The constitution of the mantle—III

Consequences of the olivine–spinel transition*

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Abstract—Evidence on the chemical composition of the mantle is reviewed. Based upon studies of the inclusions in kimberlite pipes, intrusion of peridotites in orogenic regions, and the compositions of stony meteorites and kimberlite, it is suggested that the average composition of the mantle may approximate that of a garnet peridotite. However, the upper mantle immediately below the M-discontinuity may be poorer in sialic material and close to normal dunite–peridotite in composition.

When garnet peridotite is subjected to high temperatures and pressures a series of transitions dominated by the olivine–spinel transition occurs. Besides the olivine–spinel transition, pyroxene may invert to spinel plus coesite, whilst garnet and coesite may dissolve in the spinel at higher temperatures to form a highly disordered defect solid solution. The data in Parts I and II show that these changes should occur under the P–T conditions present in the upper 1000 km of the mantle and take place over an appreciable depth range. The position and extent of this transition range depends upon the assumed temperature distribution in the upper mantle. By choosing a suitable temperature distribution, the transition region can be made coincident with region C (BULLEN) in which phase changes and inhomogeneity have been inferred on other grounds.

It is found that the proposed transition phenomena are capable of explaining the known data on seismic velocity distribution, elasticity and density in the mantle. The temperature distribution required to make the phase transition region coincident with region C is supported by recent studies of the temperature dependence of electrical conductivity in the mantle. Both convection and conduction mechanisms of heat transfer may give rise to this temperature distribution.

A specific model for the mantle is proposed.

1. INTRODUCTION

IN Parts I and II of this series a study was made of the P–T conditions governing the olivine–spinel transition in forsterite and fayalite. Attention was also given to the possibility that pyroxene might break down to a spinel under pressure. The conclusion drawn was that olivines and pyroxenes would probably undergo inversion at depths of less than 1000 km in the mantle. In this paper a study is made of the consequences of these inversions and the extent to which they can account for the known properties and structure of the mantle.

Before this can be attempted, it is necessary to discuss present data on the chemical composition of the mantle, since this will determine the relative amounts of olivine and pyroxene and the extent to which the constitution of the mantle can be interpreted on the basis of phase transitions in these minerals.

2. CHEMICAL COMPOSITION OF THE MANTLE

At an average depth of 30 km below the continents and 5 km below the ocean basins the velocity of P earthquake waves increases suddenly to about 8 km/sec, giving rise to the Mohorovicic (M) discontinuity. This velocity essentially restricts the type of rocks which may occur in this region to dunites, peridotites and eclogites. Since the former two are closely related and differ radically from

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eclogite, they will frequently be grouped together as "dunite–peridotite" in subsequent discussion.

Differentiation between eclogite and dunite–peridotite in the mantle cannot yet be made on physical grounds, therefore identification of the material beneath the M-discontinuity must depend upon geochemical and petrological arguments. At present it appears likely that most geologists favour the dunite–peridotite composition, but there have been in the past, and still are, some notable advocates of eclogites. Impetus has been given to this group by recent experiments in the high-pressure field (KENNEDY, 1956; ROBERTSON, BIRCH and MACDONALD, 1957). It has been found that many minerals common in the crust undergo polymorphic changes to denser forms when moderate pressures are applied. It seems quite reasonable to suppose that basalt would be converted to an eclogitic assemblage at some depth (as yet unknown) in the upper mantle. The important question however is whether there is sufficient material of eclogitic composition in the upper mantle to be of geophysical significance. A substantial amount of geochemical and petrologic evidence on the composition of the upper mantle is available, and is discussed below.

(a) *The significance of crustal peridotitic intrusions and of olivine nodules in basalts*

The typical mode of occurrence of peridotites, dunites and serpentines derived therefrom is in geosynclinal regions which have undergone intense deformation. Intrusion has been controlled by major tectonic features and it is believed by many (e.g. HESS, 1955) that these bodies are derived directly from the mantle. If so, this would suggest that the upper mantle, immediately below the M-discontinuity is of dunite–peridotite composition.

Ross *et al.* (1954) have shown that dunite and the common olivine nodules found in basalt all over the world possess marked geochemical similarities, strongly suggestive of genetic relationship. In particular they tend to contain Ni^2 and Cr^3 in amounts considerably greater than those found in corresponding minerals from basalts. Since these elements are strongly enriched in the earliest minerals to crystallize from a magma (WAGER and MITCHELL, 1951) this suggests that dunite–peridotites* and olivine nodules possess a primitive, pre-basaltic origin.

Further evidence supporting the deep-seated origin of peridotites and olivine nodules is provided by the composition of diopside which usually occurs in varying amounts in this association. Ross *et al.* (1954) analysed a number of diopsides from olivine bombs and peridotites and found that they nearly always contain a substantial proportion of jadeite—up to 15 per cent. This suggests that the diopside has crystallized under pressure sufficiently high to prevent crystallization of felspars, and that as a result, the soda has entered pyroxene. It follows that olivine nodules and peridotites have been derived from the mantle, since felspars are stable in the crust.

Compared to peridotites, eclogites are exceedingly rare rocks. Their environment usually also suggests a deep-seated origin under conditions of great pressure.

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* The dunite–peridotites referred to are from the typical orogenic environments. There are undoubtedly dunites and peridotites in basic complexes which have been formed by crystal settling from a parent basic magma.

This applies particularly to one of the most common modes of occurrence which is as small inclusions and schlieren in bodies of peridotite (ESKOLA, 1921). In this association the field and petrologic data are indicative of a genetic relationship between the two. If the peridotites come from the upper mantle the associated eclogites must also come from there. The relative abundances, however, indicate that eclogite could be only a minor constituent of the upper mantle. The association found in diamond pipes (next section) is in accord with this conclusion.

(b) *Inclusions in kimberlite pipes*

These have been described by WAGNER (1914) and WILLIAMS (1932) and their geologic significance discussed. The present discussion owes much to WAGNER's (1928) paper. Kimberlite pipes carrying diamonds are of frequent occurrence over 1,000,000 miles^2 of southern Africa, and are also known in India, Brazil, the United States, Siberia and Australia. In South Africa and elsewhere these pipes carry numerous xenoliths of rocks which they are known to have intruded on their journey upwards. They contain also, large numbers of xenoliths of rocks which are not known to occur in the vicinity, particularly peridotites, pyroxenites and eclogites. The presumption is that these inclusions have been derived from deeper levels in the earth, and represent a random sample of deep lying rock types cut by the pipes. This group of inclusions consists essentially of the minerals olivine, pyroxene and garnet with all gradations from peridotites through garnet peridotites and olivine eclogites to eclogite. They have been found in every known occurrence of kimberlite, and diamonds occur in these inclusions as well as in the kimberlite.

Recent thermochemical calculations by MACDONALD (1954) show that given reasonable and flexible assumptions regarding temperature in the mantle, diamond would not be stable until a depth of approximately 120 km was reached. Accordingly the kimberlites may be said to have sampled the outer mantle over very large areas down to depths of at least 120 km.

It is of great significance that in all cases, *peridotitic inclusions are found to be much more common than eclogitic inclusions.* If the sampling is representative, then the outer mantle must be dominantly of peridotitic composition, with eclogite a minor, but widely distributed constituent.

The kimberlite forming the host to the above inclusions is a rock of variable composition and degree of alteration. It is noteworthy that the dominant primary mineral is magnesian olivine, which constitutes between 50 and 75 per cent of kimberlites. This suggests that the region in the mantle where kimberlite originates is one where magnesian olivine is also abundant.

(c) *Evidence from meteorites*

There is a wide belief that the average composition of the mantle may correspond approximately to that of the average stony meteorite. Justification for this belief rests upon the observation that elemental abundances of non-volatile elements in the sun, stars and meteorites are in reasonable agreement (KUIPER, 1952), and the analogy existing between the structure and composition of the earth and that of a postulated original meteoric planet.

Most recent theories of the origin of the solar system imply an originally uniform composition for the raw material (possibly dust). Birch (personal communication) has pointed out that the radioactive heat generation in chondritic meteorites closely approximates the present total heat flow from the earth divided by the mass of the mantle. This strongly suggests that the average concentrations of potassium, uranium and thorium are the same in meteorites and in the earth. Since these are known to be among the most easily fractionated elements, this indicates that there has been little relative differentiation of composition between that of stony meteorites and that of the earth's average silicate fraction. A further argument is that the assumption of a meteoritic mantle provides a satisfactory basis for theories of magma formation (Bowen, 1928) and geochemical abundances.

Table 1. Chemical composition of chondritic meteorites
(Urey and Craig, 1952)

Component	(%)
SiO_2	47·04
MgO	29·48
FeO	15·40
Al_2O_3	3·09
CaO	2·41
Na_2O	1·21
K_2O	0·09*
Cr_2O_3	0·45
MnO	0·31
TiO_2	0·14
P_2O_5	0·26

* (Ahrens, 1954)

The average composition of the silicate fraction of chondritic meteorites is given in Table 1. The analysis has been recomputed to give a "high-pressure norm", such as would probably occur under conditions existing in the mantle. Na_2O and Al_2O_3 have been computed as jadeite and garnet, and the jadeite included with pyroxene. Cr_2O_3 and TiO_2 (as Ti_2O_3) are included with Al_2O_3 whilst MnO is grouped with MgO, FeO and CaO. This latter group is treated as one unit and no attempt has been made to divide it into different kinds of pyroxenes, since complete solid solution would probably occur above 1500°C anyway. The high pressure norm is as follows:

	(%)
pyroxene	48 (incl. jadeite, 8)
olivine	44·4
garnet	7
apatite	0·6

Thus a rock of meteoritic composition would probably crystallize as a garnet peridotite under high pressure. This would be similar to some of the garnet peridotites found as inclusions in the South African diamond pipes.

The evidence from meteorites suggests that composition of the mantle might be akin to garnet peridotite. It seems however, that the amount of pyroxene relative to olivine obtained in the norms above might be somewhat high, since olivine is far more abundant in the deep-seated peridotites, kimberlites and kimberlite inclusions.

This apparent discrepancy will be considered in detail by the author in a forthcoming paper, where it is suggested that it is probably caused by a difference in the average state of oxidation of the earth and the meteoritic planet. The earth is more reduced, containing less ferrous iron than the meteoritic average. There is also evidence suggesting that the earth's core may contain about 10 per cent of silicon metal. This would be sufficient to produce a mantle containing a substantial excess of olivine over pyroxene (if the mantle was derived from an average chondritic composition by a higher degree of reduction. For the present it may be concluded that chondritic meteorite abundances suggest a mantle equivalent to a garnet peridotite, with (subject to further interpretation) olivine the dominant phase.

(d) Chemical zoning in the mantle

Studies of crustal peridotite intrusions and kimberlite inclusions described in Sections 2(a) and 2(b) suggested that the upper mantle immediately below the M-discontinuity is dominantly of peridotitic composition rather than eclogitic. However, minor amounts of eclogite are probably widespread in this region. Furthermore the data indicated that this peridotite contained very little CaO, Al_2O_3 and Na_2O.

The study of meteorite compositions (Section 2(c)) suggested that the mantle as a whole should contain substantial amounts of CaO, Al_2O_3 and Na_2O. A supply of these components in the mantle is necessary to explain the generation of basaltic magma. It is clear that these components must therefore occur below the dunite–peridotite zone, and it was shown that the material in this region would probably crystallize as a garnet peridotite. A zonal structure for the mantle therefore seems indicated, with dunite–peridotite below the M-discontinuity, grading downwards into primary garnet–peridotite.

RUBEY (1951) has arrived at a similar conclusion from geochemical arguments. He points out that the mantle has been differentiating over geological time and supplying basalt and sialic material to the surface, resulting in continental growth. He maintains that the primary mantle material may approximate meteoritic composition (i.e. garnet–peridotite). Fractional melting of this material forms basalts which are erupted at the surface. The region where the fractional melting occurs becomes depleted in Ca, Al and Na, and therefore of dunite–peridotite composition. According to this suggestion these rocks would occur immediately below the M-discontinuity and would be responsible for the orogenic dunite–peridotite intrusions. However, they would grade downwards into normal mantle material (garnet–peridotite) which is the present source of basaltic magma.

This model is able to supply a satisfactory explanation of the role of eclogite. Fractional melting of primary garnet–peridotite provides material of basaltic composition. Probably much of the basalt magma would not reach the surface

but would crystallize as eclogite in pockets and widespread segregations in the primary garnet–peridotite and in the residual overlying dunite–peridotite. This would explain the ubiquitous but minor occurrences of eclogites in the diamond pipes. The width of the dunite–peridotite zone and the proportion of eclogite might vary considerably in different regions of the earth and there would be room for substantial chemical inhomogeneity in the upper mantle. Furthermore, systematic differences could well exist between continents and oceans. A thickness of from 100 to 200 km for the dunite–peridotite zone beneath continents would appear reasonable, whilst it might be substantially less under the oceans.

BIRCH (1952) brought forward strong evidence indicating that the mantle between 900 km and the core is homogeneous, whilst between approximately 300 km and 900 km a region of inhomogeneity occurs. This inhomogeneity may be due to changes of phase, chemical composition or both. BIRCH showed that the principal changes were probably polymorphic changes in the minerals present, leading to dense, close-packed structures. He also suggested that changes of chemical composition occurred. This would help to explain the large width of the transition zone.

In the following pages the author shows that the width of the transition zone and the known properties of the mantle can be explained in terms of phase changes alone. It is not necessary to assume any chemical changes.* The properties of the mantle will be discussed in terms of phase changes in a medium of primitive and uniform composition—akin to that of the garnet–peridotite previously advocated.

3. PHASE EQUILIBRIA IN THE MANTLE INVOLVING THE OLIVINE–SPINEL TRANSITION

In Parts I and II of this paper, some of the conditions governing the olivine–spinel transition in fosterite and fayalite were determined. Assuming plausible temperature distributions in the earth it appeared that forsterite would invert to a spinel at depths less than 1000 km, whilst fayalite was found to undergo a similar inversion at much smaller pressures (at corresponding temperatures). A thermochemical study of the stability of (MgFe) pyroxenes showed that these would break down into $(MgFe)_2SiO_4$ spinels plus coesite at maximum pressures not much greater than those required for the olivine–spinel transition in the olivine of corresponding composition. If the temperatures were sufficiently high ($\gg 1500°C$) the pressures required for pyroxene breakdown would become coincident with those required for the olivine–spinel transition.

In a mantle of the composition assumed in Section 2, transition phenomena will be dominated by the olivine–spinel transition because of the abundance of olivine. Furthermore since pyroxenes also break down to spinels under pressure, there can be little doubt as to the importance of the role which $(MgFe)_2SiO_4$ spinel plays in the mantle. However, there will be other components apart from MgO, FeO and SiO_2 present in the mantle and it therefore appears desirable to

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* At least for the major components, which are not easily fractionated. It is possible that the distribution of some trace elements which cannot fit into existing minerals and are highly mobile may not be uniform throughout the mantle. Examples would be K, U, Th.

inquire in greater detail into the sequence of changes occurring when garnet–peridotite is placed under conditions such that an olivine–spinel transition may take place. In this respect two characteristic properties of spinels will be of particular importance.

(1) The spinel structure is stable for a very large number of ions of different size, valency and electronic structure. For example, the following ions form spinels (GORTER, 1954, with additions):

$$H^1 \quad Li^1 \quad Na^1 \quad Cu^1 \quad Ag^1$$
$$Mg^2 \quad Ca^2 \quad Mn^2 \quad Fe^2 \quad Co^2 \quad Ni^2 \quad Zn^2 \quad Ca^2$$
$$Al^3 \quad V^3 \quad Cr^3 \quad Mn^3 \quad Fe^3 \quad Ga^3 \quad Rh^3 \quad Ir^3$$
$$Ti^4 \quad V^4 \quad Mn^4 \quad Ge^4 \quad Sn^4 \quad Si^4$$
$$Mo^6 \quad W^6$$

At high temperatures, spinels display a strong tendency towards solid solution among themselves. The spinel lattice is tolerant towards a very wide range of ionic substitutions. It seems quite likely that if present data on solid solution relationships were extrapolated to temperatures around from 2500°C to 3000°C, a state of complete solid miscibility would be reached between end members in most spinel systems.

(2) Spinels frequently have the ability to take compounds with ABO_3 type formulae into solid solution forming defect structures. Thus ordinary spinel ($MgAl_2O_4$) is able to form solid solutions with Al_2O_3, Fe_2O_3 and Cr_2O_3. It seems quite possible that Mg_2SiO_4 spinel would be able to dissolve some excess SiO_2 to form a defect structure (this is equivalent to dissolving some $MgSiO_3$). This process would be encouraged by high temperatures and pressures.

The possible effect of pressure and temperature on transitions in garnet–peridotite may be noted in the light of the above data. The garnet–peridotite is assumed to consist dominantly of olivine, with subsidiary pyroxene and about 10 per cent of garnet. It is emphasized however that the discussion is general and does not depend upon a detailed chemical and petrological model such as that suggested above. The following discussion applies to a mantle of any composition consisting dominantly of olivine and pyroxene, with smaller amounts of Al_2O_3, CaO, Na_2O and Cr_2O_3. The garnet–peridotite model was adopted because of reasons put forward in Section 2, and it will be convenient to discuss detailed phase changes on this model.

The olivine in the mantle contains some fayalite in solid solution—probably about 10 per cent. Because of the much lower pressure required to invert fayalite to spinel, the first spinels formed during the transition will be rich in fayalite. As pressure rises, more and more forsterite will enter the solid solution. The transition in olivine will be completed at a pressure close to that required for the pure forsterite transition.

The behaviour of pyroxene was discussed in Part II; $(MgFe)SiO_3$ will break down to spinel plus coesite at pressures somewhat higher than those required to transform olivine into spinel. At a temperature of 1500°C the pressure required to decompose pyroxene may be about one-third greater than the pressure required for the olivine–spinel transition. At higher temperatures than this the excess

pressure is decreased and may become essentially the same as that required for for the olivine–spinel transition.

Pyroxenes in the mantle will also carry some $FeSiO_3$ in solid solution. This has an effect analogous to that in olivine. $FeSiO_3$ requires smaller pressures to break down than $MgSiO_3$ and hence this transition is also spread over a transition range, forming a band. This band probably overlaps the band formed by the $(MgFe)_2SiO_4$ olivine–spinel transition.

The decomposition of pyroxene liberates coesite. At sufficiently high temperatures this may dissolve in the spinel forming a defect solid solution. The ability of spinels to form such solutions has already been discussed.

The other phase suggested to occur in the upper mantle is garnet, probably of the pyrope variety. The structures of garnet and Mg_2SiO_4 spinel are related. Both consist of oxygen ions in cubic close packing with cations filling the holes. The chief difference is that garnet contains trivalent cations, chiefly Al^3, which are not present in pure Mg_2SiO_4 spinel. It has already been pointed out, however, that all the ions which occur in garnet can also form spinels, and that spinels are capable of very wide solid solution relationships at high temperatures. Accordingly at the high temperatures occurring in the mantle it seems likely that some Ca^2, Mn^2, Cr^3, Al^3, and Ti^3 will dissolve in the spinel. This is equivalent to solid solution of the garnet phase. According to the model, there is only about 10 per cent of garnet present, and it therefore seems very possible that garnet will dissolve completely in the spinel phase at the high temperatures involved (estimated as 1500°C–3000°C in Section 7).

Summarizing this discussion it is suggested that the following transitions may occur in the material of the mantle as pressure and temperature increase with depth.

(1) Olivine → spinel	Occurs over a P–T range because of Mg–Fe solid solution
(2) Pyroxene → spinel + coesite	Occurs over a P–T range because of Mg–Fe solid solution and probably overlaps transition (1).
(3) Spinel + coesite → spinel defect solid solution	This solution encouraged by high temperatures.
(4) Spinel + garnet → spinel solid solution (or subsidiary Ca^2, Al^3, etc.)	This solid solution encouraged by high temperatures.

This discussion leads therefore to the suggestion that when the transition is completed, there will be only one phase present—essentially an Mg_2SiO_4 spinel, containing excess $Si^4 Al^3 Cr^3 Ca^2 Na^1$ and other minor constituents (including OH^{-1}) in solid solution. The temperature estimated for completion of this process is about 3000°C (Section 7). The spinel solid solution will be of a highly disordered, defect character, consisting essentially of a cubic close packing of oxygen ions, with Si^4 filling the tetrahedral holes, and all the other cations distributed randomly through octahedral holes. Under the high temperatures and pressures involved it is possible that a small percentage of Si^4 ions might also occur in octahedral

sites (disorder of ions between octrahedral and tetrahedral sites is common in spinels). Such an assemblage of ions would be as close-packed as geometry would allow and it does not seem likely that further polymorphic transitions would occur once this state was reached.

It is evident that such complex transition phenomena will take place over an appreciable pressure and temperature range. Insufficient data are available to estimate its size. It may well be in the vicinity of from 100 to 200 km at constant temperature however. Using the gradient found for the olivine–spinel transition in forsterite this would be equivalent to about 350–750°C at constant pressure.

The data obtained in Parts I and II indicated that an olivine–spinel transition and related transition phenomena should occur in the first 1000 km of the mantle for all reasonable temperature distributions. The exact position and range of the transition would depend upon the temperatures in this region.

Transition phenomena of the kind described should cause important changes in the properties of the mantle in this depth region. In the next sections a review of the physical properties of the mantle is made in order to find out whether the changes in these properties are consistent with the occurrence of the predicted olivine–spinel transition.

4. SEISMIC DATA

The JEFFREYS (1939) and GUTENBERG (1948) depth–velocity curves for the mantle are illustrated in Fig. 1. The curves differ qualitatively in the shallower
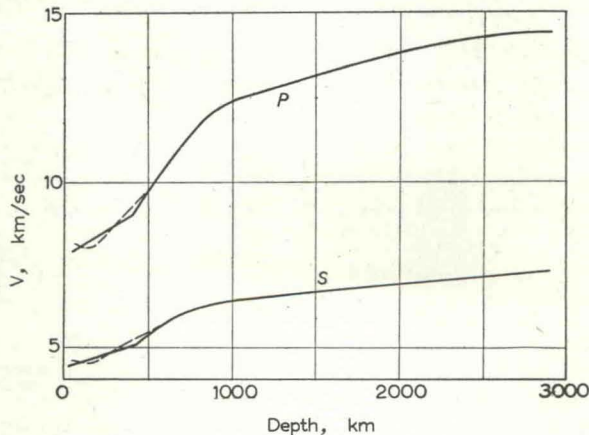

Fig. 1. Depth–velocity curves for the mantle; — JEFFREYS; – – – – GUTENBERG.

regions of the mantle but agree in the deeper regions. According to the classification made by BULLEN (1947) on the basis of these velocity distributions, three distinct regions may be distinguished in the mantle (region *A* refers to the crust):

Region B. An outer zone where wave velocity increases at a moderate rate with depth (JEFFREYS) or else it decreases slightly and then increases slowly (GUTENBERG). In JEFFREYS' solution this zone extends from 30 km to 412 km, in contrast to 30–200 km for the GUTENBERG solution.

Region C. An intermediate zone in which both solutions indicate a region

where velocity increases very rapidly with the depth until a depth of approximately 900 km is reached.

Region D. An extensive inner zone extending fron 900 km to the core at 2900 km, where wave velocity increases at a moderate and uniform rate.

The original interpretation of the velocity distribution in the mantle gave rise to the Jeffreys–Bernal hypothesis which was discussed in Part I. JEFFREYS assumed that the boundary between regions B and C was caused by a polymorphic inversion in the olivine of the mantle. It was suggested that ordinary olivine inverted to a spinel form possessing different elastic properties. In JEFFREYS' original solution, a first order discontinuity due to this phenomenon was placed at 474 km but the later solution shows a second order discontinuity at a shallower depth of 413 km.

The Jeffreys–Bernal hypothesis seemed to explain most of the features of the depth–velocity curves. Thus, on this basis, region B was assumed to consist essentially of normal olivine whereas region D was regarded as the homogeneous spinel modification. Qualitatively it was noticed that the high wave velocities of this region could be explained by the probable elastic properties of a closely packed spinel modification.

Region C could be interpreted as a region over which the transition took place, characterized by coexisting olivine and spinel. However, advocates of this hypothesis experienced some difficulty in explaining the occurrence of such a wide transition region, since a relatively sharp transition might normally have been anticipated.

Recently, BIRCH (1952) investigated the structure of the mantle from a quantitative standpoint. He compared the observed variation of seismic velocity with depth, with the variation which would be expected on thermodynamic grounds in a homogeneous medium. From this comparison BIRCH concluded that region B could be homogeneous, whilst region D was probably homogeneous. However, the rate of increase of velocity in region C was too high to be consistent with homogeneity.

BIRCH found that the ratio of initial incompressibility (K) to initial density (σ) at room temperature for the material of region D was equal to about 60 (km/sec)^2. This value is much above that of any known silicate, and is only reached by closely packed oxide structures. Accordingly he suggested that region D consists of closely packed polymorphs of normal ferromagnesian silicates. Region C could be regarded as a region where the transitions from normal to tightly packed silicates took place. Possibly also some chemical changes occurred in this zone.

It appears that BIRCH's results in the main are consistent with the Jeffreys–Bernal hypothesis. However, the wide transitional range found by BIRCH was thought not easily explicable by this hypothesis. Accordingly BIRCH suggested that perhaps other more complex polymorphic transitions besides the olivine–spinel transition and also chemical changes might be involved.

In the previous section it was shown that other polymorphic transitions are probably involved. These are closely related to, and dominated by, the olivine–spinel transition. However, there is no need to assume a change in chemical composition in the transition width. The equilibria are complicated and the width

of the transition zone can only be found by experiment. It seems reasonable to assume that it might be 100–200 km wide at constant temperature corresponding to 350–650°C at constant pressure. It could also be substantially greater.

Such a width would be narrower than the 500–700 km inferred by BIRCH for the mantle. However, when the effect of temperature increase with depth in the mantle is also taken into account, there is no difficulty in meeting the geophysical requirements. The slope of the transition in forsterite was found to be about 100 bars/°C, and the slope of the whole zone will probably approximate to this, since the transition in forsterite is the controlling factor. As the temperature rises with increasing depth in the earth, the transition pressures also become higher, resulting in a further spread of the transition zone. Accordingly the final width of the zone will depend chiefly upon the temperatures assumed to occur in the mantle. In order to spread the transition zone between 300 and 900 km a temperature difference of around 1500°C is require between top and bottom. This does not appear excessive. Temperature distribution in the mantle will be discussed in detail in Section 7.

In view of the above factors the presence of a substantial transition region would be a necessary consequence of an olivine–spinel transition in the mantle. Accordingly it may be concluded that the Jeffreys–Bernal hypothesis is able to explain the seismic data on the mantle, and is consistent with BIRCH's thermodynamic analysis.

5. ELASTICITY OF THE LOWER MANTLE (REGION D)

BIRCH deduced that the ratio of initial compressibility to density for the material of region D was about 60 (km/sec)^2 at room temperature. It is of some interest to compare this ratio with that to be expected for Mg_2SiO_4 spinel.

The compressibility of the spinel is unknown. The approximate value can be found from a study of analogous compounds, however. The compressibility of a substance is largely dependent upon the closeness with which its constituent ions or atoms are packed together. In oxygen compounds the closeness of packing of the large oxygen ions is a particularly important factor. In general, the closer the packing, the smaller the compressibility. This relation holds best for fairly close-packed compounds such as those under consideration. Anomalies may occur with the more open structures.

On these grounds, the inversion from olivine to spinel, involving as it does a considerable volume decrease, would be expected to produce a substantially smaller compressibility in the spinel modification. The initial compressibility of magnetite, which has a spinel structure is 5.5×10^{-7} bar^{-1} (BIRCH et al., 1942). In magnetite the Fe^2 and Fe^3 ions are both larger and more compressible than Mg^2 and Si^4 in Mg_2SiO_4 spinel. The initial compressibility of Mg_2SiO_4 spinel is therefore probably somewhat less than that of magnetite. The most closely packed oxide structure known is that of corundum, and as might be expected, this has the smallest compressibility. The packing in Mg_2SiO_4 spinel would approach that of corundum, but would be somewhat less. This is evident from the respective postulated densities and lattice geometry. It is unlikely that the compressibility of Mg_2SiO_4 spinel will be as low as that of corundum. From these considerations

a value for the initial compressibility of Mg_2SiO_4 between 5·5 and 3·6 seems indicated. The value selected is $4·5 \pm 1 \times 10^{-7}$ bar^{-1}. It is noteworthy that the compressibility of pyrope, the only silicate comparable in density and packing with Mg_2SiO_4 spinel has a compressibility within this range ($5·45 \times 10^{-7}$ bar^{-1})*.

Using this estimate for the compressibility of Mg_2SiO_4 spinel and taking $3·54 \pm 0·10$ g/cm³ for the density (derived from Part I), the ratio K/σ is found to be about 65 ± 15 (km/sec)², in excellent agreement with the value of 60 (km/sec)² found by Birch for the material of region D.

6. Density Variation in the Mantle

From a consideration of the distribution of moment of inertia within the earth, and depth variation of seismic velocities, Bullen (1936, 1947) has been able to calculate the density distribution within the earth. His principal results are:

(1) That the mantle must be inhomogeneous.
(2) That a substantial increase in density is required at a relatively shallow depth.

Bullen suggested that this increase in density was associated with the seismic discontinuity found by Jeffreys in the 400 km region. Using the Jeffreys depth–velocity distribution, and assuming that the density immediately below the Mohorovicic discontinuity was that of magnesian olivine (3·32 g/cm³) Bullen found, by extrapolating the densities of regions B and D that they must differ in density by 0·54 g/cm³. If the 20° discontinuity occurs at a smaller depth than 413 km the density difference between the two regions will be reduced.

In Part I, the density increase associated with the olivine–spinel transition in Mg_2SiO_4 was placed at (0·35 $\pm$ 0·10) g/cm³. This is in reasonable agreement with the geophysical value which is subject to appreciable variance according to the depth at which the transition is assumed to occur, the density assumed beneath the M-discontinuity, and the assumed density of the core. The gap between the two values could be eliminated if the spinel phase became slightly enriched in Fe_2SiO_4. Solid solution and transitions of subsidiary pyroxene and garnet of region B as previously discussed could also cause an increase in density greater than that calculated.

7. Temperature Distribution in the Mantle

In the previous section it was pointed out that the inhomogeneity in region C of the mantle could be explained by the effect of a temperature gradient spreading out the phase transition region. Although the width of the transition zone at constant $P–T$, can only be guessed at, and there is a substantial range of possible error in both the position and slope of the transition curve in forsterite, it turns out that the model implies a rather specific type of temperature distribution. The width of region C depends upon whether the Jeffreys or Gutenberg depth–velocity curves are adopted (Section 4). In the following discussion Jeffreys'

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* Birch, and Yoder (personal communication) have recently separately determined the compressibility of two samples of $MgAl_2O_4$ spinel as 4·6 and $4·1 \times 10^{-7}$ bar^{-1}. The first value refers to a sample containing a large stoichiometric excess of Al_2O_3. The higher compressibility is probably due to the large number of holes which must be present in this crystal.

curves are selected. According to them, region C begins at about 400 km. If the GUTENBERG curves, implying that region C starts at 200 km are more correct, there is little difficulty in modifying the model to accord with them.

In Fig. 2, the location of the transition phenomena in the mantle is indicated. The basic control is the position of the transition in Mg_2SiO_4 which was determined in Part II. A pressure range of 150 km for the transition region at constant
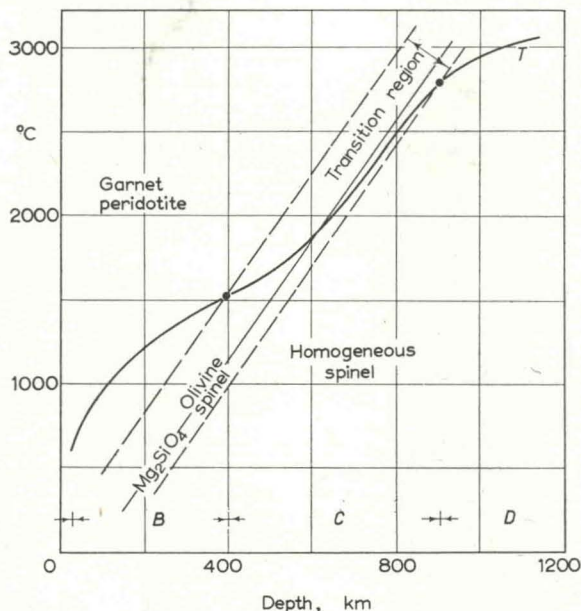

Fig. 2. Structure of mantle showing suggested relationship between temperature gradient (T) and width of transition zone.

temperature corresponding to 500°C at constant pressure, has been assumed. Accordingly the transition region takes the shape of a band with slope 100 bars/°C. Fayalite, which enters preferentially into the spinel solid solution, will spread out the transition to lower pressures. So will other components which are likely to be preferentially soluble in the spinel (CaO, Al_2O_3, Cr_2O_3, Na_2O and excess SiO_2). Accordingly most of the width of the band falls on the low pressure side of the Mg_2SiO_4 transition line. The principal transition which may extend the band to the high pressure side of this line is the breakdown of pyroxene:

$$2(MgFe) SiO_3 \rightarrow (MgFe)_2SiO_4 + SiO_2$$
$$\text{pyroxene} \qquad \text{spinel} \qquad \text{coesite}$$
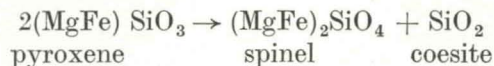
which was studied in Part II.

From Fig. 2, it may be seen that in order to have a transition region between 400 and 900 km, the internal temperature–depth curve should enter the transition zone at 400 km equivalent to 1500°C and leave it at 900 km and 2700°C. Although the above figures may be subject to substantial variance owing to experimental

error, uncertainty of the width of the transition zone, and uncertainty of the width of region C in the earth, there is one important feature which appears to remain the same no matter what reasonable combination of variables is chosen.

It is usually assumed (VERHOOGEN, 1956) that temperatures in the shallow mantle rise rather rapidly and may be in the neighbourhood of 1000°C at depths around 100 km. This necessitates a high initial temperature gradient in this zone. If the earth's temperature–depth curve is to enter the transition region at 400 km the temperature gradient must decrease rapidly (Fig. 2). This implies a relatively low temperature gradient in the region between 200 and 400 km.

When the transition region is entered, however, the temperature gradient must rise considerably in order to stay in the inhomogeneous region until 900 km. The gradient in this region must therefore be about 3°C/km. On moving out of the transition region at 900 km the gradient should lessen in order not to lead to excessively high temperatures in the core.

The previous discussion indicates that a marked increase in the earth's temperature gradient in region C is a probable consequence of the proposed model. It could be escaped by assuming the transition zone at constant pressure or temperature to be very much wider, but this appears improbable. An alternative escape from this conclusion would be to assume a mantle in which chemical composition changes markedly in region C. However, there is no need to make these assumptions. There is independent evidence suggesting that the temperature gradient may indeed increase sharply in region C, and it is possible to find plausible reasons for this behaviour.

LAHIRI and PRICE (1939) have studied the variation with depth of electrical conductivity in the mantle. They found that conductivity in the upper mantle was about 10^{-4} Ω^{-1} cm^{-1}, but in the vicinity of 600 km it rose rapidly to 10^{-2} Ω^{-1} cm^{-1}. The rate of increase of conductivity must flatten out below this depth in order to obtain a reasonable value near the core-mantle boundary. The depth at which the conductivity begins to rise is not known definitely, but may be between 300 and 600 km. More recent studies of conductivity in the mantle by RIKITAKE (1950) and MACDONALD (1957) place the beginning of the region of rapid increase around 400 km.

RUNCORN (1955) has studied the LAHIRI and PRICE distribution and concludes that currently advocated temperature distributions in a mantle composed principally of olivine will not explain the rapid increase of conductivity between 700 and 900 km. He concludes that a phase change to a more densely packed structure in this region could explain the data. The high-pressure phase is assumed to have higher electronic conductivity than the olivine modification. RUNCORN does not examine the other alternative of determining the type of temperature distribution which would cause the observed conductivities, assuming that large changes in the conductivity constants do not occur.

TOZER (manuscript) has recently completed a study of the relation between electrical conductivity and temperature in the mantle and has kindly informed the author of his results. Assuming a mantle dominantly of olivine composition, he finds that the average temperature gradient in the upper mantle is about 1·5°C/km, leading to a *maximum* temperature at 400 km of about 1700°C. In the

model a value of 1500°C is suggested for this depth. These estimates are in reasonable agreement.

TOZER has also examined the effect of phase transitions on electrical conductivity at high temperatures. He agrees with RUNCORN that an olivine–spinel transition will involve an increase in conductivity but is doubtful whether this is large enough to be responsible for the rapid rise of conductivity in region C. Making a reasonable assumption regarding the effect of phase changes on conductivity, TOZER finds that a substantial increase in temperature gradient is required somewhere below 400 km. The increase is compatible with the 3°C/km suggested in this paper for region C.

Additional considerations support this conclusion. TOZER finds from the electrical conductivity of the lower mantle that temperatures higher than 3000°C extend outwards from the core for 2000 km. This conclusion is essentially independent of the nature of the phase changes in region C. In order to reach a temperature of 3000°C at 1000 km from the 400 km region, where an average gradient of 1·5°C/km is reasonably well established, a marked increase of gradient is required. This may exceed 3°C/km.

Thus it may be seen that the evidence from electrical conductivity, which constitutes almost the only specific source of information on temperatures in the upper mantle, supports the temperature distribution in the proposed model. This distribution is required to explain region C in terms of phase changes in a chemically homogeneous mantle of garnet peridotite. Inquiry may next be directed towards the cause of this distribution.

Present ideas on temperature distribution are partially controlled by views about the mechanism of heat transport—whether it be by convection or conduction. It appears that both mechanisms are able to account for the presence of a high gradient in region C. This may be regrettable since it rules out the possibility of deciding which mechanism occurs in the earth.

Estimates of internal temperatures are commonly made by considering the cooling of a hot radioactive earth. These estimates are usually based upon the assumption of a constant thermal conductivity in the mantle. In view of recent work, this appears most unlikely. CLARK (1956, and in press), PRESTON (1956) and RINGWOOD (1956) have independently pointed out that at the high temperature occurring in the mantle, heat transport may occur by direct radiation as well as through lattice vibrations, and may well be of considerable importance. A detailed investigation of this effect has been made by CLARK, who finds that the conductivity due to radiative transfer in the upper mantle may be as much as three times the normal lattice conductivity. Below about 600 km however, radiative conductivity becomes greatly reduced because of absorption owing to the high electrical conductivity in this region. The temperature gradient is largely dependent upon the thermal conductivity and becomes greater as the conductivity decreases. According to these results, the temperature gradient should increase in the region around 600 km. The uncertainty is such as to allow appreciable variance in this depth and is in reasonable agreement with the requirements of the model.

Convection currents are considered by many to be the prime means of heat transport in the mantle. For a convection current to occur the thermal gradient

must exceed the adiabatic gradient in the mantle given by:

$$\frac{dT}{dr} = \frac{\alpha g T}{C_p}$$

where α is the coefficient of thermal expansion and C_p is the specific heat at constant pressure. In the upper mantle (region B) VERHOOGEN (1956) has estimated this gradient to approximate 0·3°C/km. For a convection current to penetrate the transition zone it is apparent however that the gradient must be much higher since a considerable increase in density occurs. At the same time, latent heat estimated in Part II as 100 cal/g is evolved. Since there is a range of transition it is sufficient for a first approximation to consider the term $\Delta v/t$ equivalent to thermal expansion in the transition range, where Δv is the total volume change in the transition (estimated as 11 per cent in Part I) and t is the temperature interval across which the transition is considered to extend at constant pressure. In Fig. 2, this has been taken as 500°C. Similarly the specific heat might be regarded as $(\Delta H/t) + C_p$ where ΔH is the latent heat of transition (estimated as 100 cal/g) and C_p is the normal specific heat. Substituting these values the adiabatic gradient in the transition region is found to be about 2°C/km, thus exceeding the normal adiabatic gradient by a factor of 6. Accordingly for a convection current to penetrate the transition region, the temperature gradient must increase as much as sixfold through the region. When (and if) a current has passed out of the transition zone the adiabatic gradient decreases to 0·3–0·2°C/km (VERHOOGEN, 1956).

The preceding discussion shows that both in a non-convecting mantle in conductive equilibrium and in a convecting mantle, the temperature gradient may increase considerably in region C. Evidence for this increase is provided by studies of the electrical conductivity of the mantle. This is in agreement with the requirements of the proposed model.

8. SUMMARY AND CONCLUSION

This study was stimulated by the Jeffreys–Bernal hypothesis which suggested that the 20°C discontinuity was caused by an olivine–spinel inversion in the mantle. In Parts I and II, the P–T conditions governing this inversion in forsterite and fayalite were investigated. It was found that natural olivine should invert to a spinel in the upper mantle, in a region where phase changes and inhomogeneity have been inferred to other grounds (region C). A thermochemical study of pyroxene, indicated that it should break down to spinel and coesite under these conditions.

A model of the mantle was suggested on geochemical and petrological grounds in which the region immediately below the M-discontinuity consisted of dunite–peridotite. This graded downwards into material of uniform and primitive chemical composition approximating a garnet–peridotite. On this model it was found that the phase transition phenomena dominated by the olivine–spinel transition should be spread out over an appreciable depth range. The precise location and width of this range was determined by temperature distribution in the mantle. By choosing a specific temperature distribution the experimental

transition range can be made to coincide with the boundaries of region C. Recent studies on electrical conductivity and temperatures in the mantle support the temperature distribution adopted.

The known properties and data on the mantle have been examined in order to find out whether they were consistent with an olivine–spinel transition in region C. The following conclusions were drawn:

(1) The olivine–spinel transition and related transition phenomena are able to explain the relevant seismic data, particularly the fact that seismic data seem to suggest a transition range.

(2) The elastic properties of the mantle below 900 km deduced by BIRCH do not agree with those of any known silicate but are in good agreement with the probable elastic properties of the spinel modification of Mg_2SiO_4.

(3) The rapid increase of density with depth below the 20° discontinuity deduced by BULLEN is in reasonable agreement with that which would be expected on the basis of an olivine–spinel transition.

(4) The temperature distribution implied by the transition phenomena is in agreement with that inferred from a study of electrical conductivity in the mantle. Both the conduction and convection mechanisms of heat transport in the mantle can account for this distribution.

It is believed that this combined evidence furnishes strong support for the Jeffreys–Bernal hypothesis and that justification exists for proposing a more specific model of the mantle than is usually attempted.

Using BULLEN's depth classification, the following model is suggested:

Region A. Crust; surface—M-discontinuity.

Region B. M-discontinuity—400 km (JEFFREYS) or 200 km (GUTENBERG). Dunite–peridotite grading downwards into garnet peridotite. Both layers contain irregularly distributed segregations of eclogite. Temperature at 400 km about 1500°C.

Region C. From 400 km (or 200 km) to 900 km. Transition zone in garnet–peridotite dominated by inversion of olivine to spinel. Pyroxene breaks down to spinel plus coesite. Coesite dissolves in spinel to form defect solid solution. Garnet dissolves in spinel. Temperature gradient increases as zone is entered and may be around 3°C/km. Temperature at 900 km approximating 3000°C.

Region D. 900 km to 2900 km. Homogeneous spinel phase consisting of a highly disordered solid solution, chemically equivalent to garnet–peridotite.

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