlite [after *O'Hara and Mercy*, 1963], and the lherzolite [after *White*, 1966].

in a narrow range. Most of the values of the  $[Fe \times 100 / (Mg + Fe)]$  ratio of this kind of olivine fall short of 15 and are concentrated around 10 [e.g., *Ross et al.*, 1954; *O'Hara and Mercy*, 1963; *White*, 1966]. The histogram of the values of this ratio for this kind of olivine in inclusions at some localities is shown, for example, in Figure 3.

We therefore use the Fe/Mg ratio of 1:9 for olivine in the upper mantle throughout the following discussions.

POLYMORPHIC CHANGE AND DISCONTINUITIES IN THE TRANSITION LAYER

*Results of high-pressure, high-temperature experiments.* We will now consider the sequence of polymorphic transitions, which appear likely to occur in the mantle under pressures and temperatures prevailing in the transition layer. In the light of the recent progress in high-pressure research, three probable types of sequences can be written:



where Ol, Py, Sp, Il, St, and M.D.S. denote, respectively, olivine, pyroxene, spinel, ilmenite, stishovite, and the most dense form of silica [see *Akimoto and Fujisawa*, 1967; *Akimoto and Ida*, 1966; *Birch*, 1952; *Ida et al.*, 1967; *Ringwood and Major*, 1966a, b, c, d; *Ringwood and Seabrook*, 1962a, b, 1963; *Syono and Akimoto*, 1968].

It is very important that in the  $MgSiO_3$ - $FeSiO_3$  system pyroxenes remain stable without exception at pressures higher than are required for olivine-spinel transition in olivines having similar Fe/Mg ratios [*Ringwood and Major*, 1966c, d]. *Ringwood and Major* [1966d] also

reported that under the maximum available pressure of their apparatus,  $(Mg_{0.75}Fe_{0.25})SiO_3$  pyroxene breaks down partially to spinel plus stishovite at about 900°C. At the same period they succeeded in synthesizing  $(Mg_{0.88}Fe_{0.12})_2SiO_4$  spinel at about 900°C with the same apparatus [*Ringwood and Major*, 1966c]; for this synthesis pressures greater than about 130 kb are required, in view of the phase diagrams of olivine-spinel transition in the  $Mg_2SiO_4$ - $Fe_2SiO_4$  system [*Akimoto and Fujisawa*, 1967]. Thus, the maximum pressure of their apparatus at that time should have reached up to 130 kb. Accordingly, it seems likely that pyroxenes with a composition around  $(Mg_{0.9}Fe_{0.1})SiO_3$  will break down, at least partially, to spinel plus stishovite at about 150 kb and 900°C.

$FeSiO_3$  pyroxene, which once broke down to spinel plus stishovite, recrystallizes to the denser structure (probably ilmenite) under pressures that are considerably higher than the pressure required for the first breakdown (*S. Akimoto*

and *Y. Ida*, private communication, 1966). It could safely be said, therefore, that among three probable types of sequences of polymorphic transitions mentioned above either of the first two sequences, which have the mineral assemblage of case IV, appears likely to occur. There are two possible cases (IV and V) of the final mineral assemblage for the lower mantle, but there would be little difference in the physical properties between them. Therefore, we adopted only case V for the lower mantle minerals in the density calculation above.

Increase of density at zero pressure ( $\Delta\rho_0$ ) in each transition is shown in Table 2. Strictly

TABLE 2. Rate of Increase of Zero-Pressure Density in High-Pressure Phase Transitions

Reaction	Rate of Density Increase, %
Mg <sub>2</sub> SiO <sub>4</sub> → Mg <sub>2</sub> SiO <sub>4</sub> Ol            Sp	10
2Mg <sub>2</sub> SiO <sub>3</sub> → Mg <sub>2</sub> SiO <sub>4</sub> + SiO <sub>2</sub> Py            Sp            St	17
Mg <sub>2</sub> SiO <sub>4</sub> → MgSiO <sub>3</sub> * + MgO Sp            Il	7.4
Mg <sub>2</sub> SiO <sub>4</sub> + SiO <sub>2</sub> → 2MgSiO <sub>3</sub> Sp            St            Il	4.6
Mg <sub>2</sub> SiO <sub>4</sub> → 2MgO + SiO <sub>2</sub> Sp            St	8.5
Mg <sub>2</sub> SiO <sub>4</sub> + SiO <sub>2</sub> → 2MgO + 2SiO <sub>2</sub> Sp            St            St	6.2
MgSiO <sub>3</sub> + MgO → 2MgO + SiO <sub>2</sub> Il                                  St	1.0
MgSiO <sub>3</sub> → MgO + SiO <sub>2</sub> Il                                  St	1.5

## Notes

Ol denotes olivine; Sp, spinel; Py, pyroxene; St, stishovite; Il, ilmenite.

\* The density estimated by Ringwood [1966, pp. 385 and 389] is used.

speaking the density increase ( $\Delta\rho$ ) at the depth of transition is less than the density increase at zero pressure ( $\Delta\rho_0$ ), because high-pressure minerals are generally less compressible, but  $\Delta\rho$  would be approximately proportional to  $\Delta\rho_0$ . The jump of physical properties associated with each transition would be directly related to the density increase  $\Delta\rho$  and so related to  $\Delta\rho_0$ .

As was previously assumed, if the mantle materials are composed mainly of olivine, the breakdown of pyroxene has little influence and makes a minor step or no step in the velocity-depth curve. Thus, there should exist two main steps in the velocity-depth curve, which correspond to olivine-spinel transition and successive breakdown of spinel, provided that a moderate temperature gradient is considered in the transition region (see Table 2).

On the other hand, if the content of coexisting pyroxene increases in the upper mantle, another seismic discontinuity corresponding to the pyroxene breakdown may become apparent at the depth between the olivine-spinel and the post-spinel transitions. At the same time, as the increase in the amount of coexisting minerals (mainly pyroxene) other than olivine becomes greater, the average rate of increase in the

density of the mantle materials as a whole in the region of the olivine-spinel transition becomes smaller. If the ratio of olivine to pyroxene is 1:1 in the upper mantle, approximate calculation shows that the average rates of the increase in the density of mantle materials are about 6 and 7% at the olivine-spinel transition and at the breakdown of pyroxene, respectively. Accordingly, three discontinuities, which correspond to the olivine-spinel transition, the pyroxene breakdown, and the post-spinel transition, could possibly be observed in the velocity-depth curve. There remains the possibility, however, that the transition region of the pyroxene breakdown would occur immediately after the region of the olivine-spinel transition. In this case, the first two steps might become combined, and the first steep rise in the velocity-depth curve would, under an adequate temperature distribution, be succeeded by the wide high-velocity gradient zone.

Ringwood and Major [1966d] and Ringwood [1967] suggested that the newly discovered garnet-pyroxene (e.g., Mg<sub>3</sub>Al<sub>2</sub>SiO<sub>3</sub>O<sub>12</sub>-MgSiO<sub>3</sub>) solid solutions would occur first at a depth of about 350 km and would cause the recently observed strong velocity gradient. Because in the present model the contents of pyroxene and garnet in the upper mantle materials are assumed to be very small, we will not discuss this problem further. Even if this phenomenon actually occurs, the depth of its occurrence will nearly coincide with the depth of the olivine-spinel transition, judging from their stability relations.

*Observed discontinuities.* It is very interesting that the recently observed seismic discontinuities are concentrated in two regions around the depths of 350 and 650 km. Some examples are listed below. (This list is not complete; for a more complete list see Anderson [1967a] and Johnson [1967].)

- 360 and 700 km (CIT 11) [Anderson and Toksöz, 1963].
- 360 ~ 440 km (CIT 11A) [Kovach and Anderson, 1964].
- 350 and 700 km (CIT 12) [Toksöz and Anderson, 1966].
- 350 and 680 km [Golenetskii and Medvedeva, 1965].
- 320 and 640 km (CIT 11CS3) [Niazi and Anderson, 1965].
- 340 km [Archambeau et al., 1966].



340 and 640 km (CIT 109P) (C. B. Archambeau and E. A. Flinn, see *Anderson* [1937c]).  
 375 km [*Kanamori*, 1967]. (See Figure 4.)  
 365 and 610 km (CIT 204) [*Johnson*, 1967].  
 (See Figure 4.)

These values are obtained by using surface wave dispersion, travel times, and apparent velocities of body waves. The apparent velocity method gives accurate velocity gradients but give slightly inaccurate values for the absolute velocities. In travel time method the absolute velocity values may be accurate but the velocity gradients are in error. In the present discussion the latest two models of *Kanamori* [1967] (oceanic near island arc) and *Johnson* [1967] CIT 204 (continental) (both models are based directly on apparent velocities) are used (see Figure 4) because the velocity gradient is of great importance in this kind of discussion.

Although the depths of the first step of the sharp velocity gradients are approximately equal, the velocity gradients of the two models used are quite different from each other within the transition layer. CIT 204 corresponds quite well to the olivine model with two main steps of velocity increase. *Kanamori's* model seems to be equivalent to the olivine-pyroxene model with all three steps coupled. Accordingly, if these two models for two different areas hold true in fine details, it seems very difficult to account for this disagreement in the velocity gradients in the transition region only by the different temperature distributions in the two areas. The disagreement may be attributed to the difference in the amount of pyroxene and garnet in the mantle materials in the two areas. There is not, however, at present sufficient knowledge of the various phase changes and

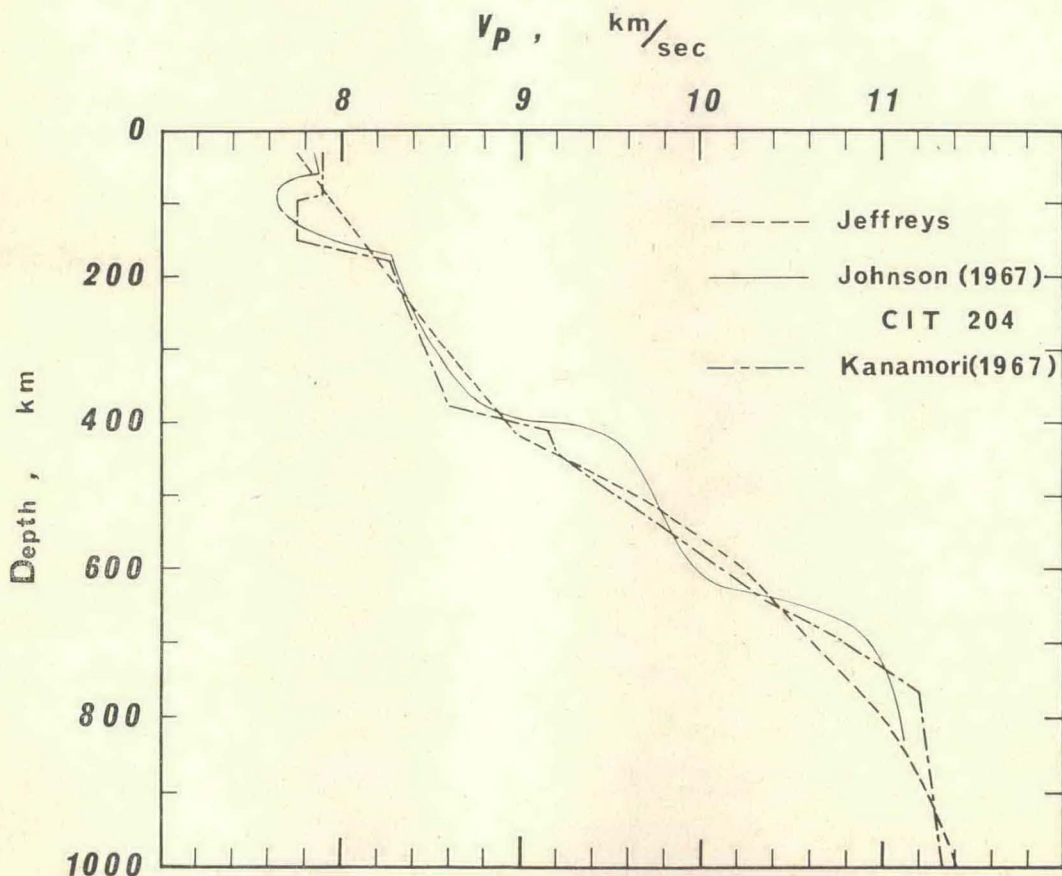


Fig. 4. The latest  $V_p$  models for the mantle after *Johnson* [1967] and *Kanamori* [1967], together with *Jeffreys'* velocity-depth curve.

the elasticity of high-pressure minerals to make a detailed discussion.

In Figure 5 the present two velocity-depth models and the olivine-spinel phase relations (in  $(Mg_{0.9}Fe_{0.1})_2SiO_4$  and  $(Mg_{0.8}Fe_{0.2})_2SiO_4$ ; arranged from Figure 1) are shown. As is seen from the figure, for the olivine-spinel transition in olivine with  $(Mg_{0.9}Fe_{0.1})_2SiO_4$ , a two-phase region 50 to 80 km thick could be expected under the temperature gradients less than  $2^\circ C/km$  through this region. As for  $(Mg_{0.8}Fe_{0.2})_2SiO_4$  olivine, the thickness would reach 110 to 140 km under the same temperature gradients. In Figure 6 the increase of zero-pressure density in pure olivine is compared with the strong velocity gradients around 400-km depth in the present two velocity models, although the over-all density increase will be slightly lowered by the coexisting minerals other than olivine.

As is seen from the figure, the width of the two-phase region of the olivine-spinel transition in the composition about  $(Mg_{0.9}Fe_{0.1})_2SiO_4$  seems approximately equal to the width of the steps at the depth of about 400 km, which appeared in the velocity-depth curves of the present velocity models. It is not necessarily clear, however, that the entire two-phase region of the olivine-spinel transition accurately corresponds to the observed high velocity gradient zone, since the zero-pressure density increases so slowly in the upper half of the two-phase region that it reaches only about 25% of the whole density increase in the olivine-spinel transition at the midpoint of this region. It seems fairly possible that the region of the sharp velocity gradient would correspond approximately to the lower half of the two-phase region.

From the discussion based on model CIT 204 using the empirical equation of state [Anderson,

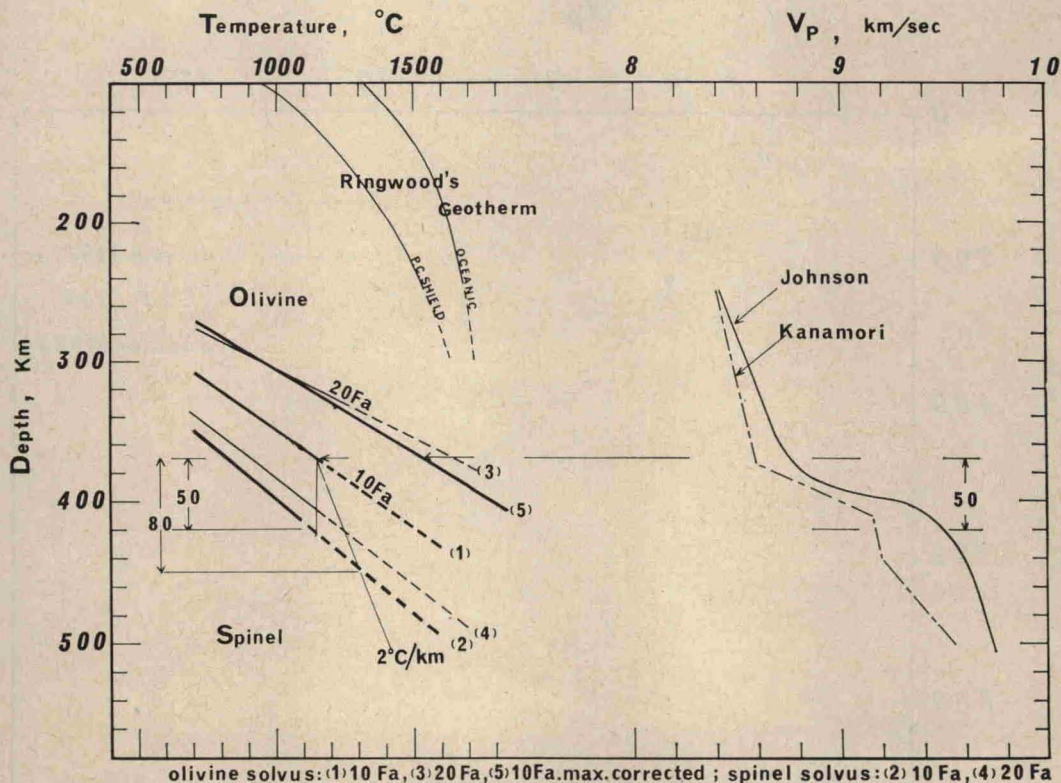


Fig. 5. Stability relations of olivine-spinel transition in 10Fa-90Fo and 20Fa-80Fo deduced from Figure 1 with the aid of the pressure-depth relation based on the Bullen model A-i, the upper sharp velocity gradient zone of the  $V_p$  models of Johnson [1967] and Kanamori [1967] and Ringwood's [1966] geotherm. Variation of the width of the two-phase region with increasing of temperature gradient is also shown.

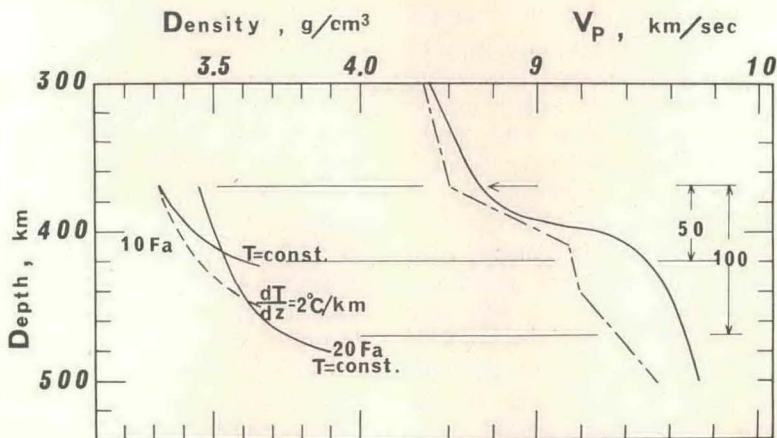


Fig. 6. The zero-pressure density increase with increasing amount of spinel in the two-phase region is compared with the anomalous velocity gradient zone.

1967b] and Birch's [1960, 1961] velocity-density relation, Anderson [1967c] pointed out that the observed velocity increases associated with each transition are slightly less than predicted for the appropriate phase change and that the whole density increase associated with the olivine-spinel transition and the spinel-oxides decomposition is fairly less than the total density increase across the transition layer of the mantle. He suggested that increasing the content of  $\text{Fe}_2\text{SiO}_4$  from 20% in the upper mantle to 40% through the transition layer is satisfactorily consistent with the CIT 204 model, provided that the earth's mantle is composed mainly of olivine. This interpretation seems disagreeable, however, from the preceding discussion of the density and the petrological evidences.

An alternative for lessening the velocity increase through olivine-spinel transition region is to add more pyroxene to the mantle materials. Coexistence of an adequate amount of pyroxene will reduce the change of bulk properties in this region. Another solution to the problem of this velocity increase in the olivine-spinel transition in the homogeneous-composition model is to consider that the transition region determined by the seismological observation would correspond to some part of the transition, not the entire transition region, as mentioned above. These would not clear away Anderson's suggestion of the difficulties in the homogeneous-composition model. In the present stage of investigation, however, the existence

of such difficulties may be the problem to solve, and the accurate knowledge of elastic properties of denser phases is an essential factor in further discussions.

#### TEMPERATURE AT TOP OF TRANSITION LAYER

From the discussions above it appears likely that the region of the anomalous velocity gradient around the depth of 400 km in the present velocity models would approximately correspond to the two-phase region of olivine-spinel transition in ferromagnesian olivine within the mantle. Consequently, the stability conditions for the two-phase region must be satisfied within this depth interval. As for the interior of the earth, pressures had been determined at each depth with sufficient accuracy, and the only adjustable parameter to satisfy the stability conditions is the temperature at the depth considered. This can be seen in Figure 5.

Before estimating the temperature, we will consider the accuracy of the measurement of pressures and temperatures in the olivine-spinel equilibrium experiment of Akimoto and Fujisawa [1967]. (The data from their work are used in this discussion.) The amount of error in the estimated pressure values for the fixed calibration points up to 100 kb would not exceed a few per cent, and the reproducibility of pressure calibration is quite good. For ordinary calibration runs, however, the construction of samples is different from construction for the phase equilibrium runs; that is, the samples for the latter runs are heated in a graphite-tube

furnace. It has been found that the presence of a graphite-tube furnace in a pressure medium makes the pressure transmission inefficient by nearly 10% to a tube-less assemblage for the pressure calibration at the room temperature and in the pressure range up to the Ba I-II transition. This inefficiency would hold true in higher pressure region. On the other hand, it is believed that at temperature higher than 1000°C the pressure medium would soften and pressure would be transmitted more efficiently [Boyd and England, 1963]. Thus, the working pressures would be increased several per cent higher than the values estimated from the calibrations at room temperature. In the phase diagrams presented by Akimoto and Fujisawa [1967] (see Figures 1 and 5 (except olivine solvus 5)), these effects are not considered. Putting all accounts together, it could be said that there is a possibility of decreasing the transition pressure shown in Figures 1 and 5 by a few per cent.

There are two sources of error in the temperature estimation. First, the simple error coming from stability of furnace temperature; this error does not exceed  $\pm 20^\circ\text{C}$  in the experiment. Second, the pressure effect on the emf of thermocouples must be considered. Accurate estimation of this effect is very difficult, because there are no quantitative results available for the range of pressures and temperatures considered here. Direct measurement of this effect has made only up to  $100^\circ\text{C}$  under relatively lower pressure [Bridgman, 1918; Bundy, 1961]. Hanneman and Strong [1965, 1966] estimated indirectly the pressure effect up to 50 kb and to  $1300^\circ\text{C}$  with Pt|Pt-10Rh, C|A, and Pt|Pt-13Rh thermocouples. If their results are true in higher-pressure range, the temperatures indicated in the phase diagrams of Figures 1 and 5 (except olivine solvus 5), which were determined with the Pt|Pt-13Rh thermocouple, must be corrected by nearly  $+100^\circ\text{C}$ , since in the experiment no correction was made for this kind of error. This indirect method of determining the pressure effect has not yet been justified by any other evidence. We tentatively adopt the value of  $+100^\circ\text{C}$  as the maximum amount of correction needed.

Now we will try to estimate the temperature at the top of the transition layer in two limiting cases. From the preceding discussions, we will

use in this attempt the assumed parameters: (1) the Fe/Mg ratio in mantle minerals is 1:9, and (2) the depth at which olivine-spinel transition begins is at about 370 km ( $\approx 125$  kb).

*Lower limit of the temperature at 370-km depth.* We will assume that (1) the pressure transmission is not affected by the existence of a graphite-tube furnace, and (2) the pressure effect on the emf of thermocouple can be considered negligible. In this case the phase relations indicated in Figure 5 can be used without corrections, and the temperature at the depth of 370 km is estimated to be  $1150^\circ\text{C}$  from olivine solvus 1 in this figure.

*Upper limit of the temperature at 370-km depth.* We will assume that (1) the existence of a graphite-tube furnace results in a 10% reduction of the pressures previously estimated, and (2) the pressure-induced correction for the emf of thermocouple reaches nearly  $100^\circ\text{C}$ . In this case the phase relation shown in Figure 5 must be modified as shown in the curve for olivine solvus 5, and the estimated temperature at the 370-km depth reaches about  $1530^\circ\text{C}$ .

Thus the temperature at the depth of about 370 km would be limited in the range

$$1150^\circ\text{C} \leq T_{370 \text{ km}} \leq 1530^\circ\text{C}$$

as long as the model of Kanamori or Johnson is considered. The temperature distributions given by Rikitake [1952] and Verhoogen [1954] fall in this range of temperatures. Extrapolated value from Ringwood's [1966b] geotherm would exceed even the highest limit of the present estimation at the 370-km depth, and Gilvarry's [1957] distribution gives lower temperature values than are given by the present estimation at that depth.

The temperature at that point will be lowered (to  $800^\circ\text{C}$  at the 320-km depth, in the lowest case, with CIT 11CS3) if other recent models referred to in the former section are taken into account, since in all these models the rapid rise of velocity around the 350-km depth always begins at a shallower depth than in the model of Kanamori or Johnson.

The temperature distribution in the olivine-spinel transition region cannot be determined strictly, since the correlation between the observed thickness of the transition region and the width of the two-phase region in the olivine-spinel transition has not yet been established

completely and since the thickness of the region estimated from the velocity-depth curve varies from about 30 to 50 km or more, although most of the thickness values are around 50 km, according to the velocity models referred above. It is clear, however, that there exists a close relation between the observed thickness and the width of the two-phase region, and if we suppose that the accurate correspondence would exist between them, the width is essentially determined by the temperature distribution and the Fe/Mg ratio in olivine. The constant temperature gives a value of about 50 km in width with a Fe/Mg ratio of 1:9, around the depth of 400 km in the mantle. To spread the thickness more than 70 km with the same chemical composition, however, the temperature at the termination of this region must be nearly 100°C higher than at its beginning.

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