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On the Compression of Stishovite

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'If this is not scientifically correct, it ought to be.' Winston S. Churchill, *Their Finest Hour*

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Summary

Currently available shock-wave compression data for single-crystal α-quartz and pore-free quartzite have been used to determine values for the isentropic bulk modulus of stishovite and its first pressure derivative. The shock-wave data reduction scheme makes use of the observed linearity in the shock-velocity–particle-velocity field over the pressure range 0·4–2·0 Mbar and the first-order Murnaghan equation of state. In addition, an accurate form of the temperature independent Grüneisen parameter (γ), consistent with the linear $U_S - u_p$ relation, has been used in the reduction of the fundamental shock-wave data to the metastable Hugoniot. The temperature derivative of the isentropic bulk modulus is provided by a least-square fit of the γ relation to available Hugoniot data directly measured on porous and fused-quartz samples in the high-pressure regime. The pertinent results are: $K^S = 3{\cdot}35 \pm 0{\cdot}19$ Mbar; $(\partial K^S/\partial P)_T = 5{\cdot}5 \pm 0{\cdot}6$; and $(\partial K^S/\partial T)_p = (-0{\cdot}35 \pm 0{\cdot}08) \times 10^{-3}$ Mbar/°K. These results are consistent with recent static-compression and ultrasonic measurements on stishovite and are related systematically to corresponding data for isostructural GeO_2 and TiO_2. Comparison of the present results with recent shock-wave analyses by other investigators suggests that the first-order Murnaghan form of the equation of state is more appropriate than the first-order Birch equation in reproducing the compression of stishovite in the zero to 2 Mbar pressure range.

An evaluation of the composition of the lower mantle in terms of the fundamental oxides, FeO, MgO, and SiO_2, using the present results for the elastic properties of stishovite, support marginally the conclusions of previous investigators regarding enrichment of FeO and SiO_2 relative to the upper mantle; however, such an interpretation is predicated on the mixed oxide assumption and should be considered in relation to alternative models.

Introduction

Several lines of evidence suggest that SiO_2 is the dominant chemical constituent of the Earth's mantle (e.g. Ringwood 1970). Moreover, it has been pointed out by Birch (1952) that the observed increase in seismic velocities within the transition zone

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of the mantle is most likely accounted for in terms of phase transformations of the constituent minerals involving primarily an increase in the co-ordination of the silica component. Therefore, since the discovery of the rutile-structure high-pressure phase of silica, stishovite, by Stishov & Popova (1961), much effort has been extended toward the determination of the elastic properties of this important material.

A variety of experimental methods have been utilized to measure the volume compression of stishovite. The isothermal compression has been measured to moderate pressures using static X-ray diffraction techniques by Ida, Syono & Akimoto (1967), Liu, Takahashi & Bassett (1969), and Bassett & Barnett (1970). However, the data and calculated bulk moduli resulting from these studies are not consistent within the indicated experimental errors. The reason for the discrepancies is not clear; presumably, they reflect systematic error inherent in the individual experimental arrangements, such as pressure distribution, and misinterpretation of the X-ray diffraction data. Shock-wave compression studies of single-crystal and polycrystal α-quartz by Wackerle (1962), Al'tshuler, Trunin & Simakov (1965), Fowles (1967), and Trunin *et al.* (1971), have provided Hugoniot data to over 6 Mbar. These data have been interpreted in the high-pressure stishovite regime in terms of an equation of state by McQueen, Fritz & Marsh (1963), Anderson & Kanamori (1968), Ahrens, Takahashi & Davies (1970), and Davies (1972). Considerable variation in the calculated elastic parameters of stishovite is also apparent in the results of these studies; however, the lack of thorough error analyses in most cases make comparison difficult. Assumptions regarding the form of the equation of state and variation of the Grüneisen parameter with volume, as well as analysis of different data sets, undoubtedly accounts for much of the variation. However, the effects of these assumptions on the resulting calculated bulk elastic properties are not clearly understood. A value for the bulk modulus of stishovite has been determined recently by Mitzutani, Hamano & Akimoto (1972) using ultrasonic techniques. Because of the small size and polycrystalline form of the specimen, a rather large estimated error has been indicated; even so, this measurement undoubtedly represents the most reliable value of the bulk modulus presently available.

An accurate value of the bulk modulus of stishovite is a critical requirement in the derivation of compositional models of the lower mantle which are based on the fundamental oxide mixture MgO–FeO–SiO_2 (e.g. Ringwood 1969; Anderson & Jordan 1970; Anderson, Sammis & Jordan 1971). A discussion of the dependency of the conclusions afforded by this assumption on the value of the bulk modulus of stishovite has been presented recently by Wang & Simmons (1972). The question as to whether the ratio FeO/(FeO+MgO) increases or decreases in the lower mantle is dependent upon the value adopted for the bulk modulus. Clearly, for meaningful conclusions, it is necessary to define the most accurate values possible for the elastic properties of stishovite, in conjunction with an appropriate estimate of error.

It is the purpose of this study to calculate the elastic properties of stishovite from presently available shock-wave data according to the linear shock-velocity–particle-velocity ($U_S - u_p$) relationship. The selection of this particular method of data reduction has several advantages. The linear form of the $U_S - u_p$ relation may be used conveniently in conjunction with the relatively simple first-order Murnaghan equation of state. In such a case, a linear fit to the metastable Hugoniot $U_S - u_p$ data yields directly the appropriate isentropic bulk modulus (K^S) and the first pressure derivative $(\partial K^S/\partial P)_S$. In addition, the standard errors in these parameters are provided by the least-square fit to the $U_S - u_p$ data. Moreover, the adoption of the linear $U_S - u_p$ form makes possible the use of a consistent and accurate relation for the volume dependent quasiharmonic Grüneisen parameter. Thus consistency is maintained throughout the data reduction process. Clearly, it is of interest and importance to compare the present results with the solutions of previous investigators who have employed different forms of the equation of state and Grüneisen parameter.

Compression data

The results of the present investigation are based primarily on the Hugoniot data from single-crystal α-quartz by Wackerle (1962), covering a range of 0·4–0·7 Mbar, and Al'tshuler *et al.* (1965), from 0·6–2·0 Mbar, and the Hugoniot data for single-crystal α-quartz and pore-free quartzite by Trunin *et al.* (1971), covering a range of 0·4–2·0 Mbar. The Hugoniot data by these investigators as represented in the pressure-density field, are indicated in Fig. 1. In addition, the value for the 'Anderson–Grüneisen' parameter was determined by a least-square fit to experimental values of the Grüneisen ratio as a function of the volume; these data were calculated by Ahrens *et al.* (1970) from porous quartz and fused quartz Hugoniot measurements provided by Jones *et al.* (1968), Shipman (1969) and McQueen (1968). These data are indicated in Fig. 2. The shock-wave compression data considered represents a pressure range of 0·4–2·0 Mbar. A necessary criterion for a satisfactory 'fit' of the selected equation of state is that it provide an adequate representation of the compression of stishovite in the zero to 0·4 Mbar range. Therefore, consistency of the calculated results with

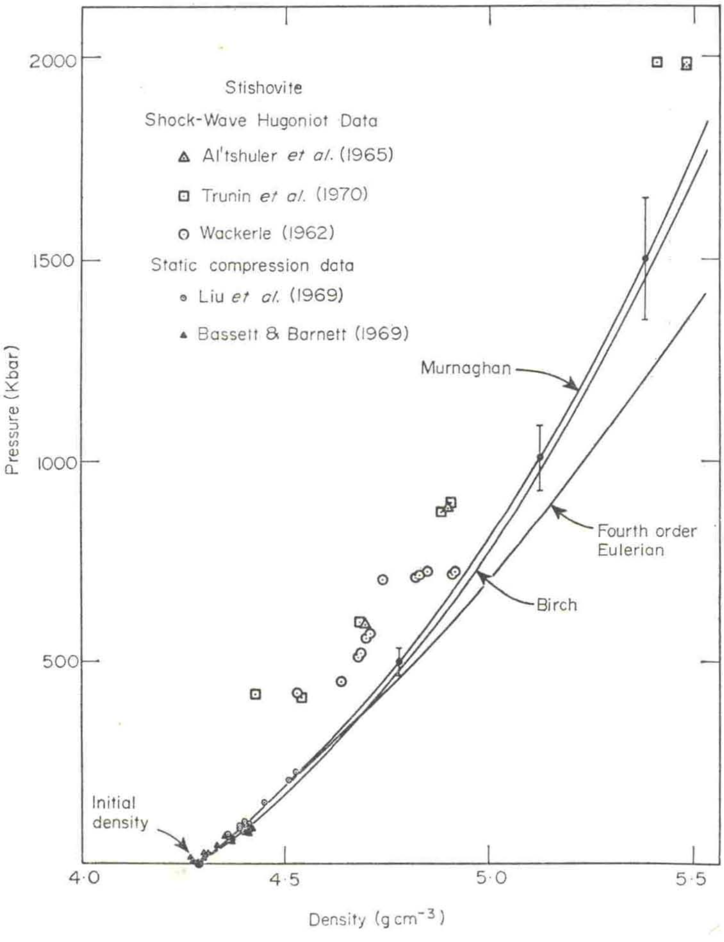

FIG. 1. Pressure-density Hugoniot data for α-quartz and quartzite in the stishovite regime. The calculated isentropes, centred at ambient conditions, are indicated for the present study (Murnaghan), Ahrens *et al.* (1970) (Birch), and Davies (1972) (Fourth-Order Eulerian).

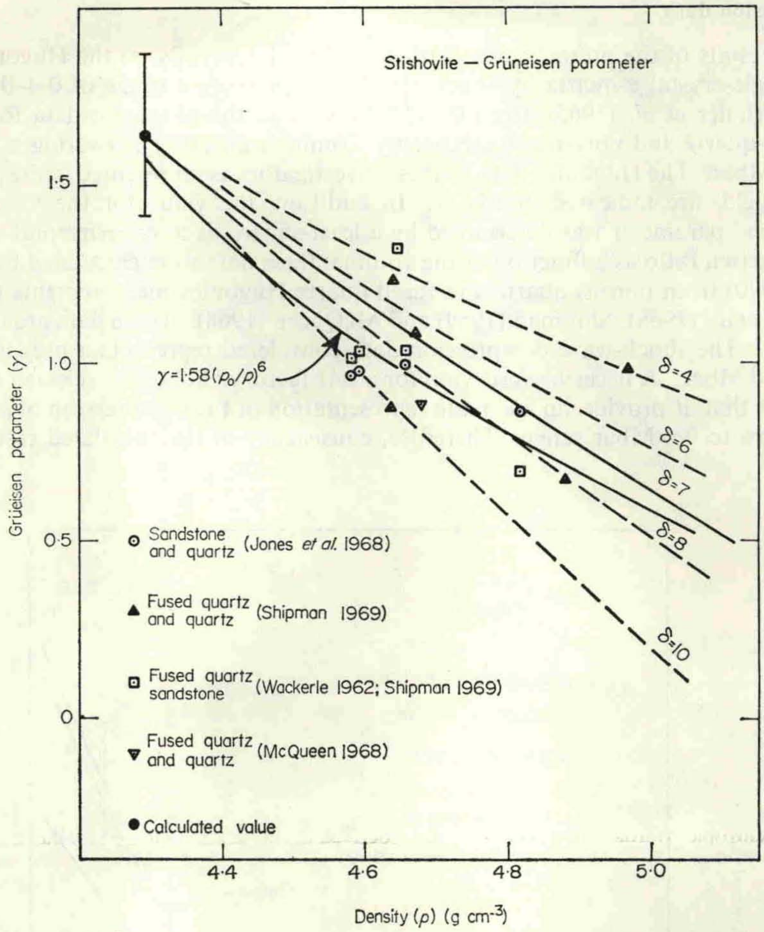

FIG. 2. Grüneisen parameter as a function of density for sandstone, fused-quartz, and α-quartz in the stishovite regime (after Ahrens *et al.* 1970).

the respective elastic properties determined independently from static-compression and ultrasonic measurements provides a means of evaluating the suitability of the equation of state used in the shock-wave analyses.

Isothermal compression measurements for stishovite using X-ray diffraction techniques provide data in the zero to 250 Kbar range. Ida, Syono & Akimoto (1967) measured the effect of pressure to 130 Kbar on the *a* and *c* lattice parameters of stishovite using a tetrahedral-anvil type of apparatus and an NaCl pressure standard. The bulk modulus derived from the data using a quadratic Bridgman equation of state is $7{\cdot}1 \pm 2{\cdot}0$ Mbar. However, it has been pointed out by Bassett & Barnett (1970), that this surprisingly high value and the anomalous behaviour of an increasing *c* axis with pressure observed by Ida *et al.* (1967), could possibly have resulted from an erroneous interpretation of the shift in the (111) reflection. The measurements of Bassett & Barnett (1970) also were carried out in a tetrahedral-anvil press on a synthetic stishovite powder with NaCl as a pressure standard. A fit of the resulting pressure-volume data in the range zero to 85 Kbar yielded a value of $3{\cdot}0 \pm 0{\cdot}3$ Mbar for the bulk modulus. The effect of pressure on the volume of stishovite to almost 250 Kbar has been measured by Liu, Takahashi & Bassett (1969) by means of a diamond anvil high-pressure cell and an NaCl marker. These data have been fit by this

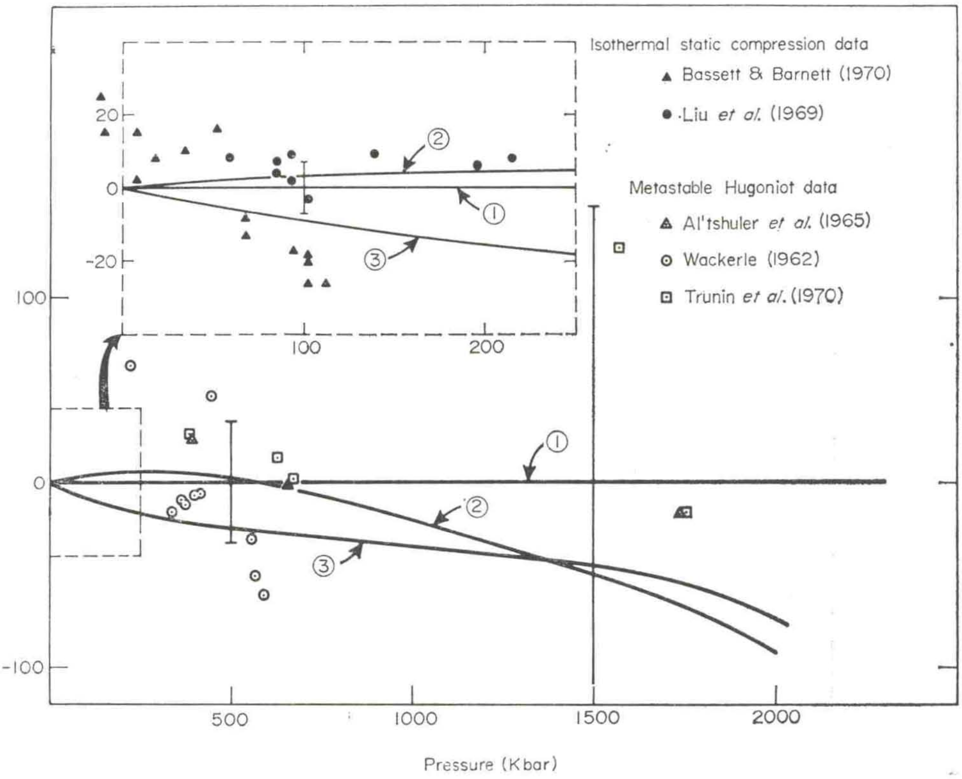

FIG. 3. Isothermal static-compression data for stishovite compared with the isentropic Murnaghan equation of state derived in this study. The values plotted represent the difference between the indicated data set or calculated equation of state and the Murnaghan equation. Curve 2 refers to a reduction of only the data of Wackerle (1962) and Al'tshuler *et al.* (1965), using the linear $U_S - u_P$ relationship; curve 3 refers to the results of Ahrens *et al.* (1970), which is based on an equivalent data set.

investigator to a Bridgman equation using a least-square procedure. The results indicate that the highest significant order is quadratic in pressure and the calculated bulk modulus and its first pressure derivative are $3{\cdot}43 \pm 0{\cdot}10$ Mbar and $3{\cdot}7 \pm 1{\cdot}2$, respectively. These results are not consistent, within the indicated experimental error, with the results of Bassett & Barnett (1970). This discrepancy has been discussed by Liu, Bassett & Takahashi (1971), who suggest that the high-pressure data of Bassett & Barnett (1970) may be systematically in error because of contact in the anvils of the tetrahedral press. Systematic error in the low-pressure data of Bassett & Barnett (1970) is evident in Fig. 3; clearly, the data do not extrapolate to the initial density of stishovite.

Mitzutani *et al.* (1972) report the first ultrasonic measurements of the compressional and shear-wave velocities of stishovite. The wave velocities were measured up to 10 Kbar in pressure using a modified pulse transmission method. The calculated isentropic bulk modulus, corrected for the effect of porosity on the P and S wave velocities, is $3{\cdot}46 \pm 0{\cdot}24$ Mbar. This value is in excellent agreement with the isothermal results of Liu *et al.* (1971). A satisfactory solution to the high pressure shock-wave data in terms of an equation of state, should require a bulk modulus favourably consistent with the results of Mitzutani *et al.* (1972) and Liu *et al.* (1971).

The method of shock-wave data reduction followed in this study is only applicable if the shock-velocity–particle-velocity relationship can be given rigorously by

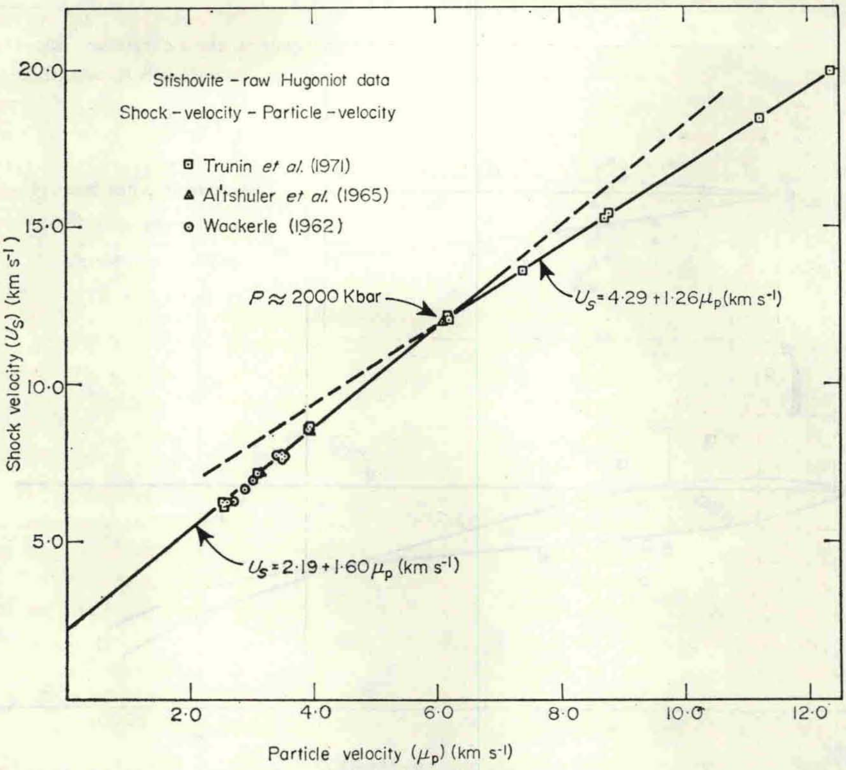

FIG. 4. Shock-velocity–particle-velocity Hugoniot data for α-quartz and quartzite in the stishovite regime. The linear segment fits are by Trunin *et al.* (1971).

$U_S = C_0 + su_p$, where C_0 is the bulk sound speed and s is a function of the initial conditions (e.g. Ruoff 1967; Pastine & Forbes 1968). Trunin *et al.* (1971) have extended the range of the shock Hugoniot data for stishovite well over 6 Mbar. These data, as well as the Hugoniot measurements of Wackerle (1962) and Al'tshuler *et al.* (1965), are indicated in Fig. 4 in the $U_S - u_p$ field. From the figure, it is apparent that the compressibility of stishovite may be represented by two linear segments; one above and one below approximately 2·0 Mbar. This observation was pointed out by Trunin *et al.* (1971), who attributed the behaviour to a change in state of the high-pressure phase, most probably melting. Therefore, the present analysis involves only the Hugoniot measurements in the range below 2 Mbar, where the data are clearly linear and continuous in the shock-velocity–particle-velocity field.

Thermochemical and other relevant data

In addition to the fundamental Hugoniot data, several other factors describing stishovite are required as initial input parameters for the reduction scheme. Chao *et al.* (1962) calculated a density for stishovite of $4{\cdot}287 \pm 0{\cdot}001$ g cm^{-3} from X-ray powder patterns of impact-metamorphosed Coconino sandstone (e.g. Kieffer 1971). This is consistent with the value of $4{\cdot}292 \pm 0{\cdot}003$ g cm^{-3} calculated from the measured lattice parameters of stishovite by Bassett & Barnett (1970) for a synthetically prepared sample. A value of $\rho_0 = 4{\cdot}288 \pm 0{\cdot}001$ g cm^{-3} was used in this study. Ahrens, Anderson & Ringwood (1970) report a preliminary value of the volumetric thermal expansion of stishovite, $\alpha = (15 \pm 2) \times 10^{-6}\,{}^{\circ}\mathrm{K}^{-1}$, measured by J. S. Weaver. Holm, Kleppa & Westrum (1967) measured the heat capacity of stishovite at constant pressure using cyrogenic calorimetry in the temperature range 5–300° K. The results at 298° K are $C_p = (0{\cdot}715 \pm 0{\cdot}002) \times 10^7\,\mathrm{erg\,g^{-1}\,{}^{\circ}K^{-1}}$. In addition, these investigators reported a measurement of the difference in enthalpy between α-quartz and stishovite at 298° K and zero pressure of $\Delta H_{298^{\circ}\mathrm{K}} = 11{\cdot}8 \pm 0{\cdot}3$ *K*cal/mole. This value represents the energy of transition ΔE_{tr}, between the specific internal energies of the low-pressure α-quartz phase and the high-pressure stishovite phase at ambient conditions. The foregoing data represent all the necessary ancillary values required by the Hugoniot data reduction procedure which is described in the following section.

Shock-wave data analysis

The pressure-density relation for a material that undergoes a shock-induced phase transformation has been described by McQueen, Marsh & Fritz (1967) and Ahrens *et al.* (1969). A convenient approach is to reduce first the experimental raw Hugoniot data to a metastable Hugoniot, which represents the experimental shock-wave data centred on the ambient initial density of the high-pressure phase. It is then possible to derive, in accordance with a selected equation of state, the isentrope and isotherm of the high-pressure phase. The isentropic and isothermal material properties are specified by the form of the equation of state. In the present analysis, it was possible to make use of the fact as previously described, that the stishovite Hugoniot data are linear in the shock-velocity–particle-velocity ($U_S - u_p$) plane, up to 2 Mbar, within experimental error. The parameters of the $U_S - u_p$ relation, when combined with the first-order Murnaghan equation, directly yield the appropriate elastic properties of the stishovite phase.

The procedure followed in this study is analogous to the reduction scheme used by Graham & Ahrens (1972) in the interpretation of Hugoniot data representing a high-pressure phase of almandine-garnet. Initially, the basic experimental Hugoniot data of the stishovite phase is transformed into corresponding points consistent with the metastable Hugoniot. The appropriate relation (e.g. McQueen *et al.* 1963), which follows from the basic definition of the volume dependent Grüneisen parameter γ and the Rankine–Hugoniot relations (e.g. Rice, McQueen & Walsh 1958), may be written in the form

$$P_M = \left\{ P_H \left[1 - \frac{\gamma}{2} \left(\frac{\rho}{\rho_0} - 1 \right) \right] - \gamma\rho(E_0 - E_0{}^h) \right\} \div \left[1 - \frac{\gamma}{2} \left(\frac{\rho^h}{\rho_0} - 1 \right) \right], \qquad (1)$$

where ρ_0, E_0 and $\rho_0{}^h$, $E_0{}^h$ refer to the initial conditions for the low and high-pressure-phase (α-quartz and stishovite), and E represents specific internal energy. The volume dependent Grüneisen parameter, required in the foregoing equation, was evaluated in this study according to the relation derived by Pastine & Forbes (1968):

$$\gamma(x) = \frac{2x(1-x)\{\delta[s(1-x)-1]+2sx\}+2x^2[1-s(1-x)]+4x(1-x)^2\,v}{\begin{array}{r} 2(1-x)^3\,v+(1-x)^2\{\delta[s(1-x)-1]+2sx\} \\ +(1-x)(1+x)[1-s(1-x)]+\dfrac{2C_p}{\alpha C_0{}^2}[1-s(1-x)]^2 \end{array}}. \qquad (2)$$

In equation (2) $x \equiv \rho_0/\rho$ (stishovite phase), C_p is the specific heat at constant pressure, and α is the thermal expansion. The relation is exact, provided that the shock-velocity may be expressed rigorously by $U_S = C_0 + su_p$ along the Hugoniot. The factor δ is the 'Anderson–Grüneisen' parameter and may be defined as

$$\delta = \frac{1}{\alpha K^S} \left(\frac{\partial K^S}{\partial T} \right)_{p=0} \qquad (3)$$

where K^S is the adiabatic bulk modulus. In addition, the parameter ν is given by

$$\nu = \frac{1}{\alpha}\left(\frac{\partial s}{\partial T}\right)_{p=0}. \tag{4}$$

Several other expressions for the volume dependent Grüneisen parameter have been in frequent use by previous investigators in the reduction of shock-Hugoniot data (e.g. Slater 1936; Dugdale & MacDonald 1953; Ahrens *et al.* 1970). The advantages of using the particular form given by equation (2) accrue from consistency in usage of the linear $U_S - u_p$ relationship, and the basic derivation of the relation in terms of the thermodynamic definition $\gamma = V(\partial P/\partial E)v$ rather than an empirical model. These aspects have been discussed by O'Keeffe (1970) and Graham & Ahrens (1972).

The use of equations (1) and (2) is dependent upon whether or not the various parameters appearing in the relations may be evaluated. Well defined experimental values of ρ_0, C_p, α, and the energy of transition $\Delta E_{tr} = E_0 - E_0{}^h$, are available for stishovite and have been indicated. The Anderson–Grüneisen parameter δ, defined by equation (3), may be calculated directly by a least-square fit of the volume dependent Grüneisen relation to the porous and fused-quartz data indicated in Fig. 2. In addition, as is apparent from the definition of δ, the resulting value may be used to calculate a value of $(\partial K^S/\partial T)_p$ for stishovite. The quantity ν appearing in equation (2) is difficult to evaluate as it is dependent upon the parameter $\partial^2 K^S/\partial T\partial P$. However, an approximation has been suggested by Pastine (1970) in the form

$$\nu \simeq \frac{s}{4}(\gamma_0 + 2 - s),$$

where γ_0 is the ambient value of the Grüneisen parameter. The above estimate is based on calculations carried out for cubic solids; however, Pastine (1970) points out that it seems likely that the accuracy of the related calculations will remain undiminished for solids of different structure.

Having defined all the appropriate input parameters for stishovite required in equation (2), it is possible to reduce the fundamental Hugoniot data to the metastable Hugoniot by means of equation (1). However, because values for C_0, s, and δ, which appear in the volume dependent Grüneisen parameter relation, are unknowns to be evaluated, an iteration procedure has been adopted. Initial values of C_0, s, and δ were arbitrarily defined in order to evaluate equation (2) and thereby afford calculation of the metastable Hugoniot. The data on the metastable Hugoniot were then transformed into the shock-velocity–particle-velocity plane using the appropriate Rankine-Hugoniot relations (e.g. Rice *et al.* 1958). It has been shown by Ruoff (1967) that if data in the $U_S - u_p$ plane can be adequately represented by $U_S = C_0 + su_p$, and if an equation of state is assumed that is based on a bulk modulus variation with pressure of the form $K^S = K_0{}^S + (\partial K^S/\partial P)_0 P$, then the following relations between the $U_S - u_p$ coefficients and the material elastic properties result:

$$K_0{}^S = \rho_0 C_0{}^2 \tag{5}$$

and

$$(\partial K^S/\partial P)_S = 4s - 1. \tag{6}$$

In this case, the bulk modulus-pressure relationship implies the familiar first-order Murnaghan equation of state (Murnaghan 1944). The parameters C_0 and s are evaluated by a linear least-square fit to the metastable Hugoniot $U_S - u_p$ data and thus afford a convenient and straightforward calculation of the error in $K_0{}^S$ and $(\partial K^S/\partial P)_S$. In addition, $(\partial K^S/\partial P)_S$ may be converted to the mixed derivative by the usual relation

$$(\partial K^S/\partial P)_T = (\partial K^S/\partial P)_S + \alpha T \gamma_0 \delta, \tag{7}$$

where T is the absolute temperature. In the iteration procedure followed, new values for C_0 and s were generated for each successive repetition; these values were used in turn to evaluate $\gamma(\rho)$ in the following iteration. The procedure was simply repeated until convergence was attained.

The foregoing procedure was initially carried out for values of the Anderson–Grüneisen parameter (δ) equal to 4, 6, 8 and 10. The resulting volume dependence of the Grüneisen parameter for each case is indicated in Fig. 2. Based on these calculated curves, a value of $\delta = 7 \pm 1$ was determined by minimizing the standard deviation of the porous and fused-quartz experimental data. This value of δ was then used for the final calculation of the elastic properties of stishovite using again the described iteration procedure. The results are: $K_0{}^S = 3{\cdot}35 \pm 0{\cdot}19$ Mbar; $(\partial K^S/\partial P)_T = 5{\cdot}5 \pm 0{\cdot}6$; and $(\partial K^S/\partial T)_p = -0{\cdot}35 \pm 0{\cdot}08$ Kbar/°K.

The values of $K_0{}^S$ and $(\partial K^S/\partial P)_T$ are based on the Hugoniot data of α-quartz from separate studies by Wackerle (1962), Al'tshuler *et al.* (1965), and Trunin *et al.* (1971). In order to weight the data from each of these sources appropriately for the final calculations, each set initially was reduced independently. Individual standard deviations in the $U_S - u_p$ plane were calculated thereby for each source; these formed the basis for weighting the various data sets in the final analysis. The metastable Hugoniot data for stishovite in the $U_S - u_p$ plane, and the linear fit providing the final elastic properties listed above, are indicated in Fig. 5. The precision in the data of Al'tshuler *et al.* (1965) and Trunin *et al.* (1971) is clearly superior to that of Wackerle (1962); the data were weighted in accordance with this observation.

The possibility exists that systematic error in the elastic properties of stishovite calculated from shock-wave data may result from an inherent 'strength effect'. This effect would occur if the material was shocked to a state along the deformational

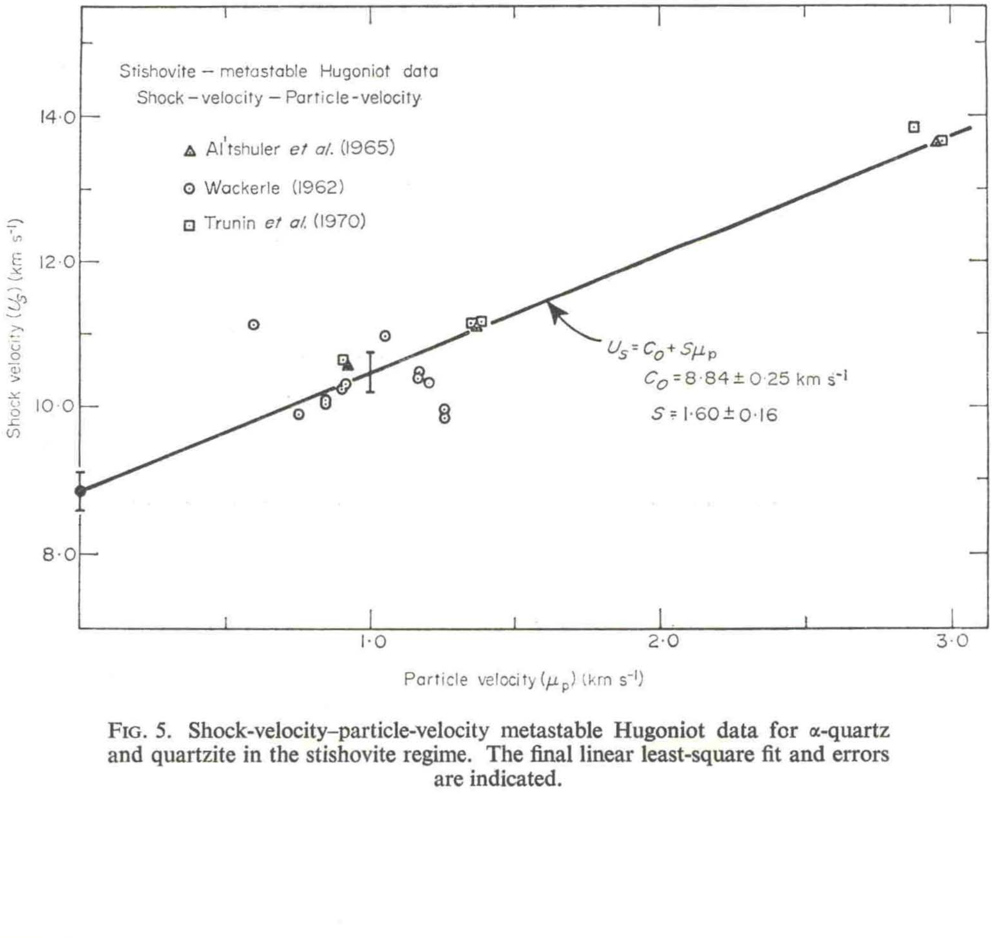

FIG. 5. Shock-velocity–particle-velocity metastable Hugoniot data for α-quartz and quartzite in the stishovite regime. The final linear least-square fit and errors are indicated.

Hugoniot, and was still able to support a finite shear stress. However, it has been suggested by Ahrens *et al.* (1969), that because the fundamental crystal structure undergoes complete rearrangement during a shock-induced phase transformation, it appears unlikely that an appreciable shear strength would characterize the high-pressure phase. In the case of α-quartz, shock-Hugoniot measurements to 230 Kbars by Fowles (1967) have demonstrated that the cohesion of the material apparently is destroyed upon yielding at the Hugoniot elastic limit (HEL); thus, there is no indication of a residual shear stress. Therefore, the assumption that shear strength offsets are negligible in the Hugoniot data of stishovite appears quite reasonable.

Equation of state considerations

The equation of state is of critical importance with respect to compositional aspects of the mantle. Several forms have been utilized to predict the compression of various materials to pressures characteristic of the lower mantle from low-pressure ultrasonic data (e.g. O. L. Anderson 1966; and Ringwood 1970); in addition, Anderson & Jordan (1970) have fit lower mantle pressure-density models directly to a particular equation of state in order to derive elastic properties characteristic of that region. Clearly, it is of significant importance to determine and understand the function of the form of the equation of state in the construction of meaningful compositional models of the Earth's interior. Because, there is abundant evidence that suggests the occurrence of silicon in the lower mantle in 6-fold co-ordination with oxygen, the equation of state of stishovite is of special interest.

A number of theoretical and empirical expressions have been proposed for the description of the equation of state of solids at high pressure. At present, theoretical equations of state contain a high degree of uncertainty because of the simplifying assumptions necessary for a tractable solution. Therefore, empirical equations have been used most extensively for geophysical applications. Most of these equations are based on a truncated Taylor expansion and can therefore be expressed in terms of an arbitrary number of parameters, corresponding to the order of the approximation. A most important implication of the use of such empirical expressions has been pointed out by Barsch & Chang (1970); since they are ' phenomenological ' equations, for a given number of parameters, which form is most appropriate for an accurate representation of experimental data over a specified pressure range can only be determined *a posteriori*, i.e. by comparison with the experimental data. This observation also has been noted by MacDonald (1969) who theoretically and statistically compared several polynomial and non-linear equations of state with experimental data sets. In this section, the results of the present analysis, incorporating the first-order Murnaghan equation of state, are compared with static-compression and ultrasonic data characterizing the zero to 250 Kbar range. In addition, the combined shock-wave, static-compression, and ultrasonic results are discussed in terms of the form of the equation of state; specifically, the shock-wave analysis of Ahrens *et al.* (1970) using the first-order Birch equation, and that of Davies (1972) involving a ' fourth-order Eülerian ' equation, are compared with the present results.

The isentrope defined by the present results according to the first-order Murnaghan equation of state

$$\rho(P) = \rho_0 \left[1+\frac{\beta^S P}{K^S}\right]^{1/\beta^S} \tag{8}$$

where $\beta^S = (\partial K^S/\partial P)_S$, is indicated in Fig. 1. Clearly, the elastic properties of stishovite, independently derived from the shock-wave Hugoniot data using the Murnaghan equation, are quite consistent with the preferred static compression data of Liu *et al.* (1971), to approximately 250 Kbar, as well as with the ultrasonic measurements of

Mitzutani *et al.* (1972). Therefore, the present reduction provides an adequate fit to the low to moderate-pressure range data. The calculated errors were based on normal error propagation involving the uncertainties in the elastic properties for stishovite determined from the shock-wave analysis.

The isentrope defined by the 'preferred' solution of Ahrens *et al.* (1970) also has been indicated on Fig. 1. These authors reduced the shock-wave Hugoniot data according to the first-order Birch equation, which may be written in the form

$$P(\rho) = \tfrac{3}{2}K^S[(\rho/\rho_0)^{7/3} - (\rho/\rho_0)^{5/3}]\left\{1 - 3\left(1 - \frac{\beta^S}{4}\right)[(\rho/\rho_0)^{2/3} - 1]\right\}, \tag{9}$$

in conjunction with an empirical function for the volume dependent Grüneisen parameter

$$\gamma = \gamma_0(\rho_0/\rho)^A \tag{10}$$

where A is an adjustable parameter. The pertinent results from the Ahrens *et al.* (1970) study are: $K^S = 3{\cdot}0$ Mbar; $(\partial K^S/\partial P)_S = 6{\cdot}86$; $(\partial K^S/\partial T)_P = -0{\cdot}50$ Kbar/°K; $\gamma_0 = 1{\cdot}58 \pm 0{\cdot}35$; and $A = 6$. This particular choice of the A parameter was predicted on the best fit to the Hugoniot data for porous and fused-quartz as indicated in Fig. 2. The physical significance of A in equation (10) may be understood in terms of the relation for γ given by equation (2). Equation (2) may be expanded in a series of the type

$$\gamma(\rho_0/\rho) = \gamma_0 - \gamma_0'(1-\rho_0/\rho) + 1/2\gamma_0''(1-\rho_0/\rho)^2 + \ldots \tag{11}$$

where

$$\gamma_0 = \alpha K^S/\rho_0 C_p$$

and

$$\gamma_0' = \gamma_0(\gamma_0 + 2 + \delta - 4s)$$

and the other parameters have been defined previously (e.g. Pastine & Forbes 1968). Expressing equation (10) in terms of an exponential expansion and comparing first order coefficients, it can be shown that

$$A \simeq \gamma_0 - \frac{1}{\alpha K^S}\left(\frac{\partial K^S}{\partial T}\right)_P - \left(\frac{\partial K^S}{\partial P}\right)_T + 1 \tag{12}$$

to first-order in compression. Substituting the appropriate values from the results of Ahrens *et al.* (1970) yields a value of $A = 6$.

Comparison of the isentrope of Ahrens *et al.* (1970) with the present results in Fig. 1 indicate equivalence within the indicated errors in the region of the shock Hugoniot data. However, examination of the Ahrens *et al.* (1970) results in comparison with the static-compression data of Liu *et al.* (1971) and the ultrasonic value of Mitzutani *et al.* (1972) suggest marginal discrepancy. The question arises as to whether the differences observed reflect real variation in the functional forms of the equations of state; or if they are simply the result of the use of different relations for the volume dependence of the Grüneisen parameter and/or different shock-wave data sets.

The conclusions of Ahrens *et al.* (1970) were based on the shock-wave Hugoniot data of Wackerle (1962) and Al'tshuler *et al.* (1965). In order to assess the extent to which the differing data sets affect the results, the present method of reduction was applied to the combined data of Wackerle (1962) and Al'tshuler *et al.* (1965) only. The results ($K^S = 3{\cdot}47 \pm 0{\cdot}28$ Mbar and $\partial K^S/\partial P = 4{\cdot}9 \pm 1{\cdot}1$) clearly are consistent with the previous calculations based on all the available shock-wave data. Fig. 3 graphically illustrates the differences in pressure ΔP between the isentropes calculated from the Wackerle–Al'tshuler (WA) data set and the Wackerle–Al'tshuler–Trunin (WAT) data set, as well as between the Ahrens *et al.* (1970) solution and the WAT results. In the range of the shock-wave data the isentropes are equivalent within the calculated error; however, in the lower pressure region the WA and WAT Murnaghan isentropes reflect the static-compression data more favourably.

The empirical form of the volume dependent Grüneisen parameter,

$$\gamma = 1{\cdot}58\ (\rho_0/\rho)^6,$$

used by Ahrens *et al.* (1970) is indicated in Fig. 2. It is apparent that the empirical form with the indicated parameters is reasonably consistent with the expression given by equation (2) when $\delta = 7$. Moreover, when the foregoing empirical relation is used in the present reduction scheme, rather than equation (2), the results are equivalent within the estimates of error. Thus, it appears that the discrepancies between the present results and the study by Ahrens *et al.* (1970) are not resolvable in terms of the Grüneisen relation or data sets; rather, the differences seem to reflect inherent dissimilarity in the forms of the equations of state and/or curve fitting procedure.

An isotherm calculated by Davis (1972) also is indicated in Fig. 1. In addition to the data considered in the present study, Davis (1972) included Hugoniot data for porous quartz samples in order to constrain the Grüneisen parameter. His preferred solution, case 2, shown in Fig. 1, involves a fit of the Hugoniot and static compression data to a fourth-order Eülerian equation of state. The results of that study are in agreement with the low-pressure data, but diverge somewhat from the present curve and that of Ahrens *et al.* (1970) in the high-pressure region. As suggested by Davies (1972), the essential differences between the analyses reflects his reliance on the porous Hugoniot data to constrain the Grüneisen parameter, while the present study utilizes Weaver's thermal expansion data. Davies (1972) also carried out an analysis using the latter alternative, the results of which, case 1, are consistent with the present study.

Comparison of the functional forms of the Murnaghan and Birch equations is possible in terms of the implied pressure dependences of the bulk modulus. The first-order Murnaghan equation is based on the assumption that the bulk modulus may be given by a linear function of pressure. In order that such an approximation be valid for a particular material implies that the sum total of the higher order terms be effectively zero over the range of pressure represented by the data. The form of the first-order Birch equation implies a fixed negative value of the quadratic term in the bulk modulus-pressure expansion. The foregoing results imply that for stishovite in the pressure range of zero to 2 Mbar, the linear relation in pressure affords a better approximation for the bulk modulus than a quadratic or higher-order expansion. A similar result was noted by Barsch & Shull (1971) in the case of NaI and KI; exact lattice-theoretical calculations for these materials indicate that the bulk modulus is more adequately represented by a linear function of pressure than a quadratic expansion over the pressure range 50 Kbar–1 Mbar.

Systematic relations of rutile-structure oxides

The elastic constants of single-crystal rutile-structure GeO_2 and TiO_2 have been measured as a function of pressure and temperature by Wang (1972) and Manghnani (1969). It is of interest to compare the present results for isostructural stishovite with the GeO_2 and TiO_2 data. A compilation of the pertinent measurements is indicated in Table 1. In Table 1 the single-crystal elastic data are represented by the Reuss average calculated by Wang (1972) and Manghnani (1969). It has been pointed out (e.g. Kumazawa 1969) that the Reuss average or single-crystal property, is to be identified with the density equation of state for the single-crystal or polycrystalline aggregate under conditions of high hydrostatic pressure. The elastic constants of polycrystalline TiO_2 have been measured by Chung & Simmons (1969) and are consistent with Manghnani's (1969) averaged values. In addition, the pertinent values for K^S, $(\partial K^S/\partial P)_T$, and $(\partial K^S/\partial T)_P$ have been plotted for stishovite, rutile, and

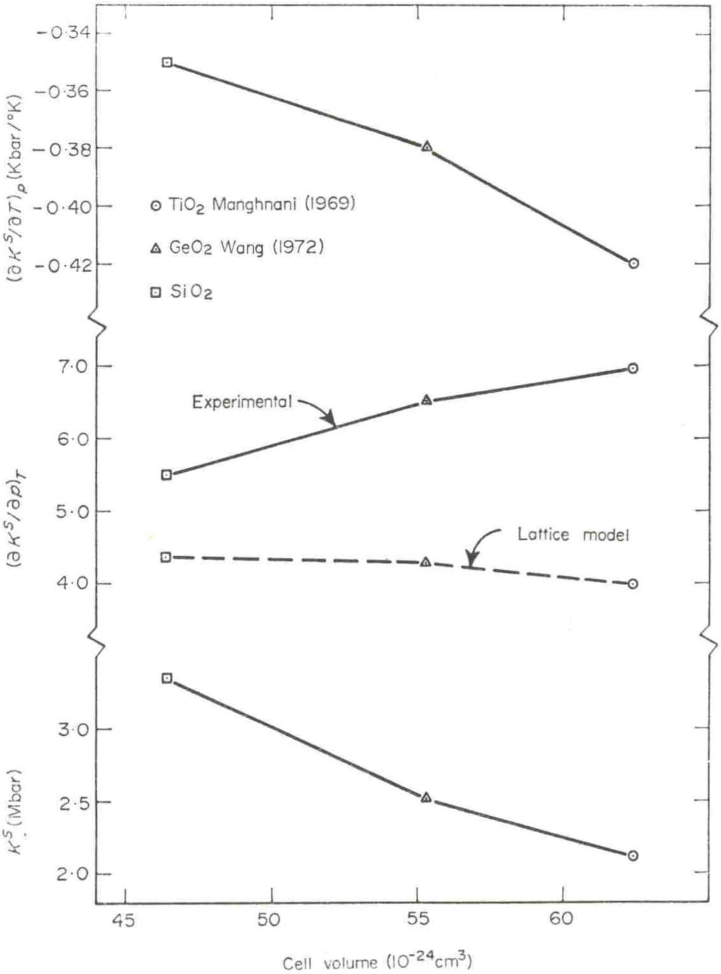

FIG. 6. Comparison of the bulk elastic properties of the isostructural oxides TiO_2 GeO_2, and SiO_2 in the rutile-structure with respect to volume per unit cell.

germania as a function of the volume per unit cell in Fig. 6. It is apparent that K^S and $(\partial K^S/\partial T)_P$ systematically decrease with increasing unit cell volume for the three isostructural oxides, while $(\partial K^S/\partial P)_S$ increases. The related behaviour between the ultrasonic and shock-wave results support, at least qualitatively, the accuracy of the latter.

On the basis of a lattice-theoretical model involving an interaction potential composed of Coulomb, van der Waals, and first and second nearest-neighbour repulsive forces, Barsch & Shull (1971) were able to explain semi-quantitatively that the first-pressure derivatives of the elastic constants of alkali halides depend almost exclusively on the ionic radius of the cation. Considering the analogous relation between the unit cell volume and $(\partial K^S/\partial P)_S$ for the rutile-structure oxides, it is tempting to relate the present results to a simple lattice model formulation. As a first approximation, the expression for the potential energy of interaction between the i^{th} and j^{th} ions may be written

$$U_{ij} = -\frac{Ze_i e_j}{r_{ij}} + \frac{A}{r_{ij}^n} \tag{13}$$

where Z represents an 'effective charge parameter'. The first term represents the usual Coulomb attraction, and the second the repulsive interaction. If the non-centrosymmetric aspects of the rutile structure are neglected, and the cohesive energy is regarded in terms of a single structural parameter represented by the volume, the total binding energy may be written

$$U(V) = -\tfrac{1}{2}N\left[\frac{\alpha_M Ze^2}{V^{1/3}} - \frac{B_n}{V^{n/3}}\right] \tag{14}$$

where α_M is the Madelung constant (defined in terms of the cube root of the volume per unit cell). The repulsion constant B_n, neglecting thermal effects, may be determined in the usual manner with respect to the ambient equilibrium volume V_0. In addition, differentiating equation (14) with respect to volume up to order three and equating the results with the definition of the bulk modulus and its first pressure derivative yields the result

$$(dK^T/dP)_T = \tfrac{2}{3}\left[\frac{9V_0^{4/3}K_0^T}{N\alpha_M Ze^2} + 4\right] \tag{15}$$

Equation (15) may be used, as a first approximation, to predict dK/dP for any primarily ionic structure if the bulk modulus K_0^T and unit cell volume V_0 are defined. A similar form has been used by Anderson & Anderson (1970) to predict dK/dP for pertinent mantle minerals.

Equation (15) has been used to predict values of $(\partial K^S/\partial P)_T$ for stishovite, rutile, and germania from the appropriate elastic and crystallographic data. The results are indicated in Fig. 6. Values of $(\partial K^S/\partial P)_T$, as calculated by equation (15), are considerably lower than the experimental results; in addition, the theoretical prediction suggests a fairly constant value of $(\partial K^S/\partial P)_T$ with respect to the various compounds, rather than the increase with increasing volume per unit cell as observed in the experimental data. The discrepancy between the experimental and theoretical results for $(\partial K^S/\partial P)_T$ suggests that the elementary lattice model, assuming the interaction potential given by equation (13), is an inadequate representation for rutile-structure compounds. Approximation of the model in terms of a single structural parameter (unit cell volume) is not consistent with the non-centrosymmetric space group of the rutile structure. In an analysis of the lattice dynamics of rutile-structure MgF_2, Katiyar (1970) found it necessary to minimize the total potential energy of the crystal with respect to the three structural parameters, a, c, and u, where the former represent the unit cell dimensions and u determines the positions of the anions. The importance of the non-centrosymmetric aspects of the rutile structure with respect to lattice dynamical models has also been pointed out by Gubanov & Shur (1966) and Sammis (1971). In addition, the inclusion of many-body forces and van der Waals and second nearest-neighbour interactions in the lattice model may be of importance for a more refined analysis. Lastly, meaningful values for the 'effective charge parameters' are not available; in the present formulation, values of Z for SiO_2, GeO_2, TiO_2 were defined using electronegativity differences in conjunction with Pauling's (1960) relation for percentage ionic character of a bond.

Implications concerning the composition of the lower mantle

The composition of the lower mantle has been discussed frequently in terms of a mixture of the fundamental oxides MgO, FeO, and SiO_2 (e.g. Ringwood 1969; Anderson & Jordan 1970). Much of the attention concerning the prevailing mineral assemblage has focused on whether the lower mantle has transformed to a state somewhat denser than the isochemical mixed oxides, or alternatively, if the lower mantle consists of a mineral assemblage with the density of isochemical mixed oxides, but with a higher iron content than the upper mantle. In order to correlate or compare possible component assemblages of the lower mantle in terms of requisite density and elastic properties, previous investigators have found it convenient to determine ρ_0 and the seismic parameter $\Phi_0 = K_0/\rho_0$ for the lower mantle by fitting various density distributions with the Birch equation. Considering the present results bearing on the equation of state of stishovite, it is pertinent to examine the procedures and results of compositional models of the lower mantle based on the assumption of a mixture of the isochemical oxides.

Anderson & Jordan (1970) fit pressure-density data for the lower mantle to the Birch equation by a least-squares procedure, thereby determining values for Φ_0 and ρ_0 representative of lower mantle material. It was assumed that the temperature gradient of the lower mantle approximates the adiabat. However, the results of the shock-wave analysis of stishovite have suggested that the compression of this material is reproduced more accurately by the first-order Murnaghan equation of state than the Birch equation. In the present case, the difference between the bulk modulus calculated by means of the Murnaghan and Birch equations is about 10 per cent. Thus the assumed form of the equation of state has a significant effect on the magnitude of the determined adiabatic constants. Until it is quite clear as to what equation of state is most appropriate for expressing the compression of lower mantle mineral assemblages, the results based on the foregoing assumptions and procedure should be regarded with caution.

In order to assess the iron content of the lower mantle, Anderson & Jordan (1970) used three different methods; these have been reviewed recently by Wang & Simmons (1972). The effect which may be associated with the selection of an inappropriate equation of state may be qualitatively illustrated by considering Anderson & Jordan's (1970) first approach.

Having determined ρ_0 and Φ_0 for a variety of lower mantle density models as outlined in the preceding section, the mean atomic weight $\overline{M}$, which reflects iron content, is derived from the seismic equation of state (Anderson 1967). This equation may be written in the form

$$\frac{\rho}{\overline{M}_i} = A_i \Phi^{n_i} \tag{16}$$

where the constants $A_1 = 0{\cdot}048$ and $n_1 = 0{\cdot}323$ refer to results obtained from 31 selected rocks and minerals, and $A_2 = 0{\cdot}0492$ and $n_2 = 0{\cdot}333$ reflect only close-packed oxides relevant to the interpretation of lower mantle data. Estimates of the composition of the upper mantle indicate an average $\overline{M}$ of about 21·1. By contrast, the estimates of $\overline{M}_1$ by Anderson & Jordan (1970) for the lower mantle, determined using the first-order Birch equation and seismic equation of state, range from about 22·4–23·4; the corresponding range for $\overline{M}_2$ is about 21·0–22·0. Thus, as Anderson & Jordan (1970) point out, marginal evidence for an increase in iron content in the lower mantle, relative to the upper mantle, is suggested. However, if the value of Φ_0 is in error by 10 per cent, this, in itself, results in a 5 per cent uncertainty in the value of $\overline{M}$. Recognition of uncertainties of this magnitude associated with the calculated values of $\overline{M}_1$ and $\overline{M}_2$ reduce the reliability of conclusions regarding iron enrichment of the lower mantle based on the foregoing procedure.

A second method used by Ringwood (1969) and Anderson & Jordan (1970) involves comparing the density and elasticity of the isochemical oxide mixture MgO–FeO–SiO_2 with lower mantle data. The conclusions resulting from this approach are obviously dependent on the uncertainties associated with the corresponding values of Φ_0 adopted for the various oxides, especially that of stishovite. Therefore, it is of interest to review the conclusions of Anderson & Jordan (1970)

Table 1

Comparison of elastic and crystallographic data for rutile-structure SiO_2, TiO_2, and GeO_2

	SiO_2	GeO_2	TiO_2
ρ_0 g cm^{-3}	4·288	6·279	4·260
$V_c{}^a$ (10^{-24}) cm^3	46·4	55·3	62·4
$K^{S\,b}$ *Kbar*	3350	2511	2109
$(\partial K^S/\partial P)_T{}^b$	5·5	6·48	6·94
$(\partial K^S/\partial T)_P{}^b$ *Kbar/°K*	−0·35	−0·38	−0·42

a Unit cell volume.
b single-crystal data is represented by the Reuss average of the C_{ij} elastic constants.

with respect to the iron content of the lower mantle in view of the value of Φ_0 for stishovite, $78{\cdot}1 \pm 4{\cdot}4$ (km s^{-1})^2, as determined in the present study.

It is assumed that the molar volumes and seismic parameters of lower mantle minerals can be considered to be molar averages of the oxides (Anderson 1969). Thus, both the composition and mineralogy of the lower mantle can be determined by comparing the density and Φ_0, inferred from the fit of lower mantle data to the Birch equation, to those predicted for the dense forms of upper mantle minerals. The basic plot of ρ_0 vs Φ_0 by Anderson & Jordan (1970) is reproduced in Fig. 7 with respect to the olivine and pyroxene systems. In addition, the appropriate values of Φ_0 and ρ_0, representing the high-pressure forms of $MgSiO_3$ and $Mg_2\,SiO_4$ calculated from the stishovite results of the present study, are indicated for comparison. The points Birch II and 200204 represent the preferred solutions of Anderson & Jordan (1970) for the values of Φ_0 and ρ_0 for the lower mantle. By combining these values inferred for the lower mantle, estimates may be made for mole per cent olivine, pyroxene, SiO_2, MgO, and FeO. In the present analysis, the following values were used for the component oxides: SiO_2, $\rho_0 = 4{\cdot}288$ g cm^{-3} and $\Phi_0 = 78{\cdot}1 \pm 4{\cdot}4$ (km s^{-1})^2; MgO, $\rho_0 = 3{\cdot}584$ g cm^{-3} and $\Phi_0 = 45{\cdot}3$ (km s^{-1})^2 (Chang & Barsch 1969); and FeO, $\rho_0 = 5{\cdot}948$ g cm^{-3} and $\Phi_0 = 27{\cdot}8$ (km s^{-1})^2 (Mitzutani *et al.* 1972). Oxide compositions were determined by linear interpolation on an MgO–FeO–SiO_2 triangle superimposed on the $\rho_0 - \Phi_0$ plot. Results of the present analysis for the Birch II and 200204 models are compared with the conclusions of Anderson & Jordan (1970) in Table 2.

Table 2

Composition of the lower mantle (mole fraction)

Model Birch II	Anderson & Jordan (1970)	Present analysis
olivine	0·57	0·05−0·68
pyroxene	0·43	0·95−0·32
SiO_2	0·39	0·47±0·04
MgO	0·49	0·38±0·03
FeO	0·12	0·15±0·03
Model 200204		
olivine	0·20	0−0·32
pyroxene	0·80	* >1·00−0·68
SiO_2	0·46	0·53±0·04
MgO	0·38	0·26±0·03
FeO	0·16	0·21±0·03

* Excess silica.

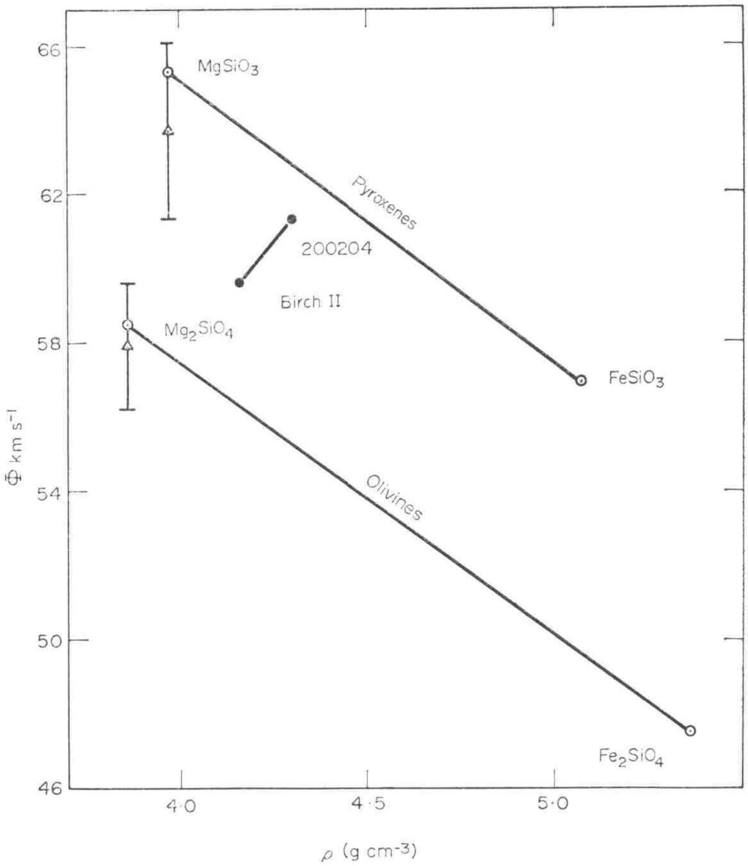

FIG. 7. Molar averaging scheme for estimating composition of the lower mantle from Φ_0 and ρ_0 values of olivine and pyroxene based on isochemical mixtures of the oxides FeO, MgO, and SiO_2 (after Anderson & Jordan 1970).

The results of the present review indicate ranges in oxide content for the two models of 47–53 mole per cent SiO_2, 26–38 mole per cent MgO, and 15–21 mole per cent FeO. The estimated uncertainties are indicated also in Table 2. When compared with the corresponding values for ultramafic rocks (White 1967) of 38 per cent SiO_2, 52 per cent MgO, and 6 per cent $FeO+\frac{1}{2}Fe_2O_3$, these results are consistent with those of Anderson & Jordan (1970) and Anderson (1970) in suggesting that the lower mantle is enriched in FeO and SiO_2 relative to the upper mantle. These results assume, of course, that the $\rho_0-\Phi_0$ points represented by the Birch II and 200204 models are representative of lower mantle material properties. In this regard, an uncertainty of ± 10 per cent in the values of Φ_0 still allows marginal recognition of the basic conclusions of Anderson & Jordan (1970). However, the possible inaccuracy in the model values of ρ_0 is not clear. Uncertainty in the calculated value of the initial ambient density for the lower mantle can arise from several sources: vertical inhomogeneity in lower mantle assemblages; a super-adiabatic temperature gradient; use of an inappropriate equation of state; and, inaccuracy associated with the selected density distribution. For example, considering the latter source only in terms of the results of Anderson & Jordan (1970), satisfactory fits were obtained for a number of density distributions yielding a range of values for ρ_0 of 4·08 (Birch I) to 4·30 (200204). This corresponds to a range in iron content of 6–21 mole per cent FeO. Thus, again, consideration of the uncertainties involved indicates iron enrichment of the lower mantle, but the evidence is marginal.

The present analysis, emphasizing the uncertainties in the equation of state and elastic properties of stishovite, suggests that the conclusions of Anderson & Jordan (1970) and Anderson (1970) concerning iron enrichment in the lower mantle are plausible within the accuracy of the material property data. Basic assumptions regarding homogeneity, temperature gradient, and density in terms of an isochemical mixture of oxides remain to be verified. In this regard, it should be emphasized that the preceding evaluation and conclusions are relevant to the explicit assumption that the lower mantle can be represented by a mixture of the component oxides, MgO, FeO, and SiO_2 only. Granting this supposition, it is reasonable to conclude that the most probable solution indicates an increase in FeO/FeO+MgO relative to the upper mantle, although this is not strictly required if the full uncertainty range is considered. An evaluation of the alternative suggestion, that the elastic properties of the lower mantle reflect phases involving more closely-packed structures than the component oxides (i.e. Ringwood 1968), is obviously not possible with the present set of material property data.

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