

Limits on the Constitution of the Lower Mantle*

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Summary

The limits on the constitution of the lower mantle which can be inferred from currently available data are investigated. The density and elasticity of the mantle are compared to those of various model mineral assemblages at zero pressure and at high pressures, the former case using extrapolations of mantle properties. The models are based on equations of state of MgO (periclase), SiO₂ (stishovite) and FeO (wüstite), and of the Twin Sisters and Mooihoek dunite high-pressure phases. The bounds on the elastic properties of mixtures are discussed. The properties of hypothetical phases denser than their isochemical simple oxide mixtures are estimated relative to those of the oxide mixtures. The uncertainties in all quantities are discussed and the interdependence of some inferred mantle characteristics is considered. The inferred silica content, temperature and phase assemblage are strongly interdependent. The inferred FeO content depends to a small extent on the phase assemblage and temperature corrections and more strongly on the presence of iron in the 'low spin' electronic state. Models which best fit the data used range between (1) an oxide mixture, or phase assemblage with similar properties, with pyroxene composition and 9 mole per cent FeO, and (2) a phase assemblage about 5 per cent denser than an isochemical simple oxide mixture with olivine composition and 6 mole per cent FeO. Combining all uncertainties and interdependences allows the FeO content to vary between about 3 and 14 mole per cent, and the temperature to vary beyond the independently estimated bounds of 2000°K and 6000°K. The possibilities of an isentropic temperature gradient, chemical homogeneity, or some iron enrichment in the lower mantle relative to the upper mantle are allowed, but not required, by the data.

Introduction

Considerable recent discussion has centred around the question of whether the Earth's mantle is chemically homogeneous or whether the lower mantle differs from the upper mantle. In particular, discussion has focused on the possibility that the lower mantle is enriched in iron relative to the upper mantle (e.g. Anderson 1967,

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1970; Wang 1968, 1970; Ringwood 1969, 1970; Anderson & Jordan 1970; Al'tshuler & Sharipdzhanov 1972b; Press 1972; Liu 1973). These and other studies have also attempted to determine such other factors as the (Mg+Fe)/Si ratio (Anderson & Jordan 1970), the temperature (Wang 1972) and the possible existence of phases denser than mixtures of dense simple oxides (Ringwood 1969, 1970; Al'tshuler & Sharipdzhanov 1972b). Unfortunately, the problem of determining the constitution of the mantle from the observed profiles of the elastic velocities and density is an under-determined one, so that various assumptions about some aspects of the mantle's constitution had to be employed in the above studies in order to determine other factors. In addition, the various material properties and empirical relations employed have often been rather uncertain, although these uncertainties have seldom been adequately discussed.

Since the question of the chemical homogeneity of the mantle is of obvious significance to theories of the origin and evolution of the Earth, as well as to current suggestions of deep mantle overturn (e.g. Morgan 1971; Richter & Johnson 1974) it would be useful to know what limits can be placed on the constitution of the lower mantle in the light of currently available data. The present paper investigates the limits on the chemical composition, temperature and phase assemblage which may be established while taking into account the under-determined nature of the problem and the uncertainties in the data. The under-determinacy manifests itself as a trade-off between some of the factors—rather than make specific initial assumptions about some of these factors, the trade-off is explicitly estimated.

The lower mantle is defined as the region of the Earth lying above the core and below the 'transition zone' of the mantle. The transition zone lies between about 400 and 1000 km depth, and is the region where the compressional elastic velocity, V_p , the shear elastic velocity, V_s , and the density, ρ , all increase with depth at an unusually high rate. Birch (1952), after examining the densities and elasticities of a variety of rocks, minerals and oxides, and considering the effects of pressure and temperature on these properties, concluded that the transition zone must involve pressure-induced polymorphic phase transitions, possibly coupled with changes of chemical composition. He also concluded that the lower mantle properties could be consistent with uniform composition and crystal structure and with a smoothly varying temperature of the order of a few thousand degrees centigrade. Finally, he concluded that the lower mantle properties could be approximated with a mixture of the dense oxides MgO (periclase), FeO (wüstite) and SiO₂ in the rutile structure (at that time, the latter was only hypothesized by J. B. Thompson, but it has subsequently been identified and named stishovite; Stishov & Popova 1961). Later, Birch (1961, 1964) deduced that a dense oxides mixture with a mean atomic weight of about 21 or 22, corresponding to about 10 per cent by weight of FeO, would be appropriate for the lower mantle.

Models of the distribution of elastic velocities in the lower mantle have changed very little in the past 20 years, and for the present context, the differences between recent models are insignificant—except in one respect: there is some evidence for a series of small discontinuities in the lower mantle (e.g. Johnson 1969), suggesting that the lower mantle is not uniform in crystal structure. Models of the lower mantle density, on the other hand, have evolved from those dependent on some kind of physical assumption (e.g. Bullen 1963; Birch 1964) to those determined entirely from the periods of free oscillation of the Earth (Dziewonski & Gilbert 1972; Jordan 1972; Jordan & Anderson 1974). The latter, of course, are the most useful for the present purpose.

A considerable number of data on the properties of materials relevant to the lower mantle has been accumulated since Birch's earlier work. A large body of shock-wave data, notably from McQueen, Marsh & Fritz (1967), has confirmed that many rock-forming silicates undergo phase changes involving large increases in density at pressures

up to several hundred kilobars, and has provided some information on the properties of the high-pressure phases (e.g. Ahrens, Anderson & Ringwood 1969; Davies & Gaffney 1973). Static compression measurements of density have been extended to a few hundred kilobars using diamond anvils and X-ray diffraction (e.g. Liu, Bassett & Takahashi 1974). The pressure and temperature dependence of the elastic properties of many materials have been determined up to the order of 10 kilobars and 1000 °C by many workers using ultrasonic methods.

Before the comparison between relevant material properties and lower mantle properties is discussed, the procedure for analysing the experimental data on material properties and casting them into a suitable form is discussed in some detail, so that the uncertainties involved in each step can be demonstrated. The various steps in this procedure are outlined below.

After a brief discussion of the theory used to interpret the data, the current status of the equations of state of the oxides MgO (periclase), FeO (wüstite) and SiO₂ (stishovite) will be discussed. Although it will be seen that there are significant uncertainties in these equations of state, particular solutions will be selected for later comparisons with other data. It can thus be decided in retrospect which were the most crucial uncertainties. The equations of state of the high-pressure phases of the Twin Sisters and Mooihoek dunities will also be discussed, and compared those of isochemical simple oxide mixtures. For this and later comparisons, the estimation of mixture properties in terms of the properties of components will be discussed. To start with, the lower mantle properties will be compared to those of mixtures of the simple oxides. The effects of varying the composition of the mixture, of temperature and of the uncertainties in the mantle properties can then be demonstrated. The utility and effect of using mixtures of the dunite high-pressure phases can also be discussed. The properties of possible phases several per cent denser than oxide mixtures are estimated here *relative* to the properties of the latter. The conclusions drawn are thus likewise relative.

The comparison of material properties with those of the lower mantle will be discussed after the various above considerations have been described. In these comparisons, the elasticity is represented by the seismic parameter, ϕ . This is derived from earth models through the relation $\phi = V_p^2 - 4V_s^2/3$, and from equations of state through the relation $\phi = (\partial P/\partial \rho)_S$, where subscript S denotes constant entropy. The comparisons can be conveniently made using ϕ -density plots at various pressures.

Theory of equations of state

The equation of state of a material, i.e. the stress-strain-temperature relation of the material, provides the conceptual framework within which the various kinds of experimental data can be incorporated and from which quantities for comparison with mantle properties can be calculated. The effects of pressure, which are dominant in the lower mantle, can be most conveniently described using the so-called 'finite strain' theory, which gives a macroscopic description using Taylor expansions in terms of strain measures. The expansion can be taken to any order demanded by the data. The 'Eulerian' strain parameter, used by Murnaghan (1937) and Birch (1938, 1952), was shown by Birch (1947, 1952) to be empirically useful in the sense that the available data demanded only two or three terms in the expansion of the strain energy. By contrast, the 'Lagrangian' strain parameter (Murnaghan 1937; Birch 1938, 1952; Thomsen 1970) seems to require at least one additional expansion term for comparable accuracy (Birch 1947; Davies 1973). The 'fourth-order' Eulerian pressure-density relation, which generalizes the well-known 'Birch-Murnaghan' equation, is (Davies 1973)

$$P = -\frac{1}{3}\rho_0(1-2E)^{5/2}(c_0 + c_1 E + c_2 E^2 + c_3 E^3), \quad (1)$$

where E , the Eulerian strain parameter for isotropic strains, is

$$E = \frac{1}{2}[1 - (\rho/\rho_0)^{2/3}] \quad (2)$$

and ρ_0 is a reference density. The parameters, c_n , in (1) may be related to the pressure, bulk modulus, $K = \rho(\partial P/\partial \rho)$, and its pressure derivatives, $K' = \partial K/\partial P$, etc., evaluated at the reference density:

$$c_0 = -3V_0 P_0, \quad (3a)$$

$$c_1 = -3V_0(-3K_0 + 5P_0) \quad (3b)$$

$$c_2 = -3V_0(\frac{3}{2}K_0 K'_0 - 18K_0 + \frac{3.5}{2}P_0), \quad (3c)$$

$$c_3 = -3V_0[-\frac{3}{2}K_0^2 K_0'' - \frac{3}{2}K_0 K'_0(K'_0 - 7) - \frac{1.43}{2}K_0 + \frac{1.05}{2}P_0], \quad (3d)$$

where $V_0 = 1/\rho_0$. The derivatives in (3b)–(3d) may be taken isothermally or isentropically, according to whether (1) is to describe an isotherm or an isentrope.

Thermal effects are of secondary importance in the lower mantle, and can be described to sufficient accuracy by the 'quasi-harmonic' approximation of lattice dynamics. This approximation has been incorporated into finite strain theory (Thomsen 1970; Davies 1973), and results in the temperature dependence of the c_n being prescribed in terms of the Grüneisen parameter, γ , and its volume derivative (Davies 1973). These, in turn, can be related, through thermodynamic identities, to the volume coefficient of thermal expansion, the specific heat and the temperature derivative of the bulk modulus. Other identities, involving the foregoing quantities, relate the isothermal and isentropic derivatives in (3). The details of these relations, and of their application, are given elsewhere (Davies 1973).

The above equation of state formulation, or its generalization to general stresses and strains (Davies 1974), implicitly describes all thermoelastic properties, and therefore allows static compression, shock compression, ultrasonic and thermal expansion data to be incorporated into a coherent framework. An expression for Hugoniot (the locus of shock states) has been given elsewhere (Davies 1973), but it is convenient here to use a slight variant, in which the Hugoniot pressure, P_H is related to the pressure on an isentrope, P_S , rather than on an isotherm, P_T :

$$P_H = [P_S - \gamma\rho(\Delta U + E_t)]/[1 - \frac{1}{2}\gamma(\rho/\rho'_0 - 1)]. \quad (4)$$

Here, ρ'_0 is the initial density of the shocked medium, E_t is the transformation energy of any phase change occurring during the compression, U is the internal energy and

$$\Delta U = - \int_{V_0}^V P_S dV$$

is the change in U along the isentrope. In the evaluation of ΔU , V_0 is the specific volume at zero pressure of the phase achieved upon shock-compression. The volume dependence of P_S is given by (1), and a formula for the volume dependence of γ , in terms of the 'thermal' parameters, has been given previously (Davies 1973).

In the procedure outlined earlier, a family of isotherms can be calculated by evaluating the parameters c_n at a series of temperatures and inserting these values into (1). In practice, because of the limited accuracy of the extrapolations, this can result in isotherms which cross at high pressures. It would still be useful to know the relative properties on different isotherms, even though the absolute errors may be comparable to the effects considered. Therefore, an alternative method of calculating isotherms relative to each other at high pressure is given here. In the quasi-harmonic theory, thermal effects on the pressure are described by the Mie-Grüneisen equation:

$$P = P_l + \gamma\rho U_q, \quad (5)$$

where P_1 is the pressure exerted by the static lattice of atoms, and U_q is the quasi-harmonic vibrational contribution to the internal energy, U . In the Grüneisen approximation, γ is independent of temperature. Then,

$$P(T) = P(T_0) + \gamma \rho \Delta U_q, \quad (6)$$

where $\Delta U_q = U_q(T) - U_q(T_0)$, and T_0 is a reference temperature. Differentiating (5),

$$\phi(T) = \phi(T_0) + \gamma \left(1 + \gamma - \frac{d \ln \gamma}{d \ln V} \right) \Delta U_q, \quad (7)$$

where we have used the result (Leibfried & Ludwig 1961) that $(\partial U_q / \partial \rho)_S = \gamma U_q / \rho$. At the high temperatures of interest here, U_q is quite adequately approximated by the Debye model, the volume dependence of the Debye temperature being given by a formula closely related to that for γ (Davies 1972, 1973).

Equations of state of oxides

By combining the ultrasonically determined parameters given by Spetzler (1970) with the shock-wave data of Carter *et al.* (1971), the equation of state of MgO at high pressures and temperatures has been determined in terms of the theoretical framework given above (Davies 1973). The ultrasonic data are sufficient to determine all parameters except $\zeta = K_0 K_0''$, which was determined from the Hugoniot data.

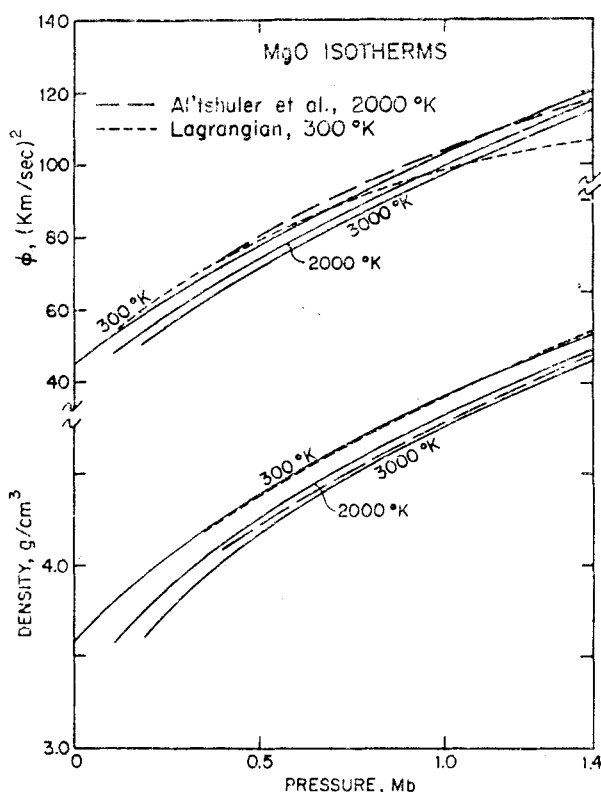


FIG. 1. Isothermal density and ϕ vs pressure for MgO calculated from data of Spetzler (1970) and Carter *et al.* (1971). Results using Lagrangian strain equations and from Al'tshuler & Sharipdzhanov (1972b) are also shown.

The density and ϕ as a function of pressure calculated from these parameters for 300 °K, 2000 °K and 3000 °K are shown in Fig. 1. An indication of the accuracy of these curves can be obtained from a comparison with the 300 °K curves (short-dashed, Fig. 1) calculated using the equation analogous to (1) in terms of the 'Lagrangian' strain parameter, η (Davies 1973). Inaccuracies of less than 1 per cent in density and 5 per cent in ϕ are indicated. Al'tshuler & Sharipdzhanov (1972a) have also given a determination of the MgO equation of state. Their tabulated values of ρ and the bulk sound speed, $C = \phi^{\frac{1}{2}}$, along a geotherm, combined with their estimates of temperature effects, have been used to estimate the 2000 °K values of ρ and ϕ which are shown (long-dashed) in Fig. 1. These curves deviate from the others by more than the estimated errors, but they are based on different ultrasonic parameters and different functional forms.

In a detailed analysis of static compression, shock-wave and thermal expansion data for stishovite (Davies 1972), three different fits to the data were obtained from different interpretations of the data. The first (Case 1) was constrained to fit Weaver's (1971) value for the volume coefficient of thermal expansion ($18 \times 10^{-6} \text{ } ^\circ\text{K}^{-1}$) and resulted in an equation of state resembling those of Ahrens, Takahashi & Davies (1970) and Graham (1973). In Case 2, a better fit to the Hugoniot data up to about 1.5 Mb and 15000 °K was obtained with a lower value of the thermal expansion coefficient ($13 \times 10^{-6} \text{ } ^\circ\text{K}^{-1}$), and in Case 3, all of the Hugoniot data (to much higher temperatures and pressures) were reasonably fit with a value of $12 \times 10^{-6} \text{ } ^\circ\text{K}^{-1}$. It was suggested that Case 2 might be the most appropriate for geophysical application, since below the Debye temperature (about 1000 °K) γ might be temperature dependent

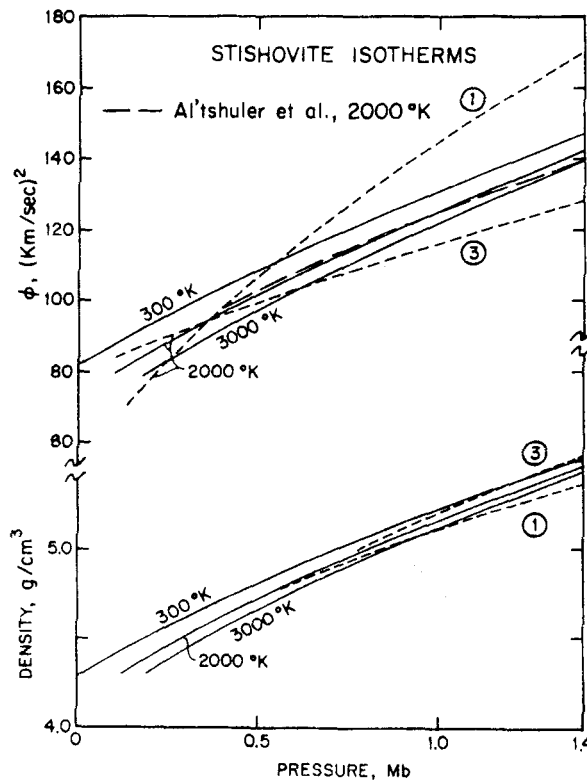


FIG. 2. Isothermal density and ϕ for stishovite from Davies (1972), Case 2. Results at 2000 °K for Cases 1 and 3 (Davies 1972) and from Al'tshuler & Sharipdzhanov (1972b) are also shown.

because all of the modes of vibration of the stishovite lattice might not be excited, while at extremely high temperatures a different value of γ might be appropriate because a different phase might be involved. Since then, Weaver, Takahashi & Bassett (1973) have shown that somewhat lower room temperature values of the coefficient of thermal expansion would be compatible with his data, while Trunin *et al.* (1970) have suggested that all of the Hugoniot data above about 2 Mb might involve a liquid phase. The first development casts further doubt on the Case 1 solution, while the second suggests that only a rather limited selection of the Hugoniot data is appropriate to the stishovite equation of state, thus rendering it even more uncertain.

In Fig. 2, the 300 °K, 2000 °K and 3000 °K isotherms from Case 2 are illustrated (solid curves), along with the 2000 °K isotherms from Cases 1 and 3 (short-dashed) and estimated from Al'tshuler & Sharipdzhanov (1972a) (long-dashed). The density from Al'tshuler & Sharipdzhanov is almost coincident with that from Case 2, and is not shown. If the spreads between the curves of Cases 1 and 3 are taken as indications of the uncertainties, then at 1 Mb the density is uncertain by about 1 per cent, while ϕ may have up to 15 per cent uncertainty. For the subsequent discussion in this paper, the Case 2 equation of state will be used, although it will emerge that the uncertainties in the stishovite equation of state are probably larger than any others to be considered.

The measurement of the equation of state of wüstite is complicated by its non-

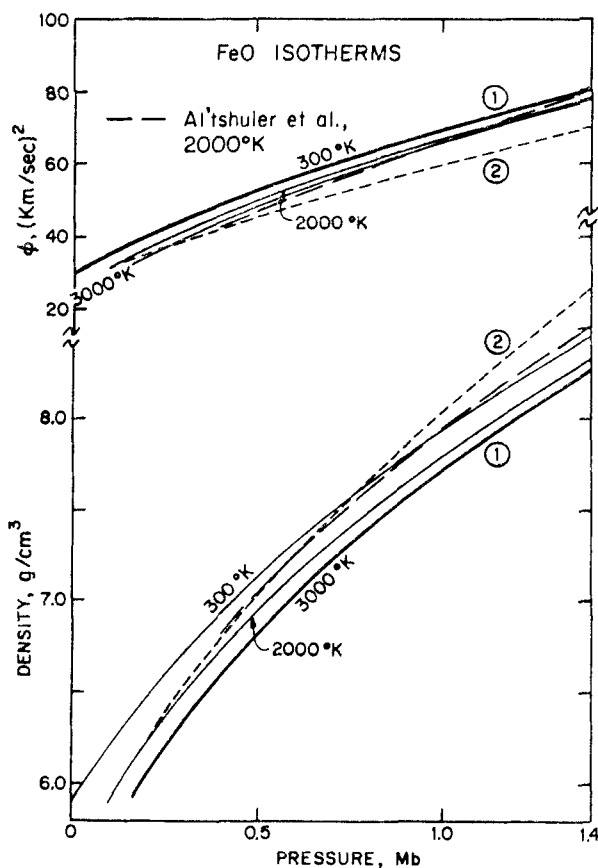


FIG. 3. Estimated isothermal density and ϕ for FeO (wüstite) using parameters of Case 1 (Table 1(a)). Heavy lines have no significance. Curves for 2000 °K for Case 2 and from Al'tshuler & Sharipdzhanov (1972b) are also shown.

stoichiometric character. Recent ultrasonic measurements by Mizutani *et al.* (1972a) on $\text{Fe}_{.98}\text{O}$ (density 5.84 g cm^{-3}) gave a bulk modulus of 1.74 Mb . This is somewhat higher than the value of about 1.5 Mb inferred from the static compression data of Clendenen & Drickamer (1966) for $\text{Fe}_{.95}\text{O}$. The former value will be used here for FeO , with an estimated density of 5.91 g cm^{-3} . The value of dK/dP can be estimated from tentatively established systematic behaviour of dK/dP with density and mean atomic weight (Anderson *et al.* 1968; Davies & Gaffney 1973) to be about 4.5. The values of γ and its logarithmic volume derivative have simply been assumed to be 1.5 here. Isotherms calculated using these parameters are shown in Fig. 3. Also shown are 2000°K curves calculated using $dK/dP = 3.5$ and those estimated from the tabulations of Al'tshuler & Sharipdzhanov (1972a). There is a large spread in the densities at high pressure, but reasonable agreement between the values of ϕ which is probably fortuitous. Since no more than about 15 mole per cent of FeO is likely to be present in the lower mantle, these fairly large uncertainties in the equation of state of wüstite are less important than the uncertainties in the equations of state of the major components.

The parameters of the equations of state of periclase, stishovite and wüstite discussed in this section are summarized in Table 1. Since only the third-order version of (1) is used for wüstite (and for the dunite high-pressure phases discussed below), the values of $\zeta = K_0 K''_0$ are not explicitly given in Table 1.

Table 1

(a) Parameters of component equations of state

| Oxides | | ρ_0 (g cm^{-3}) | K_0 (Mb) | K'_0 | ζ $= K_0 K''_0$ | γ_0 | $\frac{d \ln \gamma}{d \ln V}$ |
|------------------|-----|------------------------------------|---------------|--------|--------------------------|------------|--------------------------------|
| MgO | | 3.584 | 1.605 | 3.89 | -1.5 | 1.52 | 1.55 |
| SiO ₂ | (1) | 4.287 | 3.415 | 4.86 | -2.24 | 1.61 | 5.7 |
| | (2) | 4.287 | 3.499 | 3.53 | -1.94 | 1.30 | 3.1 |
| | (3) | 4.287 | 3.547 | 2.83 | -1.68 | 1.22 | 1.9 |
| FeO | (1) | 5.91 | 1.74 | 4.5 | — | 1.5 | 1.5 |
| | (2) | 5.91 | 1.74 | 3.5 | — | 1.5 | 1.5 |
| Dunites | | | | | | | |
| Twin Sisters | (a) | 4.03 | 2.353 | 3.58 | — | 1.5 | 1.5 |
| | (b) | 4.08† | 2.473 | 3.57 | — | 1.5 | 1.5 |
| | (c) | 4.03 | 2.601† | 2.95† | — | 1.5 | 1.5 |
| | (d) | 4.03 | 2.452 | 3.59 | — | 1.0† | 1.5 |
| | (e) | 4.03 | 2.044 | 4.46† | — | 1.5 | 1.5 |
| Mooihoek | (a) | 4.82 | 2.635 | 3.58 | — | 1.5 | 1.5 |
| | (b) | 4.64† | 2.184 | 3.57 | — | 1.5 | 1.5 |
| | (c) | 4.64† | 2.496† | 2.605† | — | 1.5 | 1.5 |
| | (d) | 4.82 | 2.837 | 3.59 | — | 1.0† | 1.5 |
| | (e) | 4.82 | 2.386 | 4.47† | — | 1.5 | 1.5 |

† Varied from case (a).

(b) Additional equation of state parameters

| Oxides | \bar{M} | θ_D (°K) | ρ'_0 (g cm^{-3}) | E_r (10^9 erg g^{-1}) |
|------------------|-----------|--------------------|-------------------------------------|--|
| MgO | 20.16 | 770 | 3.584 | 0 |
| SiO ₂ | 20.03 | 1000 | 2.65 | 7 |
| FeO | 35.7 | 800 | 5.91 | 0 |
| Dunites | | | | |
| Twin Sisters | 21.0 | 800 | 3.32 | 7 |
| Mooihoek | 25.1 | 800 | 3.78 | 3 |

Equations of state of dunites

The Hugoniot data of McQueen *et al.* (1967) for high pressure phases of Twin Sisters and Mooihoek dunites are some of the most relevant data to the lower mantle. A number of interpretations of these data (McQueen *et al.* 1967; Wang 1968; Anderson & Kanamori 1968; Ahrens *et al.* 1969; Davies & Anderson 1971) have concluded that these phases resemble isochemical mixtures of periclase, stishovite and wüstite. Using a fresh approach to the interpretation, based on estimates of the Hugoniots of hypothetical phases, Davies & Gaffney (1973) re-affirmed this interpretation of the Twin Sisters dunite data, but concluded that it was less likely for the Mooihoek dunite. The preferred interpretation was of a phase in the calcium ferrite structure with most of the Fe^{++} ions in octahedral sites and having the 'low-spin' electronic configuration. This phase is estimated to be 1 or 2 per cent denser than the isochemical mixture of oxides.

Based on these interpretations, uncertainties in the equations of state of these phases are investigated here. The predicted values of the equation of state parameters (Davies & Gaffney 1973) are retained here, except for the bulk modulus, which has been adjusted slightly to give a least-squares fit to the Hugoniot data. The effects of varying the initial density, dK/dP and γ_0 will be shown.

Fig. 4 shows the Hugoniot data of the dunites compared with three fitted Hugoniot curves: (a) the basic interpretation discussed above, (b) using a different initial density, and (c) allowing both K and dK/dP to be determined by the Hugoniot data. The initial densities of each case are indicated by the arrows in Fig. 4. These examples illustrate how poorly constrained most of the parameters are. The parameters for these cases are given in Table 1. In Figs 5 and 6, the 2000 °K isotherms are shown for these cases and for two others: (d) with a different value of γ_0 , and (e) with a different value of dK/dP . These parameters are also given in Table 1. From Fig. 5, it can be seen that the density of the Twin Sisters dunite is constrained to within about 1 per

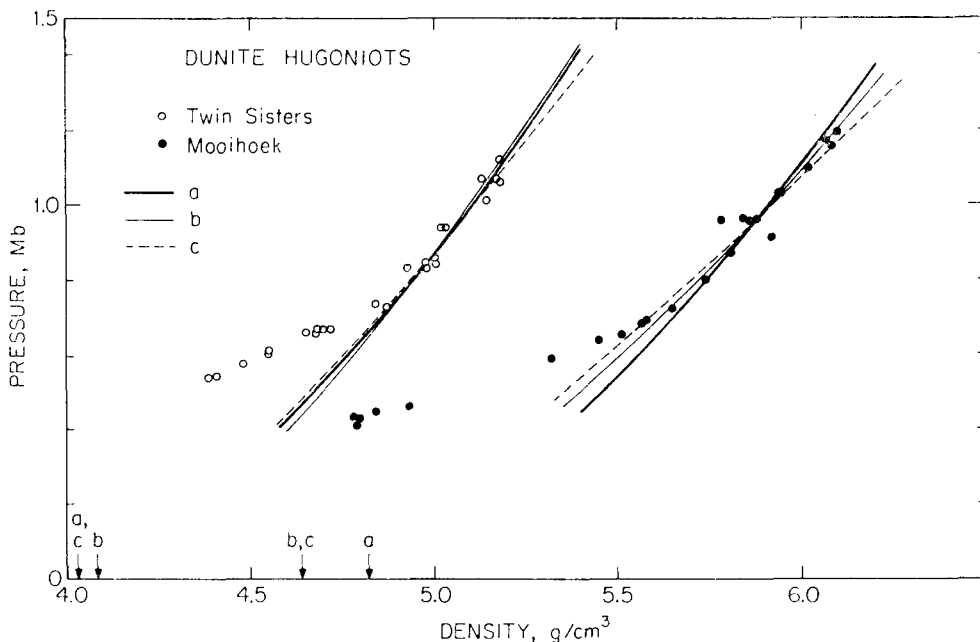


FIG. 4. Hugoniot data for dunites (McQueen *et al.* 1967) and various fitted Hugoniots (Table 1(a)). Cases (a) were used for later discussion. Arrows indicate initial density assumed for different cases.

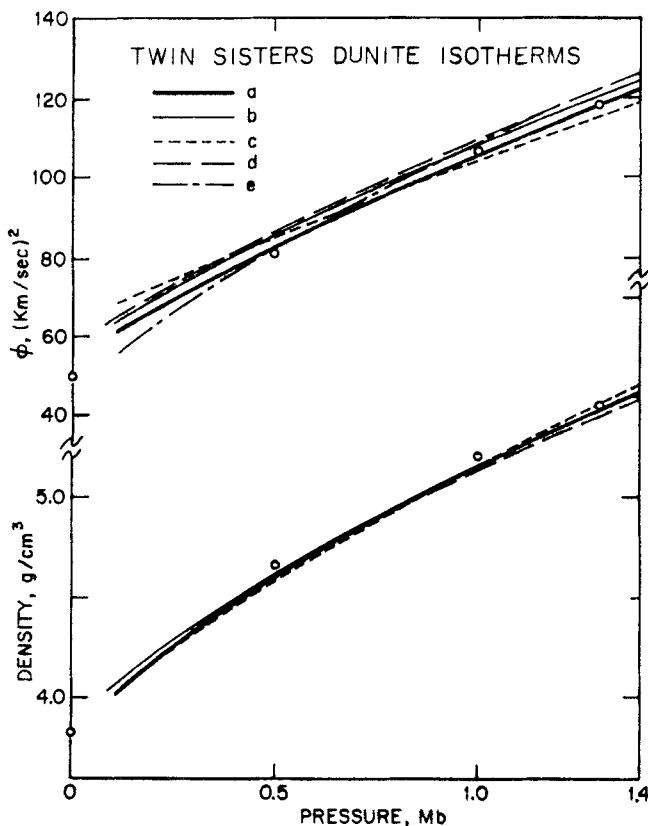


FIG. 5. Isothermal density and ϕ of Twin Sisters dunite from various cases (Table 1(a)). Open circles are estimates of isochemical oxide mixture properties at various pressures.

cent and the ϕ to within about 5 per cent. For the Mooihoek dunite, Fig. 6, the constraints are not so good, but if the estimated density of the calcium ferrite phase (4.82 g cm^{-3}) is assumed to be appropriate, the remaining uncertainties are about 1 per cent or less in density and less than 10 per cent in ϕ .

A stronger test of the interpretation of these data than just the values of ρ_0 and K_0 can be made here by comparing the calculated 2000 °K properties with those of isochemical oxide mixtures (estimated according to the method given in the next section) at high pressures. In Figs 5 and 6, the estimated mixture properties at several pressures are indicated by the open circles. The values of ϕ are in reasonable agreement. The density of the Twin Sisters dunite is slightly less than the oxide density at higher pressures, while that of the Mooihoek dunite is slightly greater. Thus the interpretations assumed here are less decisively supported by the high pressure test, but the discrepancies are within the previously estimated uncertainties of the quantities involved. Also, the conclusion remains that the Mooihoek dunite is in a denser phase, relative to the isochemical oxide mixtures, than the Twin Sisters dunite.

Equations of state of mixtures

The properties of a mixture are not uniquely determined by the properties of the components, but depend also on the geometrical character of the mixture. Since the

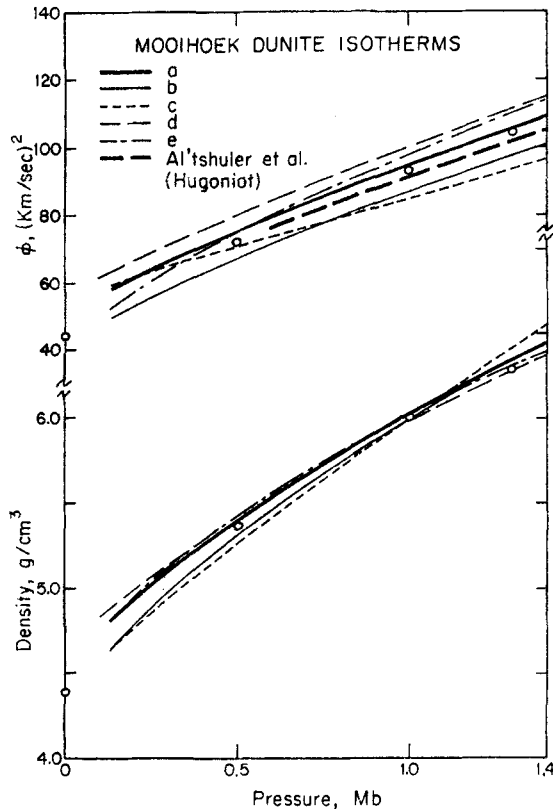


FIG. 6. Isothermal density and ϕ of Mooihoek dunite from various cases (Table 1(a)). Open circles are estimates of isochemical oxide mixture properties at various pressures.

geometrical characteristics of many mixtures are poorly known or unknown, the problem of specifying the properties of a mixture has been approached by trying to establish bounds on the properties in terms of the component properties. Some unique solutions have also been obtained for special geometries and other special cases. In the present context, the density and elasticity of mixtures are to be compared to the results of shock-wave data and to the observed density and elasticity of the lower mantle. For the shock-wave data, nothing is known about the geometry of any mixture that might be involved, and any assumptions about it would be rash. For the lower mantle, the assumption of 'random' geometry might traditionally have been regarded as very reasonable, but recent observations suggesting significant lateral variations in lower mantle properties (Kanasewich *et al.* 1973; Julian & Sengupta 1973, for example) and suggestions that the lower mantle might be undergoing large-scale motions (Morgan 1971) in turn suggest that the lower mantle might be far from a random mixture.

It was shown by Hill (1952) that the averages of elastic moduli proposed by Reuss (1929), who assumed uniform stress, and by Voigt (1928), who assumed uniform strain, were in fact lower and upper bounds, respectively, on the elastic moduli of a mixture of perfectly elastic components. Hill proposed that the arithmetic or geometric means of these bounds might be useful, and the former has become known as

the Voigt–Reuss–Hill (VRH) average. The Voigt and Reuss averages are, respectively,

$$c_V = \sum v_i c_i, \quad (8)$$

$$1/c_R = \sum v_i/c_i \quad (9)$$

where c_i is the elastic modulus and v_i the volume fraction of the i th component.

More recently, Hashin & Shtrikman (1963) have shown that these are not the best-possible bounds. They have derived more restrictive bounds, and shown these to be the best possible (assuming the geometry to be completely unknown) by solving a particular geometry for which the mixture properties can coincide with either bound. Their bounds on the bulk modulus and shear modulus, G , of a two-phase mixture of isotropic components, with moduli K_i and G_i , have the form

$$K_1^* = K_1 + v_2/[1/(K_2 - K_1) + v_1/(K_1 + 4G_1/3)], \quad (10)$$

$$G_1^* = G_1 + v_2/[1/G_2 - G_1] + 2v_1(K_1 + 2G_1)/5G_1(K_1 + 4G_1/3), \quad (11)$$

with the other bounds obtained by permuting subscripts 1 and 2 everywhere.

These averages are illustrated in Fig. 7, which is a ϕ – ρ plot at zero pressure, for the system MgO–FeO–SiO₂. The Voigt, Reuss and VRH averages have been calculated for the bulk compositions MgSiO₃, Mg₂SiO₄, FeSiO₃, Fe₂SiO₄, MgFeSi₂O₆ and MgFeSiO₄, and are indicated by the large error bars and their midpoints. Ranges

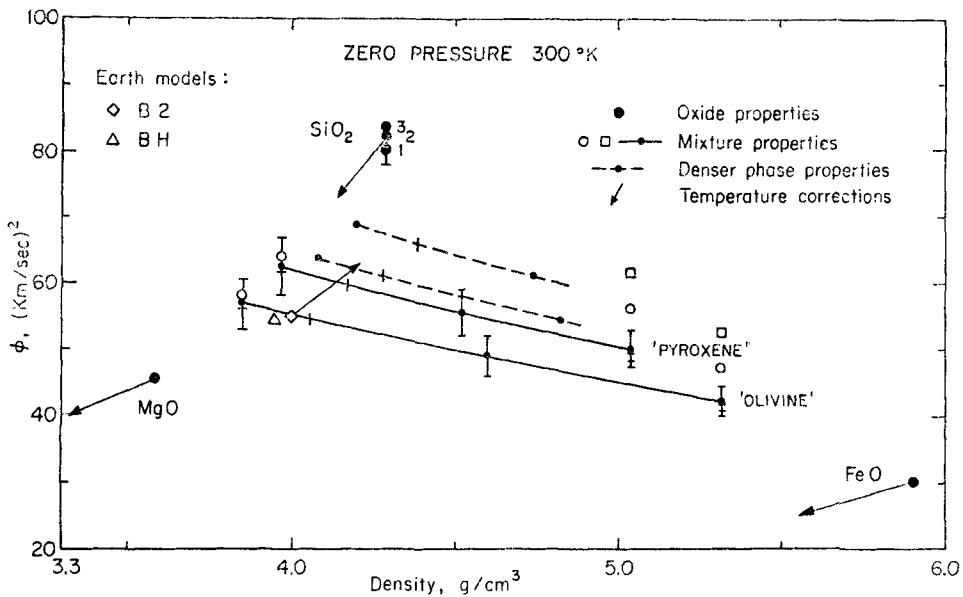


FIG. 7. Zero pressure, 300 °K ϕ -density plot for oxides, mixtures and earth models. SiO₂ (stishovite) points are for Cases 1–3 (Table 1(a)); FeO (wüstite) points for Case 1 (Table 1(a)). Solid curves join VRH average properties of oxide mixtures of olivine and pyroxene compositions with varying iron content. Error bars extend between Voigt (upper) and Reuss (lower) bounds. Inner error bars are HS bounds. Open circles are 'molar average ϕ 's' (Anderson 1969) and open squares are averages of Davies & Gaffney (1973). Dashed curves are estimates for denser phases of corresponding compositions. Vertical ticks indicate FeO contents of 10 mole per cent. Earth models plotted are model II (Birch 1964) (BII) and Haddon & Bullen (1969) (HB), as extrapolated to zero pressure by Anderson & Jordan (1970). Downward arrows are calculated temperature corrections from 300 °K to 2000 °K. Upward arrow is estimated correction to model BII appropriate for a 1700 °K decrease in temperature.

of up to 15 per cent in ϕ , for the MgO–SiO₂ compositions, are allowed by these bounds. The Hashin–Shtrikman (HS) bounds have been calculated for the two-phase compositions MgSiO₃, Mg₂SiO₄, FeSiO₃ and Fe₂SiO₄. These are indicated by the interior error bars—they are almost coincident for the MgO–SiO₂ system. This near-coincidence occurs because the periclase and stishovite shear moduli are nearly identical: 1.31 Mb for periclase (Anderson *et al.* 1968) and 1.30 for stishovite (Mizutani, Hamano & Akimoto 1972b.) It was shown by Hill (1964) that the bulk modulus of a mixture is uniquely determined if the shear moduli of the components are equal. This is easily corroborated from the HS bounds, which are coincident in this case. In the FeO–SiO₂ system, the HS bounds are separated by about 2 to 3 per cent (the shear modulus of wüstite is 0.51 Mb; Mizutani *et al.* 1972a). It is notable that the VRH average is close to, but outside, the HS bounds in these cases.

Unique bulk and shear moduli have been derived by Kröner (1967) for the case of a ‘perfectly disordered’ aggregate. When this average was computed for the MgO–SiO₂ system, it was found to lie outside the HS bounds. Since the case of equal shear moduli has been solved by completely independent methods with identical results, as discussed above, one is led to suspect an error in Kröner’s derivation. In any case, the assumption of ‘perfect disorder’ constitutes a special assumption about the geometry of the mixture, and it therefore may not be appropriate in the present context, as discussed previously.

Anderson (1969) proposed that the ϕ value of many complex oxides was close to the molar average of the ϕ values of the component simple oxides, and subsequently (e.g. Anderson & Jordan 1970) used this average to predict the properties of compositions appropriate to the lower mantle. The Voigt average is equivalent to averaging the quantity $m_i V_i K_i$, where m_i is the number of moles and V_i is the molar volume of the i th component. If M_i is the formula weight, then it is easily shown that

$$m_i V_i K_i = m_i M_i \phi_i = m_i n_i \bar{M}_i \phi_i$$

where n_i is the number of atoms per formula and \bar{M}_i is the mean atomic weight. Then the Voigt average is equivalent to

$$\phi = \sum \frac{m_i n_i \bar{M}_i}{n \bar{M}} \phi_i \quad (12)$$

Anderson’s scheme averages $m_i \phi_i$, rather than $m_i M_i \phi_i$. A variation on Anderson’s scheme was used by Davies & Gaffney (1973)—the quantity $m_i n_i \phi_i$ was averaged. From (12), this can be seen to be equivalent to the Voigt average when the components have the same mean atomic weights, as is nearly the case with MgO (20.16) and SiO₂ (20.03). Neither scheme, however, gives sufficient weight to FeO ($\bar{M} = 36$). Results of these schemes are compared to the previous ones in Fig. 7. Anderson’s scheme (open circles) gives results reasonably close to the HS bounds for the MgO–SiO₂ system, but too high for iron-rich compositions. The Davies & Gaffney scheme (squares) gives the same as the Voigt average for the MgO–SiO₂ system, but much too high values of ϕ for iron-rich compositions. For the relatively small iron contents which seem to apply to the mantle, either scheme gives reasonable, though slightly high, values of ϕ .

In later sections, it is desired to calculate the properties of mixtures at high pressures. Since the pressure dependence of the shear moduli of all of the components are not known, it is most convenient to use the VRH average, which has been shown to give results reasonably close to the HS bounds.

Properties of very dense phases

It has been suggested (e.g. Ringwood 1969) that phases may exist in the deep mantle

which are a few per cent denser than the isochemical mixture of oxides. For instance, pyroxene stoichiometries may exist in the perovskite structure, which would be 5–7 per cent denser than the mixed oxides, and olivine stoichiometries may exist in the K_2NiF_4 structure, about 5 per cent denser, or the $CaFe_2O_4$ (calcium ferrite) structure. Ringwood (1969) estimates the density of the latter phase to be 5–7 per cent denser than the mixed oxides, but Gaffney & Anderson (1973) have re-examined the systematics and concluded that there may be very little difference from the oxides density when the small Mg^{++} ion is present. In the present context, the important point is that phases have been hypothesized which are about 5 per cent denser than the oxide mixtures, and the particular structures involved are not important.

An estimation of the relative effects on ρ and ϕ of polymorphic phase transitions has been given by Davies & Gaffney (1973). Fig. 8 reproduces their plot of ϕ vs ρ for a number of oxides and silicates. The few phase transitions represented (in SiO_2 and fayalite) were augmented by the estimated properties (open circles) of dense oxide mixtures of $(Mg, Fe)SiO_3$ and $(Mg, Fe)_2SiO_4$ and garnet stoichiometries. The mixture properties were estimated according to the method described in the last section, and ϕ is therefore overestimated, especially for iron-rich compositions. However, the slopes of the lines joining similar compositions are consistent enough to give an estimate of the increase in ϕ to be expected to accompany an increase in density due to a phase transition: roughly $30 \text{ (km s}^{-1}\text{)}^2$ per 1 g cm^{-3} increase in density, and less for iron-rich compositions. Note that this slope is lower than that of the line joining MgO and stishovite, and would be lower still with better estimates of ϕ for the oxide mixtures.

The trend suggested here has been used to estimate the values of ϕ relative to those of oxide mixtures for phases roughly 5 per cent denser than the oxide mixtures. Results at zero pressure are illustrated in Fig. 7 by the dashed lines, which represent the offset which the 'pyroxene' and 'olivine' lines would undergo during such a

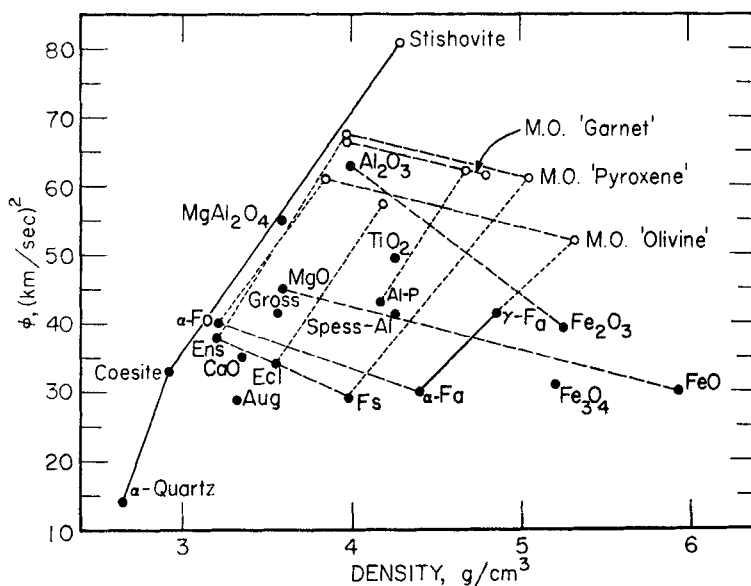


FIG. 8. Zero pressure, room temperature ϕ -density plot for various oxides and silicates (solid circles) and for dense oxide mixtures (open circles) of olivine, pyroxene and garnet compositions, using molar averages. Lines of positive slope join real or hypothetical polymorphs. Dashed lines of negative slope join isochemical mixtures formed by iron substitution. Estimates of ϕ for iron-rich mixtures may be too high. (After Davies & Gaffney 1973).

phase transition (the iron-rich ends of these lines have been omitted). Similar estimates will be made in the next section for high pressures.

The effect of an electronic spin transition is to decrease the ionic radius. The density will therefore certainly increase, but the effect on ϕ is much less clear. The value of ϕ estimated from the above trend at an appropriate density would presumably be an upper limit, since an intrinsically smaller ion is involved. Gaffney & Anderson (1973) have considered the effect and concluded that ϕ may be comparable to that of the corresponding high-spin phase. This will be taken here to be a lower limit.

Comparison with the lower mantle

The results of the preceding discussions will now be assembled and compared with each other and with the lower mantle. A selection of recent models of ϕ and ρ versus pressure for the lower mantle is shown in Fig. 9. The models of ϕ are, of course, derived from seismic observations, as are the density models of Jordan (1972). The density models BII (Birch 1964) and HB (Haddon & Bullen 1969) were derived with the aid of some physical assumptions, although the latter was adjusted to fit some data on the free earth oscillations. For comparison, the 2000 °K isotherms of MgO and stishovite are also shown in Fig. 9.

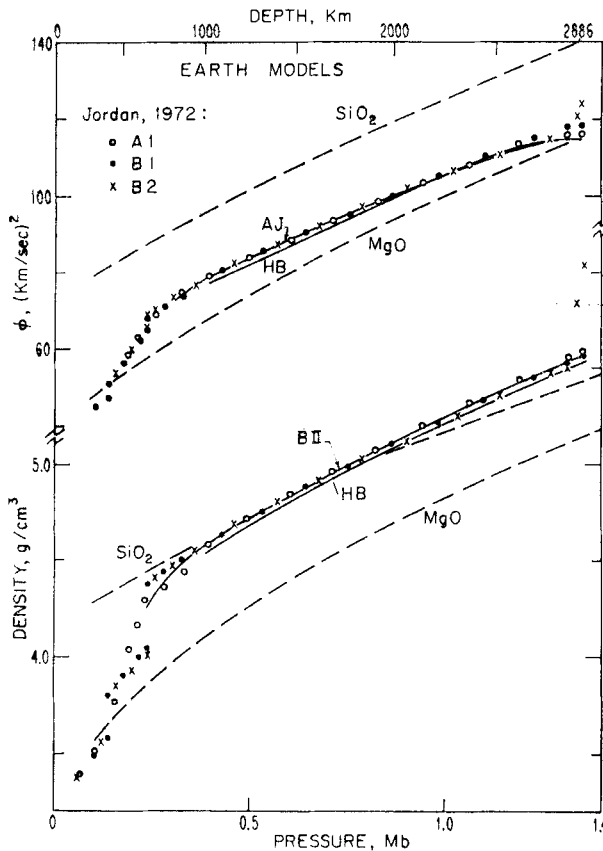


FIG. 9. Density and ϕ from various mantle models. Models A1, B1 and B2 are from Jordan (1972), BII from Birch (1964), HB from Haddon and Bullen (1969) and AJ from Anderson & Julian (1969). The 2000 °K properties of MgO and SiO₂ (stishovite) are shown for comparison.

Anderson & Jordan (1970) extrapolated a series of models of the lower mantle to zero pressure. The results of two such extrapolations are included in Fig. 7— for the models BII and Bullen & Haddon (1967a, b). The former model is quite close to model B1 of Jordan (1972) and the latter to model HB. The temperature to be associated with these extrapolated points is unknown. An estimate of the effect of a 1700 °K decrease in temperature is shown by the arrow extending from these points. This was obtained by averaging the effects of a 1700 °K increase in temperature (from 300 to 2000 °K) on periclase and stishovite. These are shown by the respective downward extending arrows.

From Fig. 7, estimates can be made of the compositions necessary to fit the (zero pressure) lower mantle points for particular temperatures and phase assemblages. Thus, for instance, if the extrapolated lower mantle temperature is 2000 °K, then the BII point corrected to 300 °K would lie at the tip of the upward arrow. This would correspond to an olivine stoichiometry in a dense phase or phase assemblage, with a small amount of iron included. The vertical ticks on the 'olivine' and 'pyroxene' lines correspond to 10 mole per cent of FeO. Thus the above case would require about 6 mole per cent of FeO, or $(\text{Mg}_{.91}, \text{Fe}_{.09})_2\text{SiO}_4$. Alternatively, this case could correspond to a mixture of oxides, or phases with similar properties, with a silica content slightly in excess of that of pyroxene (about 60 mole per cent) and about 8 mole per cent FeO. Higher mantle temperatures would imply a larger correction to 300 °K and would therefore correspond to higher silica contents, but to very similar iron contents.

Plots of ϕ vs ρ , analogous to Fig. 7, are shown in Figs 10–12 for pressures of 0.5, 1.0 and 1.3 Mb and at 2000 °K (Fig. 7 is at 300 °K). The earth models plotted are

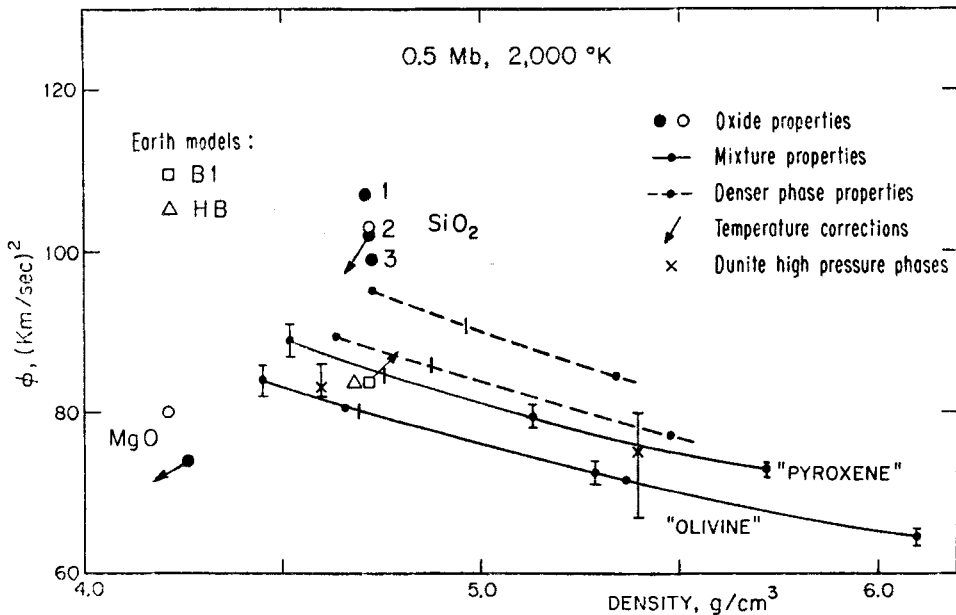


FIG. 10. ϕ -density plot at 0.5 Mb, 2000 °K for oxides, mixtures and earth models. Symbols are similar to those of Fig. 7. Open circles denote MgO and SiO₂ (stishovite) properties from Al'tshuler & Sharipdzhanov (1972b). Dunite high-pressure phase properties (Cases a) are included (crosses); bars indicate range of all cases. Adjacent points on 'olivine' curve are estimated isochemical oxide mixture properties. Earth model B1 is from Jordan (1972) and HB is from Haddon & Bullen (1969). Arrows indicate corrections for temperature changes of 1000 °K.

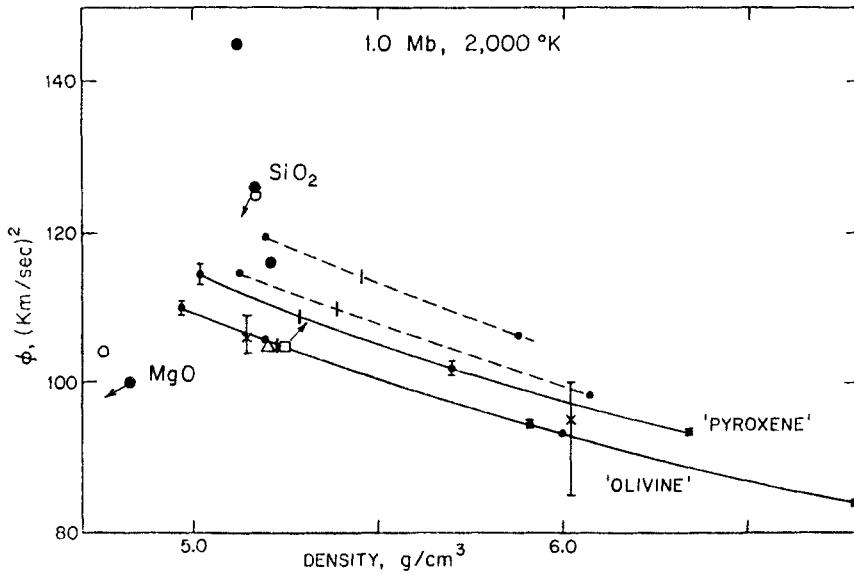


FIG. 11. ϕ -density plot at 1 Mb and 2000 °K for oxides, mixtures and earth models. Symbols as in Fig. 10. Solid SiO₂ circles are for (upper to lower) Cases 1, 2 and 3, respectively (Table 1(a), Davies 1972).

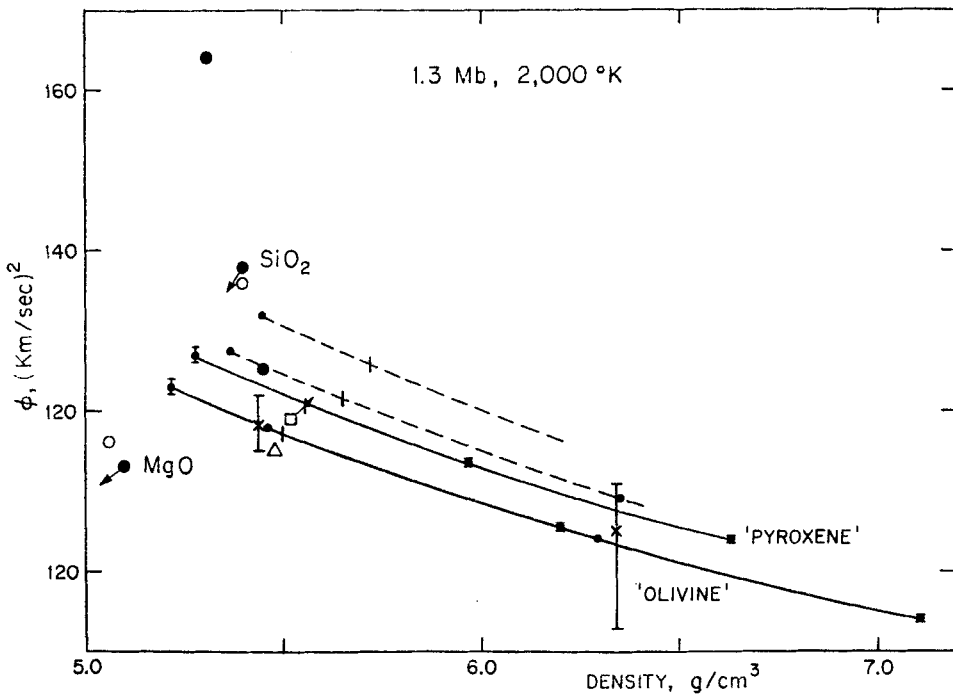


FIG. 12. ϕ -density plot at 1.3 Mb and 2000 °K for oxides, mixtures and earth models. Symbols as in Figs 10 and 11.

B1 (Jordan 1972) and HB (Haddon & Bullen 1969), and the temperature correction shown is for a decrease of 1000 °K. Only the Voigt and Reuss bounds on the mixture properties are given, as discussed previously. In addition to the periclase and stishovite properties calculated by Davies (1972, 1973), those estimated from the tabulations of Al'tshuler & Sharipdzhanov (1972a) are shown (open circles). The properties of the Twin Sisters and Mooihoek dunites, derived according to the previous discussion, are indicated by the crosses. The density of the Twin Sisters dunite is slightly less, and that of the Mooihoek dunite slightly greater, than the 'olivine' density of corresponding iron contents, shown by points.

Figs 10–12 can be used to estimate the compositions corresponding to various temperatures and phase assemblages at high pressures. It may be seen that similar iron contents are deduced at high pressures as were deduced at zero pressure. Thus, oxide mixtures require 8–11 mole per cent FeO, while the denser phases require 6–9 mole per cent FeO to fit the lower mantle points of model B1. The trade-off between silica content, phase assemblage and temperature can be illustrated by deducing the temperature required to fit the lower mantle points for particular compositions and phase assemblages. These temperatures are plotted against pressure in Fig. 13 for oxide mixtures and denser phases of olivine and pyroxene stoichiometry and for dense phases of a pyrolite composition (Ringwood 1970). The reversals in the gradient of some of the profiles only reflect some of the uncertainties in the temperatures, and are not significant. Although there is a wide spread in the temperatures, it is difficult to decide which possibility is the most likely, even if all of the uncertainties are ignored.

Some estimates of temperature in the upper mantle are included in Fig. 13.

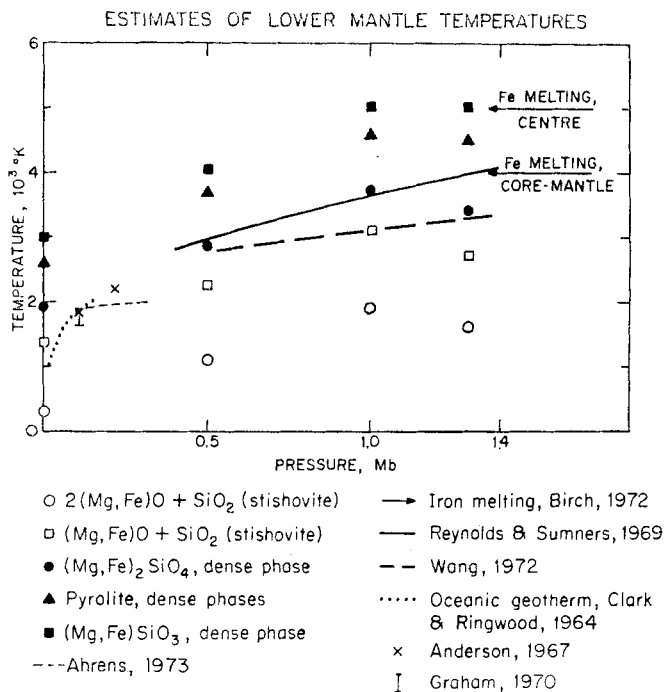


FIG. 13. Various estimates of lower mantle temperatures. Circles, squares and triangles show the temperatures required in order that the indicated model mineral assemblage properties fit the density and ϕ of earth model B1 (Jordan 1972). Iron-melting temperatures at the core–mantle interface and at the centre of the Earth were estimated by Birch (1972).

These are the 'oceanic' geotherm calculated by Clark & Ringwood (1964) and the estimates by Anderson (1967) and Graham (1970) of the temperatures at the transition zones of the upper mantle. Also shown are the lower mantle geotherm assumed by Reynolds & Sumners (1969), and subsequently assumed by Al'tshuler & Sharipdzhanov (1972b), and that estimated by Wang (1972) on the assumptions that the temperature gradient is isentropic and that the lower mantle can be modelled by the Twin Sisters and Mooihoek dunites. Upper limits to the temperatures in the Earth are provided by the melting temperatures of the solid parts of the Earth. Birch (1972) has revised the estimates by Higgins & Kennedy (1971) of the melting curve of iron, and his estimates of the iron-melting temperatures at the Earth's centre and at the core-mantle boundary are shown in Fig. 13. These estimates may be uncertain by as much as 1000 °K (Birch 1972). Another recent estimate of the iron-melting curve by Leppaluoto (1972), in which the equation of state of the liquid is taken into account, gives a melting temperature at the Earth's centre of about 7000 °K, also with large uncertainty. Estimates of the melting temperature of the lower mantle vary widely. At the core-mantle boundary, Clark (1963) estimated a melting temperature of about 7000 °K, while Uffen (1952) and Kennedy & Higgins (1972) estimate about 5000 °K. Kennedy & Higgins (1972) pointed out that the relevant temperature to be considered is the solidus of the lower mantle, and that this may be 1000 °K or more below the melting temperatures of pure components. From the preceding discussion, it can only be concluded that temperatures in the lower mantle should range from about 2000 °K to perhaps 5000 to 6000 °K. Thus the mixed oxides model of olivine stoichiometry would be ruled out, but none of the others illustrated in Fig. 13 would be. When other uncertainties are considered, even this one may not be ruled out.

The formal uncertainties are smallest at zero pressure (Fig. 7), but the interpretation of the extrapolated lower mantle points depends on the assumption that the composition of the lower mantle is homogeneous and that the temperature varies fairly smoothly. At higher pressures, there is not this difficulty with the lower mantle points, but the equations of state of the various components become more uncertain. The uncertainties in the properties of high-pressure phases are smallest at pressures around 0.5 Mb (Figs 2, 5 and 6) and increase rapidly at higher pressures. Thus the comparison of lower mantle properties with component properties is probably best made at 0.5 Mb pressure (Fig. 10). The comparison at zero pressure is also useful, with the above qualification.

The most serious uncertainty is in the properties of stishovite. At 0.5 Mb, this is sufficient to cause uncertainties of about 10 mole per cent in silica content, 2 mole per cent in FeO content and 700 °K in temperature. At higher pressures it would allow strong compositional gradients—at 1.3 Mb (Fig. 12) the silica content could be as low as 30 mole per cent and the FeO content as high as 16 mole per cent.

Although the Voigt and Reuss bounds allow significant variations in the mixture properties, the observation made previously that the VRH average is quite close to the HS bounds reduces this to a secondary source of uncertainty, especially at high pressures.

If, instead of referring to the mixture properties, the properties of Twin Sisters dunite are made the basis of the comparison, the FeO content would be increased by 2–3 mole per cent, while the silica content would be changed very little.

Electronic spin transitions in iron would mean that less iron was required in the lower mantle. Octahedral co-ordination of the iron is probably required to produce spin transition (Gaffney & Anderson 1973), and not all candidates for dense phases have any or all iron in octahedral sites. An extreme case is probably obtained by assuming that the iron occurs as FeO in the wüstite structure, in which it is all octahedrally co-ordinated. Gaffney & Anderson (1973) estimate that the spin transition would increase the density of wüstite from about 5.9 g cm^{-3} to about 7.5 g cm^{-3} .

If ϕ did not increase by much, the main effect of this would be that the present estimates of iron content would be reduced by about half. If an increase in ϕ comparable to that in the other phase changes considered occurred, then the effect would be similar to that of the phase changes already considered, i.e. a reduction in both the FeO and silica contents.

A final source of uncertainty is that of the models themselves. The uncertainties in ϕ are considerably less than the uncertainties of the ϕ of the components, but there is a significant uncertainty in the density. The models discussed by Anderson & Jordan (1970) were derived by a variety of methods, and the zero-pressure extrapolated densities they obtained range from 3.90 to 4.13 g cm^{-3} . This would correspond to a range of over 10 mole per cent of FeO content. The use of free-oscillation data has led to better constraints on the density. Thus the difference between models HB and B1 is about 0.05 g cm^{-3} , corresponding to a range of 2–3 mole per cent of FeO. Continuing improvements in the free-oscillation data will presumably further reduce this range of uncertainty.

Discussion

The limits which can be placed on the constitution of the lower mantle can be summarized by describing the more likely models found here and by then exploring the range of possible variations about these models.

The models which give the best fit of the particular component properties used here to the lower mantle properties are an assemblage of the very dense phases with an olivine stoichiometry, or an oxide mixture, or phase assemblage with similar properties, with a pyroxene stoichiometry. Very dense phase assemblages of a pyrolite or even a pyroxene composition are also possible, but an oxide mixture of olivine stoichiometry implies temperatures which may be too low. The iron content required in the oxide mixtures is about 9 mole per cent of FeO, while for the very dense phase assemblages it is about 6 mole per cent.

The silica content, phase assemblage and temperature are all interdependent. Thus an oxide mixture with as much as 70 mole per cent silica is possible if fairly high temperatures are assumed (Fig. 13), or a denser phase assemblage with as little as 30 mole per cent silica is possible with lower temperatures. The uncertainty in the ϕ of the components, especially of stishovite, may add another 10 mole per cent to the range of silica contents at 0.5 Mb pressure (about 1200 km depth). The uncertainties at greater depths and pressures are even greater, and large variations in the silica content with depth cannot be ruled out. The uncertainties at 0.5 Mb do not seem to be sufficient to admit an oxide mixture of olivine stoichiometry, but at greater depths it is probably admissible.

The dependence of the iron content on the phase assemblage found here depends in turn on the periclase–stishovite join in the $\phi - \rho$ plots being steeper than the loci of relevant polymorphs in these plots (Figs 7, 10–12). As discussed previously, the slopes of polymorph loci may have been overestimated, if anything. Nevertheless, the details of the iron-content dependence on phase assemblage will probably depend on the individual phases involved. Thus, all that should be concluded at this stage is that the inferred iron content may vary by a few mole per cent, depending on the particular phase assemblage. Of the other factors affecting the iron content, uncertainties in the component properties and in the lower mantle density each contribute about 2 mole per cent uncertainty in the FeO content, and the presence of ‘low-spin’ iron could reduce by up to one half the inferred FeO content, although the effect is likely to be somewhat less than this. Reference to the dunites would increase the FeO content by about 2 mole per cent. Thus the extreme range of FeO content deduced at 0.5 Mb would be from about 3 mole per cent to about 14 mole per cent, with the most likely range between 6 and 10 mole per cent.

If the lower mantle is assumed to be homogeneous in composition and phase assemblage, and its temperature is assumed to vary smoothly with depth, then stronger constraints follow from the zero-pressure extrapolated properties. Only the oxide mixture of pyroxene composition and the denser phase assemblage of olivine composition are clearly acceptable. These would have FeO contents of about 8 and 6 mole per cent respectively. One of the largest uncertainties at zero pressure is in the temperature corrections. With these included, the temperatures of these models are accurate to perhaps 500 °K, and the FeO content to about 2 mole per cent. A pyrolite composition in a very dense phase assemblage is possibly just acceptable by these criteria.

Al'tshuler & Sharipdzhanov (1972b) noted a trend in recent studies towards FeO contents of 13–15 weight per cent (or about 9–11 mole per cent), in agreement with their own determination of 14 weight per cent derived from a mixed oxides model, and in reasonable agreement with the results of this study for oxide mixtures. However, in dismissing the possibility of denser phase assemblages, Al'tshuler & Sharipdzhanov did not take sufficient account of the interdependence of phase assemblage, temperature and silica content.

Anderson (1970), Anderson & Jordan (1970) and Anderson, Sammis & Jordan (1971) deduced FeO contents of the lower mantle in the range 12–18 mole per cent. These higher values seem to have resulted mainly from the high density of some of the models used (especially model CIT 200204, Anderson & Smith 1968), but also in part from using either oxide mixtures or dunites as references—denser phases were not considered.

The determination by Wang (1972) of temperatures in the lower mantle (Fig. 13) was given uncertainties of 800 °K. However, by using the dunites as references, Wang did not take sufficient account of the effects of changes in silica content and phase assemblage.

Conclusions

The limits on the constitution of the lower mantle which have been obtained here embrace most of the claims which have recently been made concerning the lower mantle. Thus, its composition may be similar to that of the upper mantle. Graham (1970) deduced an FeO content for the upper mantle of 7 mole per cent from an olivine model, and Ringwood's (1970) pyrolite contains 8.5 weight per cent of FeO plus Fe₂O₃ (or about 6 mole per cent of FeO, equivalently). In a detailed study of the upper mantle and transition zone, Ahrens (1973) found the Fe/(Fe+Mg) ratio to be about 0.15 ± 0.05 for a model with about 25 per cent garnet-pyroxene component. This corresponds to about 9 ± 3 mole per cent of FeO. A moderate enrichment of FeO in the lower mantle is possible, but the high values of 16–18 mole per cent FeO obtained by Anderson (1970) and Anderson *et al.* (1971) from the Earth model CIT 200204 are beyond the limits found here. The question of iron enrichment deeper in the lower mantle cannot really be resolved at present. Ringwood's (1969, 1970) suggestion that very dense phases may be present in the lower mantle is quite plausible. The presence of very dense phases would probably not be consistent with any iron enrichment in the lower mantle. The temperatures in the lower mantle are very indeterminate in the present approach. Silica contents ranging from olivine to pyroxene compositions are easily accommodated within the present limits. A homogeneous composition and isentropic temperature gradient in the lower mantle are consistent with the present limits, but substantial compositional gradients and superadiabatic temperature gradients cannot be ruled out because of the increasing uncertainty of the component properties at higher pressures and greater depths.

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References

- Ahrens, T. J., 1973. Petrologic properties of the upper 670 km of the earth's mantle; geophysical implications, *Phys. Earth Planet. Int.*, **7**, 167-186.
- Ahrens, T. J., Anderson, D. L. & Ringwood, A. E., 1969. Equations of state and crystal structures of high-pressure phases of shocked silicates and oxides, *Rev. Geophys.*, **7**, 667-707.
- Ahrens, T. J., Takahashi, T. & Davies, G. F., 1970. A proposed equation of state of stishovite, *J. geophys. Res.*, **75**, 310-316.
- Al'tshuler, L. V. & Sharipdzhanov, I. I., 1972a. Additive equations of state of silicates at high pressures, *Bull. (Izv.) Acad. Sci. USSR, Earth Physics (Engl. Transl.)*, No. 3, 167-177.
- Al'tshuler, L. V. & Sharipdzhanov, I. I., 1972b. Distribution of iron in the earth and its chemical differentiations, *Bull. (Izv.) Acad. Sci. USSR, Earth Physics (Engl. Transl.)*, No. 4, 231-239.
- Anderson, D. L., 1967. Phase changes in the upper mantle, *Science*, **157**, 1165-1173.
- Anderson, D. L., 1969. Bulk modulus—density systematics, *J. geophys. Res.*, **74**, 3857-3864.
- Anderson, D. L., 1970. Petrology of the mantle, *Mineral. Soc. Am. Spec. Pap.*, **3**, 85-93.
- Anderson, D. L. & Jordan, T. H., 1970. The composition of the lower mantle, *Phys. Earth Planet. Int.*, **3**, 23-35.
- Anderson, D. L. & Julian, B. R., 1969. Shear velocities and elastic parameters of the mantle, *J. geophys. Res.*, **74**, 3281-3286.
- Anderson, D. L. & Kanamori, H., 1968. Shock-wave equations of state for rocks and minerals, *J. geophys. Res.*, **73**, 6477-6502.
- Anderson, D. L., Sammis, C. & Jordan, T., 1971. Composition and evolution of the mantle and core, *Science*, **171**, 1103-1112.
- Anderson, D. L. & Smith, M., 1968. Mathematical and physical inversion of gross earth data (abstract), *Eos. Trans. Am. geophys. Un.*, **49**, 282.
- Anderson, O. L., Schreiber, E., Liebermann, R. C. & Soga, N., 1968. Some elastic constant data on minerals relevant to geophysics, *Rev. Geophys.*, **6**, 491-524.
- Birch, F., 1938. The effect of pressure upon the elastic properties of isotropic solids, according to Murnaghan's theory of finite strain, *J. appl. Phys.*, **9**, 279-288.
- Birch, F., 1947. Finite elastic strain of cubic crystals, *Phys. Rev.*, **71**, 809-824.
- Birch, F., 1952. Elasticity and constitution of the earth's interior, *J. geophys. Res.*, **57**, 227-286.
- Birch, F., 1961. Composition of the Earth's mantle, *Geophys. J. R. astr. Soc.*, **4**, 295-311.
- Birch, F., 1964. Density and composition of the mantle and core, *J. geophys. Res.*, **69**, 4377-4388.

- Birch, F., 1972. Melting relations of iron, and temperatures in the Earth's core, *Geophys. J. R. astr. Soc.*, **29**, 373–387.
- Bullen, K. E., 1963. *Introduction to the theory of seismology*, Cambridge University Press.
- Bullen, K. E. & Haddon, R. A., 1967a. Earth oscillations and the earth's interior, *Nature*, **213**, 574–576.
- Bullen, K. E. & Haddon, R. A., 1967b. Derivation of an earth model from free oscillation data, *Proc. nat. Acad. Sci.*, **58**, 846–852.
- Carter, W. J., Marsh, S. P., Fritz, J. N. & McQueen, R. G., 1971. The equation of state of selected materials for high-pressure references, in *Accurate characterization of the high-pressure environment*, 147–158, ed. E. C. Lloyd, *N.B.S. Spec. Publ.* 326, U.S. Dept. of Commerce.
- Clark, S. P., 1963. Variation of density in the earth and the melting curve in the mantle, in *The Earth Sciences*, 5–42, University of Chicago Press.
- Clark, S. P. & Ringwood, A. E., 1964. Density distribution and constitution of the mantle, *Rev. Geophys.*, **2**, 35–88.
- Clendenen, R. L. & Drickamer, H. G., 1966. Lattice parameters of nine oxides and sulphides as a function of pressure, *J. chem. Phys.*, **44**, 4223–4228.
- Davies, G. F., 1972. Equations of state and phase equilibria of stishovite and a coesite-like phase from shock-wave and other data, *J. geophys. Res.*, **77**, 4920–4933.
- Davies, G. F., 1973. Quasi-harmonic finite strain equations of state of solids, *J. Phys. Chem. Solids*, **34**, 1417–1429.
- Davies, G. F., 1974. Effective elastic moduli under hydrostatic stress—I. Theory, *J. Phys. Chem. Solids*, in press.
- Davies, G. F. & Anderson, D. L., 1971. Revised shock-wave equations of state for high-pressure phases of rocks and minerals, *J. geophys. Res.*, **76**, 2617–2627.
- Davies, G. F. & Gaffney, E. S., 1973. Identification of high-pressure phases of rocks and minerals from Hugoniot data, *Geophys. J. R. astr. Soc.*, **33**, 165–183.
- Dziewonski, A. M. & Gilbert, F., 1972. Observations of normal modes from 84 recordings of the Alaskan earthquake of 1964 March 28, *Geophys. J. R. astr. Soc.*, **27**, 393–446.
- Gaffney, E. S. & Anderson, D. L., 1973. Effect of low-spin Fe^{2+} on the composition of the mantle, *J. geophys. Res.*, **78**, 7005–7014.
- Graham, E. K., 1970. Elasticity and composition of the upper mantle, *Geophys. J. R. astr. Soc.*, **20**, 285–302.
- Graham, E. K., 1973. On the compression of stishovite, *Geophys. J. R. astr. Soc.*, **32**, 15–34.
- Haddon, R. A. & Bullen, K. E., 1969. An earth model incorporating free earth oscillation data, *Phys. Earth Planet. Int.*, **2**, 35–49.
- Hashin, Z. & Shtrikman, S., 1963. A variational approach to the theory of the elastic behaviour of multiphase materials, *J. Mech. Phys. Solids*, **11**, 127–140.
- Higgins, G. & Kennedy, G. C., 1971. The adiabatic gradient and melting point gradient in the core of the earth, *J. geophys. Res.*, **76**, 1870–1878.
- Hill, R., 1952. The elastic behaviour of a crystalline aggregate, *Proc. Phys. Soc.*, **A65**, 349–354.
- Hill, R., 1964. Theory of mechanical properties of fibre-strengthened materials: I. Elastic behaviour, *J. Mech. Phys. Solids*, **12**, 199–212.
- Johnson, L. R., 1969. Array measurements of P velocities in the lower mantle, *Bull. seism. Soc. Am.*, **59**, 973–1008.
- Jordan, T. H., 1972. *Estimation of the radial variation of seismic velocities and density in the earth*, Ph.D. Thesis, California Institute of Technology, Pasadena, California.

- Jordan, T. H. & Anderson, D. L., 1974. Earth structure from free oscillations and travel times, *Geophys. J. R. astr. Soc.*, **36**, 411–459.
- Julian, B. R. & Sengupta, M. K., 1973. Seismic travel time evidence for lateral inhomogeneity in the deep mantle, *Nature*, **242**, 443–447.
- Kanasewich, E. R., Ellis, R. M., Chapman, C. H. & Gutowski, P. R., 1973. Seismic array evidence of a core boundary source for the Hawaiian linear volcanic chain, *J. geophys. Res.*, **78**, 1361–1371.
- Kennedy, G. C. & Higgins, G. H., 1972. Melting temperatures in the earth's mantle, in *The Upper Mantle*, ed. A. R. Ritsema, *Tectonophysics*, **13**, 221–232.
- Kröner, E., 1967. Elastic moduli of perfectly disordered composite materials, *J. Mech. Phys. Solids*, **15**, 319.
- Leibfried, G. & Ludwig, W., 1961. Theory of anharmonic effects in crystals, *Solid State Phys.*, **12**, 175–444.
- Leppaluoto, D. A., 1972. Melting of iron by significant structure theory, *Phys. Earth Planet. Int.*, **12**, 175–181.
- Liu, L., 1973. Chemistry of the earth's lower mantle, *J. geophys. Res.*, **78**, 3501–3504.
- Liu, L., Bassett, W. A. & Takahashi, T., 1974. Effect of pressure on the lattice parameters of stishovite, *J. geophys. Res.*, **79**, 1160–1164.
- McQueen, R. G., Marsh, S. P. & Fritz, J. N., 1967. Hugoniot equation of state of twelve rocks, *J. geophys. Res.*, **72**, 4999–5036. Also, in Clark, S. P. (editor), 1966. *Handbook of physical constants*, *Geol. Soc. Am. Mem.*, **97**, New York.
- Mizutani, H., Hamano, Y., Akimoto, S. & Nishizawa, O., 1972a. Elasticity of stishovite and wüstite (abstract), *Eos, Trans. Am. geophys. Un.*, **53**, 527.
- Mizutani, H., Hamano, Y. & Akimoto, S., 1972b. Elastic-wave velocities of polycrystalline stishovite, *J. geophys. Res.*, **77**, 3744–3749.
- Morgan, W. J., 1971. Convection plumes in the lower mantle, *Nature*, **230**, 42–43.
- Murnaghan, F. D., 1937. Finite deformations of an elastic solid, *Am. J. Math.*, **59**, 235–260.
- Press, F., 1972. The earth's interior as inferred from a family of models, in *The Nature of the Solid Earth*, 147, ed. E. C. Robertson, McGraw-Hill, New York.
- Reuss, A., 1929. Berechnung die Fließgrenze von Mischkristallen auf Grund der Plastitätsbedingung für Einkristalle, *Z. Angew. Math. Mech.*, **9**, 49.
- Reynolds, R. T. & Sumners, A. L., 1969. Calculations on the compositions of the terrestrial planets, *J. geophys. Res.*, **74**, 2494–2511.
- Rice, M. H., McQueen, R. G. & Walsh, J. M., 1958. Compression of solids by strong shock waves, *Solid State Phys.*, **6**, 1–63.
- Richter, F. M. & Johnson, C. E., 1974. Stability of a chemically layered mantle, *J. geophys. Res.*, **79**, 1635–1639.
- Ringwood, A. E., 1969. Phase transformations in the mantle, *Earth Planet. Sci. Lett.*, **5**, 401–412.
- Ringwood, A. E., 1970. Phase transformations and the constitution of the mantle, *Phys. Earth Planet. Int.*, **3**, 109–155.
- Spetzler, H., 1970. Equation of state of polycrystalline and single-crystal MgO to 8 kilobars and 800 °K, *J. geophys. Res.*, **75**, 2073–2087.
- Stishov, S. M. & Popova, S. V., 1961. A new dense modification of silica, *Geokhimiya*, **10**, 923–926.
- Thomsen, L., 1970. On the fourth-order anharmonic equation of state of solids, *J. Phys. Chem. Solids*, **31**, 2003–2016.
- Trunin, R. F., Simakov, G. V., Podurets, M. A., Moiseyev, B. N. & Popov, L. V., 1970. Dynamic compressibility of quartz and quartzite at high pressure *Izv. Earth Physics*, **1**, 13–20. English transl., 1971, *Phys. Solid Earth*, **1**, 8–12.
- Uffen, 1952. A method of investigating the melting point gradient in the earth's mantle, *Trans. Am. geophys. Un.*, **33**, 893.
- Voigt, W., 1928. *Lehrbuch der Krystallphysik*, 962, Teubner, Leipzig.

- Wang, C., 1968. Constitution of the lower mantle as evidenced from shock wave data for some rocks, *J. geophys. Res.*, **73**, 6459–6476.
- Wang, C., 1970. Density and constitution of the mantle, *J. geophys. Res.*, **75**, 3264–3284.
- Wang, C., 1972. Temperature in the lower mantle, *Geophys. J. R. astr. Soc.*, **27**, 29–36.
- Weaver, J. S., 1971. *Thermal expansion of stishovite*, Ph.D. Thesis, Part I, University of Rochester, Rochester, N.Y.
- Weaver, J. S., Takahashi, T. & Bassett, W. A., 1973. Thermal expansion of stishovite (abstract), *Eos, Trans. Am. geophys. Un.*, **54**, 475.