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EVALUATION OF EQUATION OF STATE DATA

Thomas J. Ahrens, et al

California Institute of Technology
Pasadena, California

January 1970

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Thomas J. Ahrens

Final Report

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DEFENSE ATOMIC SUPPORT AGENCY
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13. ABSTRACT

Equations of state, or constitutive equations, provide a complete mechanical as well as thermodynamic description of material. An equation of state relates stress or pressure, strain or density, and one or more thermodynamic variables, such as internal energy, or temperature, for a specific material. Equations of state for earth materials are necessary for the calculation of intense stress-wave propagation and seismic coupling resulting from explosions or impacts on or within the earth's crust. Because of the wide range of dynamic pressures which are induced within the vicinity of a nuclear explosion, the equations of state which are of interest will describe the response of a medium over a range of conditions from thousands of kilobars and tens of thousands of degrees down to a fraction of a bar and ambient temperature; the latter conditions correspond to large distances from the disturbance.

The present program has been concerned with the analysis of a large body of published data obtained by shock-wave techniques which describe the dynamic behavior of a number of earth materials below 2 megabars. Most of these data are expressed in terms of Hugoniot curves, however the authors have used additional data such as composition of the rocks or minerals involved, thermodynamic properties, and attempted to examine the systematics of the equations of state of these materials. The authors have also reduced the shock-wave data which, in general, are in terms of a pressure-volume-energy relation to the more conventional pressure-volume-temperature variables.

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I. Introduction

Equations of state, or constitutive equations, provide a complete mechanical as well as thermodynamic description of material. An equation of state relates stress or pressure, strain or density, and one or more thermodynamic variables, such as internal energy, or temperature, for a specific material. Equations of state for earth materials are necessary for the calculation of intense stress-wave propagation and seismic coupling resulting from explosions or impacts on or within the earth's crust. Because of the wide range of dynamic pressures which are induced within the vicinity of a nuclear explosion, the equations of state which are of interest will describe the response of a medium over a range of conditions from thousands of kilobars and tens of thousands of degrees down to a fraction of a bar and ambient temperature; the latter conditions correspond to large distances from the disturbance.

The present program has been concerned with the analysis of a large body of published data obtained by shock-wave techniques which describe the dynamic behavior of a number of earth materials below 2 megabars. Since most of these data are expressed in terms of Hugoniot curves, we have used additional data such as composition of the rocks or minerals involved, thermodynamic properties, elastic properties, crystal structure and strength measurements, and attempted to examine the systematics of the equations of state of these materials. We have also reduced the shock-wave data which, in general, are in terms

of a pressure-volume-energy relation to the more conventional pressure-volume-temperature variables.

II. A Review of Equation of State Data for Earth Materials Pertinent to Seismic Coupling

Equation-of-state data are obtained in the very high pressure range -- the hydrodynamic regime -- with both explosive and hypervelocity impact shock wave techniques. Because the magnitude of the principal stresses (for example, the radial stress in spherical shock propagation) far exceeds any possible stress differences supportable by the medium, a fluid-like behavior is usually assumed in this regime. Although the formulation of the equation of state in this regime lacks the complications arising from material strength, the fact that many minerals, in particular the silicates (and rocks containing silicate minerals) undergo solid-solid (polymorphic) transitions (Boyd, 1964 and Ringwood, 1969) turns the formulation of a complete equation of state into a challenging problem. In addition, as a result of the high temperatures which accompany the high pressures in the hydrodynamic experiments, descriptions of partial or complete transformation of rocks or minerals into liquids and/or gases are required.

At distances far enough from the source that the dynamic stress levels are below the dynamic yield strength of the medium, an elastic type of behavior is usually assumed, as a first approximation, for the material. In the elastic regime the equations of state are usually

derived from laboratory low amplitude shock, acoustic (ultrasonic), and quasi-static pressure-volume experimental data.

Over a range of intermediate stress levels (e.g. tens to hundreds of kilobars), dynamic yielding of rocks and minerals is usually encountered. Experimentally it is observed that for a range of shock stresses, a single shock wave transmitted into the material will break into an elastic and a deformational shock front. These shock fronts are thought to represent the onset of dynamic uniaxial compressions; these are achieved by essentially elastic and deformational strain, respectively. Of special importance in this regime is the relation of stresses parallel and perpendicular to the stress wave propagation direction during and after the material has been encompassed by the deformational shock front.

Relevant to the development of complete equations of state for rocks and minerals are contributions from the following sources:

1. Shock wave experiments
2. Experiments on the strength of rocks and minerals
3. Static pressure-volume experiments
4. Dynamic elastic and anelastic experiments
5. Thermodynamic measurements
6. Consideration of the form of equations of state

The contributions from these sources are outlined below:

1. Shock wave experiments

The type of shock wave data most available for solids including rocks and minerals are Hugoniot curves. The Hugoniot*, which is usually depicted in the pressure-volume plane, represents the locus of states that a material may achieve upon shock compression from some initial state. This locus represents a property of the material and is not intrinsically related to the technique employed in achieving the shock states. The Hugoniot curve which is most often measured is termed the principal Hugoniot; this corresponds to an initial material state at normal temperature and pressure. However, Hugoniot curves other than the principal Hugoniot can be, and have been, measured.

Hugoniot data are obtained in a series of experiments in which plane shock waves (for which the pressure profiles are approximated by step functions) are driven into a series of material samples. These plane shock waves produce dynamic one-dimensional compression in the solid. The quantities usually measured in such experiments, either by optical or electronic techniques, are the shock and particle velocities. These velocities, and the initial density, when introduced into the Rankine-Hugoniot conservation equations give the shock pressure, density, and change in internal

*Often called the dynamic adiabat in the Soviet literature

energy produced by the shock wave. This type of experiment is repeated using varying incident shock pressures, thereby tracing out the entire Hugoniot curve. The Hugoniot curve then represents a pressure-density curve along which the internal energy varies in a known way. This is somewhat different than the case of an isotropic or an isothermal pressure-density curve for which the entropy and temperature are fixed, respectively.

At least one shock pressure range exists in all rocks and minerals in which the final high pressure shock state is achieved by two (and in some cases more) shock fronts. Multiple shock fronts arise from dynamic yielding or shock-induced polymorphism. In the case of dynamic yielding, the amplitude of the resulting shock front is called the Hugoniot elastic limit (HEL). The HEL represents the maximum normal stress that the material can withstand under one-dimensional compression without internal rearrangement taking place at the shock front. The HEL is thus an important measure of the stress which the material may withstand under shock compression. It therefore serves as a useful parameter in formulation of an equation of state which takes into account the strength of the material. HEL data have been compared to static and quasi-static strength data in order to formulate a complete yield criteria.

Hugoniot data for rocks and minerals are often tabulated in terms of the quantities measured in the experiments, shock and particle velocity, as well as in terms of pressure and density; the latter are useful in formulating complete equations of state.

MgO
MgO-ADIABATS
γ=1.46
γ=1.48
γ=1.50
γ=1.52
γ=1.54
γ=1.56
γ=1.58
γ=1.60
Pressure, kb
70
60
50
40
30
20
10
0
0.277
0.279
0.281
Volume
0.283
cm³/g
0.285
0.287
0.289
400°K
600°K
700°K
900°K
1000°K

Figure 4

Hugoniot data reported to 1963 which included a few rocks are tabulated by Rinehart (1965). A more recent and complete tabulation, which includes recent Soviet and Los Alamos results, is given by van Thiel (1966). Data gathered by McQueen and co-workers for a large number of non-porous rocks and minerals within the hydrodynamic regime is collected in Birch (1966) and some are described in detail by McQueen et al (1967b). Additional data in this regime are available from the work of Trunin et al (1965), Al'tshuler (1965) and Jones et al (1968). Hugoniot data for various rocks and minerals in the dynamic yielding regime are reported by Ahrens et al (1966), Ahrens (1969b), and Peterson et al (1969). Hugoniot data for porous rocks of interest to the Ferris-Wheel program are summarized in Flanagan (1966). Shock measurements on various porous geologic materials performed at Sandia Corporation and Los Alamos have been summarized by Bass (1966) and McQueen (1968). Our analysis of the shock-wave data has largely concentrated on developing equations of state at high-pressures for non-porous rocks and minerals.

Recently, experimental data delineating the release adiabats for high-pressure shock states of several geologic materials have become available. The release adiabat curves represent the succession of states through which a mass element brought to high pressure by a shock front, i.e. shocked to a Hugoniot state, passes through upon being returned to ambient pressure and achieving

a post-shock volume. Hence, a family of release adiabat curves exists for each Hugoniot curve.

A limited number of release adiabat data have been reported by Weidermann (1964), Anderson et al (1966), for porous materials and for solid materials by Ahrens (1968), Ahrens et al (1968), Rosenberg et al (1968), and Peterson et al (1969). Although this type of data is somewhat more difficult to obtain experimentally, it is of considerable interest from materials which upon shock compression, either undergo irreversible mechanical crushing or irreversible phase changes accompanied by large changes in volume.

2. Experiments on the Strength of Rocks and Minerals

A considerable body of data relating to the mechanical strength properties of rocks as a function of rock structure, stress state, strain rate, and moisture content, has recently been summarized by Walsh and Brace (1969). Earlier tabulations of the data in this area are available through the AFCRL Bibliography of Rock Deformation (Riecker et al, 1965, 1966). Data on the strength of a wide class of rocks and minerals under stresses up to ~ 40 kb have been summarized by Handin (1966). The work of Brown et al (1967) who have obtained stress-strain curves from various rocks under one-dimensional static compression -- the same geometry as in shock experiments -- is also of special interest. In addition, we have found the recent work of Towle and Riecker (1968) on the shear strength of minerals at high temperature and pressure useful in reducing the shock-wave data (See Section III-2).

3. Static Pressure - Volume Measurements

We have found that comparison of high-pressure volume data with Hugoniot data is useful for evaluating the effect of material strength under shock loading conditions. Isothermal-pressure-volume data for series of porous and solid rocks and minerals have been obtained with piston-cylinder type apparatus. These have been reported by Stephens (1964), Stephens and Lilley (1966), LaMori (1967) and La Mori (1968). The earlier data of Bridgman (tabulated in Birch, 1966) most of which is below 30 kb, is in several instances the only static data available for a given mineral. Drickamer (Perez-Albuerne, and Drickamer, 1965, Lewis and Drickamer, 1966) and McWhan (1967) have obtained an important series of pressure-volume curves for oxides to approximately 40 kb using high pressure X-ray techniques. More recently the work of the high-pressure X-ray group at Rochester (Bassett et al, 1968; Bassett and Barnett, 1959; Mao et al, 1969; Liu et al, 1969) have significantly increased our knowledge of the pressure-volume behavior of high pressure polymorphs of the silicates.

4. Dynamic Elastic and Anelastic Experiments

The measurements of elastic wave velocities and elastic moduli of rocks and minerals are summarized by Birch (1966), and Anderson and Liebermann (1966), and for a wide range of compounds by Simmons (1965) and for oxides, Anderson et al (1968). Measurements of elastic moduli to pressures of 10 kb at temperatures of 800°C are now possible and have been carried out for selective materials

which may be used with ultrasonic measuring techniques (see for example, Spetzler, 1969 a, b).

The attenuation of stress waves in the seismic or so-called elastic regime is controlled by the small intrinsic anelastic properties of geologic materials as well as the extrinsic loss of energy due to internal interfaces such as joints, faults, and bedding surfaces which occur in virtually all crustal rocks. Data for various engineering materials and for rocks obtained from laboratory measurements to about 1964 are reviewed by Knopoff (1965a). Additional data particularly for porous and sedimentary rocks are included in a data compilation given by Bradley and Fort (1966). Various anelastic mechanisms in the earth have been discussed by Savage (1964), Gordon and Nelson (1966), and Merkulova (1966). More recently, a review of pertinent anelastic data for ceramics and geologic materials has been prepared by Jackson and Anderson (1969).

5. Thermodynamic Measurements

The specification of states which are displaced from the normally measured pressure-volume curves in the pressure-volume plane, such as the principal Hugoniot, requires supplementary data such as the Gruneisen ratios and the volume expansion coefficient. Also, shock temperature calculations require knowledge of specific heat, usually assumed to be a function of volume and temperature. In order to extend the equation of state through a regime where a

solid-solid transition, melting or perhaps vaporization takes place, supplementary data such as the enthalpy of the appropriate species are required.

Thermodynamic data for minerals at standard conditions are given by Robie (1966 and 1968). Thermal expansion data for minerals are tabulated by Skinner (1966). High temperature enthalpies for many of the species found in earth materials are available in the Janaf Tables (Stull et al, 1965). Debye-temperatures and the acoustic Gruneisen's ratio are extrapolated from ultrasonic data such as summarized by Anderson and Liebermann (1966), Anderson (1968), and Anderson et al (1969).

6. Equations of State

Hugoniot and other forms of equation of state are usually formulated in terms of expressions containing 1, 2, or more adjustable parameters. These relate pressure to density along a particular curve (Hugoniot) or a thermodynamic path (adiabat or isotherm). States along different pressure-volume curves, such as, for example, two states differing in internal energy, E, and pressure, P, at the same, V, are often related by the Mie-Gruneisen equation

$$P - P_K = \frac{\gamma}{V} (E-E_K) \qquad (1)$$

P_K and E_K are the pressure and energy along some reference curve. Here γ is the Gruneisen ratio which may, at high temperatures, be independent of temperature. (For silicates, $\gamma = (\partial P/\partial E)_V$, at around room temperature, probably depends on temperature as well as volume.) For metals it is often assumed that γ depends only on volume. Among the more often used equations of state are the Murnaghan equation

$$P = (K_o/n)[x^{3n}-1] \tag{2}$$

and the Birch-Murnaghan second order equation

$$P = A(X^7-X^5) - B\,(X^7-X^5)(X^2-1) \tag{3}$$

which as Thomson (1969) has pointed out, corresponds to assuming a Eulerian form for the strain in finite strain theory. Here K_o and n, and A and B are adjustable parameters and

$$X = (\rho/\rho_o)^{1/3} = (V_o/V)^{1/3} \tag{4}$$

where ρ_o and ρ are the initial and final density and V_o and V are the initial and final volume. Equation 3 may be written as

$$P = \frac{3K_o}{2} [X^7 - X^5][1 - \xi(X^2 - 1)] \qquad (5)$$

where $K_o = 2A/3$ is the bulk modulus, $\xi = B/A$ and $K_o' = (dK_o/dP)_o = 4 - \frac{4}{3}\xi$. Thomsen has recently discussed an alternate form of equation 5 corresponding to expressing the strain in the theory of finite strain in Lagrangian form. The equation which results is

$$P = \frac{3}{2} K_o [X - X^{-1}] [1 - \frac{3}{4} K_o' (X^{-2} - 1)] \qquad (6)$$

Equation 6 gives a similar pressure-volume curve as Equation 5 for compressions, ρ/ρ_o, of less than 1.2. Some difficulties are, however, noted in applying this equation to pressure volume data; these are described in Section III-4. In the above equations the zero-pressure bulk modulus, K_o is related to a bulk sound speed, C_o, and seismic parameter, ϕ, by

$$K_o/\rho_o = C_o^2 = \Phi \qquad (7)$$

As indicated, K_o' is the pressure derivative of the bulk modulus. In practice it is simpler to use the Birch-Murnaghan equation to fit a series of P-V data or a series of calculated P-V points than it is to use the Murnaghan equation because in equation 2 the exponents of X are fixed and hence evaluation of the parameters A and B involves only the solution of a series of linear simultaneous

equations.

It should be noted that both the Birch-Murnaghan and Murnaghan equations place restraints on the high-order parameter $\partial K/\partial P$ along the curve which they define in the P-V plane. The Murnaghan equation $\partial K/\partial P$ is a constant while in the Birch-Murnaghan equation the derivative $\partial^2 K/\partial P^2$ is fixed by the form of equation 5.

Another two-or three-parameter equation may be obtained from the often-used linear or quadratic shock (U_s) and particle velocity (U_p) relation

$$V_s = C_o + S_1 U_p + S_2 U_p^2 \tag{8}$$

where C_o represents the bulk sound speed and S_1 and S_2 are equation of state parameters. In a case of a two-parameter, linear equation ($S_2 = 0$) it follows from the Rankine-Hugoniot shock equations that

$$P = C_o^2 \, (V_o - V)/[V_o - S_1 (V_o - V)^2] \tag{9}$$

Equation 9 is particularly well-suited for fitting raw Hugoniot data. However, the thermodynamic strains posed by the linear U_s and U_p relation, which have been recently discussed by Ruoff (1967) reduces the usefulness of this relation by forms of equations of state other than the Hugoniot. For the three-parameter equation

$$P = \frac{C_o^2\ (1-V/V_o)}{V_o\ [1-S_1\ (1-V/V_o)]^2} \left[\frac{1 + S_2 P V_o (1-V/V_o)}{2C_o} \right]^2 \qquad (10)$$

Recently, Pastine and Forbes (1968) have shown that for a Mie-Gruneisen type of equation of state, i.e. $(\partial\gamma/\partial E)_V = 0$ the coefficients in the expansion of γ with volume ratio is given by

$$\gamma = \gamma_o - \gamma'\ (1-X^3) + \frac{1}{2}\gamma''\ (1-X^3)^2 - \frac{1}{6}\ \gamma'''\ (1-X^3)^3 + \ldots \qquad (11)$$

The coefficients of equation 11 are related to thermodynamic properties of the material which are measured at ambient pressure and high-temperature. The ambient value of Gruneisen's ratio, γ_o is related to the thermodynamic properties.

$$\gamma = \alpha K_s/\rho\ C_p \qquad (12)$$

where α is the coefficient of thermal expansion, K_s is the adiabatic bulk modulus, and C_p is the specific heat at constant pressure. The first coefficient in equation 11 is given by

$$\gamma' = \gamma_o \left(\gamma_o + 3 - \frac{2}{\alpha C_o} \left(\frac{\partial C_o}{\partial T} \right)_{P=0} - 4S_1 \right) \qquad (13)$$

where S_1 is either obtained experimentally from shock-wave experiments or from ultrasonic measurements using the relation

$$S_1 = \frac{1}{4}\left[\left(\frac{\partial K_s}{\partial P}\right)_s + 1\right] \tag{14}$$

Recently, Thomsen (1969) has formulated a three-parameter equation of state also based on finite strain theory which treats the Gruneisen parameter γ, $(\partial K/\partial T)_p$, and $\partial^2 K/\partial P^2$ in a self-consistent way. This three-parameter relation is given by

$$P = 3\tilde{K}\,(\tilde{a}/a)\left[\eta - \frac{3}{2}\eta^2\Gamma + \frac{3}{2}\eta^3\Lambda\right] + E_T\tilde{a}/(a\tilde{V})\ \mathrm{x}$$

$$\left\{\tilde{\gamma} + 3\eta\left[\lambda - \tilde{\gamma}^2\,(1 - T\,C_V/E_T)\right]\right\} \tag{15}$$

where

$$\eta = \frac{1}{2}\,[X^{-2}-1] \tag{16}$$

$$\tilde{a}^2 = a_o^2\left(1 - \frac{2}{3}\,\alpha\,E_{TO}/C_V\right)$$

$$\Lambda = \tilde{K}\,K_o'' - \left(K_o' - \frac{2}{3}\right)\Gamma - \frac{4}{9}\frac{\tilde{a}}{a_o} \tag{17}$$

$$- \frac{4}{9}\frac{E_{To}}{\tilde{V}\tilde{K}}\left[\tilde{\gamma}\Gamma - 2\lambda + 2\tilde{\gamma}^2\left(1 + T\,C_{VO}/E_{TO}\right)\right]$$

$$\tilde{K} = K_{os} - \left(\frac{\partial K_s}{\partial T}\right)_{P=0} E_{TO}/C_{VO} \tag{18}$$

$$\tilde{\gamma} = \frac{\alpha_o \tilde{K} \tilde{V}}{C_{VO}} \left(\frac{a_o}{\tilde{a}}\right)^2 \tag{19}$$

$$\Gamma = K_o' \left(\frac{\tilde{a}}{a_o}\right)^2 \tag{20}$$

Here a is a measure of a length the unit cell, α is the volume expansion coefficient, K is the bulk modulus and the primes indicate differentiation with respect to pressure. Also E_T is the thermal vibration energy and C_V is the specific heat at constant volume, the subscripts o indicate standard conditions. Because the Mie-Gruneisen assumption, $\gamma = \gamma(V)$, is implicit in equations 14 through 20, equation 15 is expected to be useful for geologic materials at or above Debye-temperature of the material. This equation, therefore, has considerable promise in describing these materials at high temperatures and in the hydrodynamic regime.

III. Analysis of Equation of State Data

The major emphasis in research carried out during the past year has been the analysis of a large body of available shock-wave data for rocks, minerals, and earth forming oxides. In the analysis of the

data we have attempted to use the physically significant parameters and incorporate supplementary data such as crystal structure, atomic weight, elastic moduli at normal and elevated temperatures and pressures, as well as thermodynamic properties and strength of material data. The research performed on this contract has been presented in detail in five manuscripts which are in various stages of publication as indicated below.

1. Equation of state and crystal structure of high-pressure phases of shock silicates and oxides, Thomas J. Ahrens, Don L. Anderson, and A. E. Ringwood, Reviews of Geophysics, 7, 667-708, 1969.
2. Equation of state and pressure dependence of the shear strength of two oxides under shock compression, Geoffrey Davies and Thomas J. Ahrens, to be published.
3. The Equation of state of stishovite, Thomas J. Ahrens, T. Takahashi, and Geoffrey Davies, J. Geophys. Res., in press, 1970.
4. Calculation of Gruneisen's ratio of Periclase to 10 kb and 1200°K from Ultrasonic Data, Thomas J. Ahrens, and Hartmut A. W. Spetzler, to be published.
5. Heat of Formation of O^{2-}, Edward S. Gaffney and Thomas J. Ahrens, J. Chem. Phys., 51, 1088-1091, 1969.

The results obtained in these papers are outlined and summarized below:

1. Equation of State and Crystal Structures of High Pressure Phases of Shocked Silicates and Oxides

The raw Hugoniot data for minerals (Figure 1) may often be represented as lying in one or more of the three regimes which are designated as the low pressure phase, mixed phase, and high pressure phase (hpp) regime.

In this paper the shock wave data for rocks and minerals obtained by McQueen and Marsh (1966), Mc Queen et al (1967b), Al'shuler et al (1965), Trunin et al (1965), Wackerle (1962), and Ahrens et al (1967b) were analyzed in order to obtain equation-of-state properties and infer, especially from the zero-pressure density, the crystallography of the high pressure phase (hpp). With the exception of stishovite (SiO_2) there is no direct knowledge of the crystallography of the hpp produced in the shock experiments.

For many of the subject materials the low-pressure regime corresponds to stress-volume-energy states in material that has yielded under one-dimensional compression and has thus been shocked into states which are in an effectively hydrostatic state of stress, i.e., the principal stresses are nearly equal. In some cases, however, for example, Al_2O_3 and MgO, significant stress differences appear to be present at Hugoniot states up to substantial stress levels. These are discussed below. The mixed phase region is assumed to represent a mixture of both the high and low pressure phase material while states in the high-pressure regime are

assumed to represent material that has been wholly converted to the high-pressure phase. In this paper we analyzed the shock data in the high pressure region. Although in practice it is often difficult to ascertain the lower pressure limit of this regime. It should be noted that the states lying in the high pressure regime are achieved by direct shock transition from the low pressure, initial phase which is at standard conditions. Thus, no assumption of the equation of state of the low pressure phase material need be made.

The parameters in the Birch-Murnaghan equation were obtained for the 24 materials analyzed along the raw Hugoniot centered at zero pressure, the metastable Hugoniot of the shock-induced hpp and the adiabat and 25°C-isotherm of the hpp (Table 1 and 2). Of all the minerals and rocks for which data are analyzed, all but three (Al_2O_3 - corundum, MgO - periclase, and MnO_2 - pyrolusite) appear to have at least one major phase transition between 0 and 800 kb. Because of the marked decreases in volume (typically 20-50%), the zero-pressure density of the hpp's were obtained by restraining the hpp adiabat, calculated from the Hugoniot data, so that the zero-pressure density, ρ_o, zero-pressure seismic parameter, ρ_o, and mean atomic weight, $\overline{M}$, satisfied the equation

$$\rho_o/\overline{M} = A\ \Phi_o^n \qquad (20)$$

suggested by Anderson (1967), here A = 0.048 and n = 0.323. (A recent revision of his analysis (Anderson, 1969) suggests values of A = 0.0492 and n = 1/3 are more appropriate. The new value of A and n give values of zero-pressure density which are 1 to 4% lower than those reported here.) When this restraint is applied to the shock data for corundum, periclase, pyrolusite, and stishovite, for which the zero-pressure derivatives are known, the error in the inferred zero-pressure density varies from -0.8% for stishovite to +2.8% for MgO. The transformation energy E_{tr}, at standard pressure and temperature is also employed in the analysis. In general, transformation energies are estimated from independent thermochemical data for the same or analogous transitions. Uncertainties of ~ 50% in E_{tr} result in uncertainties of only ~ 1% in the calculated zero-pressure densities. The sensitivity of calculated equation-of-state parameters to assumptions which are made concerning both the initial (zero-pressure) value of Gruneisen's ratio (γ), and the dependence of γ on compression were tested. Since the initial value of γ can vary by almost a factor of 2, depending upon whether the Slater or the Dugdale-McDonald value is used, it is found that the assumption of the initial value of γ affects the calculated equation-of-state to a much greater degree than the assumed dependence of γ on compression. For example, in Fe_3O_4 a change in γ from 0.34 to 0.63 (Slater to Dugdale-McDonald) changes the inferred zero-pressure density of the hpp by only ~ 0.3% and the zero-pressure bulk modulus by ~ 1.5%.

The probable crystallography of the oxide and silicate phases produced at high shock pressures, is inferred from the calculated zero-pressure density and indirect lines of evidence, such as high-pressure petrologic studies of analog systems (e.g., germanates, titanates) under static conditions as well as the classical rules of crystal chemistry. Except for stishovite, shock recovery experiments have not as yet yielded samples of the hpp's that are actually produced in shock experiments. Statements as to the probable crystallography of the hpp's are therefore necessarily subject to considerable uncertainty. This uncertainty largely depends on the availability of data for appropriate analog systems. The oxides, Al_2O_3, MgO, and MnO_2, do not appear to have significant phase transitions up to ~ 1200 kb. Rutile, TiO_2, appears to transform from an initial density of 4.25 g/cm^3 to a hpp with a zero-pressure density of 5.71 g/cm^3. As previously inferred by McQueen et al. (1967a) this hpp probably has the fluorite structure. Although similar transformations are known to occur in GeO_2 and PbO_2, the analogous transformations are not detected in the analysis of the SiO_2 shock data (available to 2000 kb and presumably representing stishovite above ~ 400 kb). The hpp of hematite, Fe_2O_3, density 5.96, vs. 5.27 g/cm^3 for the low pressure phase, is inferred to have the perovskite structure although the B-rare earth structure (Sc_2O_3) is another possibility. Spinel, $MgAl_2O_4$, transforms to a phase which has zero-pressure density of 4.19 g/cm^3, which compares with a density of 3.86 g/cm^3 for the isochemical mixed oxides. We infer a structure for this

phase similar to that of $CaFe_2O_4$. The hpp of magnetite, Fe_3O_4, has a density of 5.54 as compared with 5.20 g/cm^3 for the low-pressure phase. This phase may represent either a disproportionated product of FeO + Fe_2O_3 (perovskite) or possibly the orthorhombic $CaFe_2O_4$ structure.

The minerals, albite, oligoclase, and microcline all appear to transform to the hollandite structure, density ~ 3.85 g/cm^3 (Ringwood et al. (1969). Although this transformation does not appear to be completely over the range of data in the pure mineral samples, the zero-pressure density of the high-pressure products of Westerly granite (3.96 g/cm^3) and anorthosite (3.51 g/cm^3) are consistent with a mixture of stishovite and feldspar (in the hollandite structure) existing at high pressure.

In the case of olivines, since the hpp zero-pressure density is typically some 20% higher than the starting material, the olivine-spinel transition (usually involving a density increase of less than 10%) is clearly overdriven. Although the hpp densities are close to those which would occur if this mineral were to disproportionate either to the oxides-periclase, wustite and stishovite-or to ilmenite and rock salt structure, in the range Fo_{90} to Fo_{10}, it appears most likely that the Sr_2PbO_4 structure [Wadsley et al, 1968] is produced. In the case of pure forsterite, with an initial density of 3.21 g/cm^3, a hpp material having a density of 4.31 g/cm^3 is obtained. This compares to 4.12 g/cm^3 for the hpp of Twin Sisters dunite (Fo_{90}). A somewhat higher density of the magnesia end-member may represent the formation of the K_2NiF_4 rather than the Sr_2PbO_4 structure. The K_2NiF_4

structure is taken by the olivines Ca_2GeO_4 and $MgCaGeO_4$ (Ringwood and Reid, 1969). This result should, however, be taken with caution as only a few less reliable Hugoniot points are reported for this material.

The Hugoniot data for bronzitite (En_{90}) gives a hpp zero-pressure density of 3.74 g/cm^3 as compared to a starting density of 3.27 g/cm^3. The hpp is thought to represent a garnet or ilmenite structure or possibly a disproportionation into spinel plus stishovite. The relatively low zero-pressure bulk modulus inferred for the hpp material (~ 2100 kb) suggests that the experimental data may not all lie within the high pressure phase regime.

As in the case of pure forsterite, the data for pure enstatite are also less reliable. These also give significantly higher densities than the material containing more FeO. The inferred zero-pressure density of the hpp, 4.20 g/cm^3, correlates well with the expected zero-pressure density, of 4.25 g/cm^3 for the perovskite structure.

Sillimanite and andalusite have hpp zero-pressure densities of 4.00 and 3.95 g/cm^3. These values probably represent the disproportionation reaction products, Al_2O_3 and SiO_2 (stishovite). This mixture would have a theoretical zero-pressure density of 4.09 g/cm^3.

The equation-of-state parameters of the hpp's display several trends which are believed significant. We find that the

second order parameter ξ in the Birch-Murnaghan equation is nearly zero for the oxides MgO and Al_2O_3. For stishovite, we find $\xi = 0.73$ and $K'_{os} = (dK/dP)_s = 3$ (a later analysis yields a value of K'_{os} of 7, Ahrens et al, 1969a) while for the hpp of olivines and pyroxenes values of ξ closer to 1 with values of K'_{os} of 2 to 3 are obtained. The value of dK/dP calculated along the adiabat and Hugoniot curves (the latter representing higher temperatures), decrease with increasing compression. The rate of decrease of K' with density inferred from the Birch-Murnaghan equation is similar for all the oxides and hpp's of the silicates. These vary from -0.5 to -0.7 cm^3/g. Increasing the density upon substitution of FeO for MgO gives values for the change of (dK/dP) with density in the range -0.3 cm^3/g to -1.6 cm^3/g. The values of γ for the hpp's are between 0.5 and 1.0. These are related to K'_{ot} which is also generally lower for the hpp's and decrease with compression and increasing iron content.

Since the Hugoniot data for MgO and Al_2O_3 indicate that no significant phase transition has taken place in these materials, the zero-pressure densities were constrained to their zero-pressure values for the purpose of further analysis. The resulting bulk moduli obtained were higher than the ultrasonic values of 1622 and 2521 kb. Since no internal rearrangement takes place at the shock front (presumably due to the lack of a phase transition), strength effects will produce a Hugoniot curve for MgO, Al_2O_3, and MnO_2, which is offset in shock stress above the hydrostatic curve.

Upon correcting the raw Hugoniot data for MgO, ceramic and crystalline Al_2O_3, for residual strength effects (by relating the net shear stress at high shock pressures, to that existing at the Hugoniot elastic limit (Ahrens et al , 1968a)) an analysis of the hydrostatic Hugoniot was performed. A corrected Hugoniot yields values for the zero-pressure adiabatic bulk modulus of 1675, 2563, and 2919 kb for MgO, ceramic, and crystalline Al_2O_3. These are in good agreement with the ultrasonic data. (A more recent analysis of the shock data in which the shear strength is allowed to increase with mean principal stress gives similar results (Davies and Ahrens, 1969).) The good agreement in both bulk moduli and $(dK_{os}/dP)_s$ is consistent with the result that MgO and Al_2O_3 do not undergo phase changes over the range of the shock data and furthermore that these materials support significant levels of shear stress above shock pressures of 150 and 300 kb, respectively.

2. Equation of State and Pressure Dependence of Shear Strength of Two Oxides under Shock Compression

Isotherms and a family of release adiabats are calculated from the periclase (MgO) and corundum (Al_2O_3) Hugoniot data. A strength correction which depends on pressure and temperature in accordance with the empirical relation proposed by Towle and Riecker (1968), is used to bring the zero-pressure and high-temperature densities into self-consistent agreement with the high-temperature thermal expansion and ultrasonic data (Table 3.).

Assuming a linear dependence of shear strength, S, with pressure according to

$$S = S_o \cdot (1 + \varepsilon P) \tag{21}$$

as suggested by Towle and Riecker, has improved agreement of the shock data for single crystal corundum with the zero-pressure and high temperature ultrasonic data. Here S is the strength at hydrostatic pressure P, S_o is the initial strength and ε is a constant. For a periclase, the agreement between the high temperature parameters of the adiabats calculated and those observed has also been improved by the amount comparable to that obtained earlier (Ahrens et al, 1959c) by assuming a constant strength which is independent of pressure. In this case, errors in the analysis and in the data may be of the same order as the effects obtained. For ceramic corundum this agreement increases with increasing temperature and cannot be substantially reduced using this method. The pressure dependence of a shear strength obtained from this analysis of shock-wave data is indicated in Table 4 and is in surprisingly good agreement with the pressure dependence of the shear modulus which has been hypothesized by Towle and Riecker. In the analysis of the shock wave data, we have again assumed the Birch-Murnaghan form (equation 5) for the pressure-volume curve. The errors introduced by employing this assumption rather than using some higher order equation or another two-parameter formula

are difficult to determine. One possible way to estimate the errors involved is to compare the results obtained with those obtained by other equations of state such as the Murnaghan equation or equations derived from different interionic potentials. Thomsen (1969) quoted an equation derived from finite strain theory using the Lagrangian definition of strain rather than the Eulerian definition. This two-parameter equation as given by equation 6 was fitted to the Hugoniot data; but resulting values of K_o are in poor agreement with the ultrasonic data and the values of K_o' were unrealistically large, i.e., 10 to 15. Thus, this equation appears to be a very poor representation of the binding forces involved. The accuracy of the Birch-Murnaghan equation is still not determined, but because of its success representing much of the shock-wave data probably gives K_o to within about 5%. As indicated in Table 4 the pressure dependence of the shear strength obtained for periclase and corundum is comparable to the first-order pressure dependence of the shear modulus and supports the hypothesis of Towle and Riecker (1968).

3. Equation of State of Stishovite

With the recent availability of new Hugoniot data for sandstone (Jones et al, 1968), fused quartz (McQueen, 1968; Shipman and Isbell, 1969) we have reanalyzed the high-pressure data for SiO_2 in the high regime where quartz has transformed to stishovite. Combining these new data with those of Wackerle (1962) and Al'tshuler (1965) for quartz (Figure 2), and using the procedure outlined by

McQueen et al (1963) an independent determination of the Gruneisen ratio at high pressures is obtained (Figure 3). Using this determination of γ and the recently available data for the zero-pressure density, transformation energy of quartz to stishovite, specific heat and thermal expansion coefficient for stishovite an isothermal and adiabatic equation of state is constructed (Table 5). Stishovite has a surprisingly high zero-pressure Gruneisen ratio of approximately 1.7. This compares to $\sim$ 0.9 obtained earlier by McQueen et al (1963) and ourselves (Ahrens et al, 1969c). We find that the value 0.9 is consistent with the earlier calculations, but only at higher pressures. It appears that the rapid decrease of γ along the Hugoniot from a value of $\sim$ 1.7 at standard temperature and pressure to 0.9 kb, may largely be a temperature effect.

4. Calculation of Gruneisen's ratio of Periclase to 70 kb and 1200°K from Ultrasonic data

The recent availability of high-temperature and high-pressure ultrasonic data from minerals such as MgO, has permitted a cricital evaluation of thermodynamic Gruneisen's ratio as a function of temperature and pressure. In this analysis we apply a form of the Gruneisen ratio

$$\gamma = V(\partial P/\partial E)_V \qquad (22)$$

directly to the ultrasonic, thermal expansion, and enthalpy data. The zero-pressure adiabatic bulk modulus, K_{os} and its pressure derivatives $(\partial K_{os}/\partial P)_T$ have been determined ultrasonically by Spetzler (1969b). After correcting Spetzler's mixed derivatives to adiabatic conditions, and applying the thermal expansion data for MgO, a series of pressure-volume adiabats were constructed using the data of Victor and Douglas (1958) for the high-temperature enthalpy of MgO. Gruneisen's ratio was then calculated as a function of pressure and volume (Figure 4).

The most interesting result of these calculations is the marked decrease of γ with increasing temperature at constant volume (10% at normal volume).

The often employed assumption of the Mie-Gruneisen equation of state which implies that γ is only a function of volume, may be in error below the Debye temperature (940°K). If the Mie-Gruneisen assumption were true the lines of constant γ shown in Figure 2 should be vertical. As can be seen they are actually nearly parallel to the adiabats (or isotherms) in this pressure and temperature range. Because of the increased excitation of optical phonon modes with temperature between 300 and 1200°K, the Gruneisen ratio of MgO appears to be more dependent on temperature than volume in this regime.

According to the phonon dispersion curves given by Peckham (1967) the maximum acoustic vibration frequency is $\sim 15.5 \times 10^{12}$ cps.

The relation $T = h\nu/k$ gives a temperature for excitation of all the acoustic modes of 755°. The average acoustic Gruneisen ratio give theoretical values of 1.39 to 1.41.

The resulting Gruneisen ratio for the transverse and longitudinal optic modes give an average of 1.31 ± 0.06. If at 744°K only the acoustic modes are excited, we expect $\gamma_{th} = \gamma_{ac} = 1.40$. At high temperatures (above 1056°), both the acoustic and optic modes should show a lower composite Gruneisen ratio given by $\gamma_{th} = 1/2 (\gamma_{ac} + \gamma_{op}) = \sim 1.36$. The value of the thermodynamic Gruneisen ratio which is measured (~ 1.56) is somewhat higher than the theoretical estimate of 1.40. The theoretical estimate does however indicate a decrease in gamma with increasing temperature. We suggest this result arises from the successive excitation of the low γ optical modes with increasing temperature. Above ~ 1056° the Gruneisen ratio should become nearly independent of temperature and the Mie-Gruneisen equation should be valid.

5. Heat of Formation of O^{2-}

As part of our continued interest in the nature of the high pressure phases produced in shocked silicates and oxides a series of Born-Mayer-type calculations were used to calculate the lattice energies of simple oxides (MgO, BeO, CaO, and ZnO). Repulsion and other non-Coulombic contributions to the lattice energy are obtained using thermodynamic and recent ultrasonic data for the bulk moduli and the isothermal pressure-temperature derivatives of the elastic constants. Using thermochemical data for the

heat of formation of MgO, CaO, and BeO and their cations, the heat of formation of O^{2-}, $\Delta H_f^\circ(O^{2-})$, is calculated to be 197 ± 5 kcal/mole. Using the largest value of $\Delta H_f^\circ(O^{2-})$, obtained for MgO, presumably the most ionic of the crystals treated, a value of 202.3 kcal/mole is obtained. These values are believed to be more accurate than earlier values given by Morris (1958) and by Huggins and Sakamoto (1957) who obtained 210 ± 6 and 221 ± 15 kcal/mole. The anomalously low value calculated for $\Delta H_f^\circ(O^{2-})$ for ZnO is believed to result from a substantial covalent contribution in the Zn-O bond in this oxide.

IV. Recommendations

The results of our analysis indicate that further or continued work should be carried out in several areas relating to equations of state of rocks and minerals. These research areas are outlined below:

A. Strength effects at low and high pressures. New dynamic data describing the stress differences supported by earth materials upon passage of intense stress waves should be obtained. Knowledge of the stress differences supportable by a medium is of importance for the following two reasons: 1) The value of the difference in principal stresses present under dynamic conditions are critical to the reduction of Hugoniot or release adiabat shock data and to formulation a complete hydrostatic equation of state of the material, 2) Stress differences supported by the media under dynamic

conditions directly enter into the numerical calculations of the stress wave propagations and are needed to formulate a complete rheological model of the material under varying dynamic conditions.

Further work along the lines suggested by Walsh and Brace (1969) and Cherry (1968) involving correlation of data from static and quasi-static strength tests with dynamic data would appear profitable. We have found that the comparison of a hydrostatic equation of state inferred from high-pressure and high-temperature ultrasonic data are also useful in evaluating stress differences at high pressures (Davies and Ahrens, 1969). Comparison of piston-cylinder measurements with shock-wave data, such as is performed by Peterson et al (1969) appears to be another promising technique to evaluate strength effects.

Another approach to the strength problem is the performance of small-scale one-dimensional intense stress wave propagation experiments in spherical or planar geometry. In these experiments one or more of the critical flow of variables are measured as a function of time and thus, for example, pressure or particle velocity profiles are obtained. The various rheological models for a real material may then be tested by comparing the observed flow variable profiles with numerical calculations. Some experiments along these lines have been carried out by C. Godfrey and coworkers (personal communication, 1968) in spherical geometry.

Another important area in which experimental data are especially lacking is that of the effect of water content and porosity on dynamic yielding and the stress differences supportable under dynamic conditions.

B. Equation of State Data

Although knowledge of the principal Hugoniots of rock forming minerals is far from complete and should be continued, a considerable body of data is now available for the oxides and silicates. Data pertaining to testing various mixing laws for employing equation of state data for minerals and oxides to predict the response of rocks of arbitrary composition is important. Some work along these lines has recently been carried out by McQueen (1968) and co-workers. The effect of water or a concentration of heavily hydrated minerals on the equation of state should also be examined experimentally and theoretically in future work.

C. Gruneisen's Ratio

The availability of thermodynamic and ultrasonic data at high temperatures and moderate pressures for individual mineral species is important in fixing parameters such as Gruneisen's ratio under standard conditions. As recently pointed out by several authors including Anderson (1968) and Knopoff and Shapiro (1959), knowledge of the Gruneisen parameter of high pressure is vital to the calculation of states lying away from the principal Hugoniot as well as a formulation of a complete equation of state. Judging from results of our analysis of the high-pressure data for Gruneisen's ratio data for stishovite (Ahrens et al, 1969a) shock wave experiments on porous minerals such as those of Jones et al (1968) on SiO_2 and Carter et al (1969) on MgO appear to be

a promising source of data for Gruneisen's ratio at high pressure. In this regard the shock wave measurements themselves, as well as the preparation of uniform samples and the precise measurements of their initial density, present challenging experimental problems. The new techniques in which a large, but known, pulse of energy is radiatively deposited in a sample and the rise in pressure is then measured may also be a useful tool for generating new Gruneisen ratio data (Graham and Hutchison, 1967).

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Table 1

Parameters Used to Reduce Shock Wave Data

Starting Material	Initial Density (g/cm^3)	Mean Atomic Weight (g/mole-atom)	Number Of Data Points	Lowest Pressure (kb)	Highest Pressure (kb)	Transition Energy (10^{10} erg/g)
Al_2O_3-Corundum Crystal[a]	3.987	20.39	11	516	1480	0.0
Al_2O_3-Ceramic[a,b]	3.829	20.39	10	635	1131	0.0
MgO-Periclase[a]	3.58	20.16	19	202	1258	0.0
MgO-Periclase[c]	3.425	20.16	3	345	2581	0.0
SiO_2-α-Quartz[c,d]	2.654	20.03	15	414	1974	0.804
MnO_2-Pyrolusite[a]	4.31	28.98	17	183	1202	0.0
$MgAl_2O_4$-Spinel[a]	3.42	20.32	9	740	1158	0.03
Al_2SiO_5-Sillimanite[a]	2.71	20.3	11	584	1099	0.44
Al_2SiO_5-Andalusite[a]	3.08	20.3	12	594	1158	0.44
Fe_3O_4-Magnetite[a]	5.120	33.08	10	853	1310	0.13
Fe_2O_3-Hematite[a]	5.00	31.9	10	896	1421	0.71
Mg_2SiO_4-Forsterite[a]	3.05	20.1	6	664	1035	0.67
$MgSiO_3$-Enstatite[a]	2.71	20.1	4	300	637	0.85
Bronzitite (Mont.)[a]	3.28	21.2	13	655	1090	0.85
Twin Sisters Dunite (Wash.)[a]	3.32	20.9	13	831	1123	0.67

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Table 1 (Continued)

Starting Material	Initial Density (g/cm^3)	Mean Atomic Weight (g /mole)	Number Of Data Points	Lowest Pressure (kb)	Highest Pressure (kb)	Transition Energy (10^{10} erg/g)
Olivinite I[e]	3.31	21.2	4	755	5050	0.67
Hortonolite Dunite (S. Africa)[a]	3.79	25.1	15	687	1190	0.3
Fayalite (Rockport)[a]	4.25	29.1	5	696	1137	0.3
Eclogite (Healdsburg)[a]	3.41	22.3	6	817	1078	0.85
Anorthosite (N.Y.)[a]	2.73	21.0	14	331	952	0.86
Oligoclase (Muskwa Lake)[f]	2.63	20.49	7	464	674	0.97
Albitite (Pa.)[a]	2.61	20.4	7	410	904	0.99
Microcline (Ontario)[f]	2.561	21.4	5	296	576	1.28
Westerly Granite (Mass.)[a]	2.63	20.6	8	408	919	0.8

[a] McQueen and Marsh (1966); McQueen et al. (1967)

[b] Ahrens et al. (1968a)

[c] Altshuler et al. (1966)

[d] Wackerle (1962)

[e] Trunin et al. (1965)

[f] Ahrens et al. (1968b)

Table 2. Equation of State Parameters, High Pressure Phases

Starting Material[a]	Hugoniot: Apparent Density ρ_{oH} (g/cm^3)	Hugoniot: Apparent Bulk Modulus K_{oh} (kb)	Hugoniot: ζ_h	Hugoniot: K'_{oh}	Adiabat: Calculated Density ρ_o (g/cm^3)	Adiabat: Grüneisen Ratio γ_o	Adiabat: Bulk Modulus K_{os} (kb)	Adiabat: ζ_s	Adiabat: K'_{os}	Isotherm: Bulk Modulus K_{ot} (kb)	Isotherm: ζ_t	Isotherm: K'_{ot}	Mixture Hugoniot: Bulk Modulus K_{om} (kb)	Mixture Hugoniot: ζ_m	Mixture Hugoniot: K'_{om}
Al_2O_3-Corundum Crystal[b]	3.95	2968	0.478	3.23	3.96[b]	1.1[b]	2931[b]	0.66[b]	3.12[b]	2917[b]	0.66[b]	3.13[b]	2903	0.42	3.31
Al_2O_3-Ceramic[b]	4.03	3233	0.403	3.46	4.04[b]	1.1[b]	32[illegible][b]	0.64[b]	3.15[b]	323[illegible][b]	0.63[b]	3.16[b]	3224	0.63	3.10
MgO-Periclase[b,c]	3.69	2318	0.417	3.44	3.70[b]	1.1[b]	2336[b]	0.62[b]	3.18[b]	2319[b]	0.61[b]	3.19[b]	231[illegible]	0.464	3.37
MgO-Periclase[b,d]	3.77	2526	0.191	3.75	3.82	1.1	2668	0.58	3.22	2650	0.576	3.23	2624	0.396	3.47
SiO_2-α-Quartz[b]	4.26	4272	0.498	4.66	4.32[b]	0.62[b]	420[illegible][b]	0.84[b]	2.88[b]	4167[b]	0.84[b]	2.67[b]	4176	0.74	3.00
MnO_2-Pyrolusite	[illegible].20	3011	1.25	2.33	[illegible].29	0.67	3400	1.74	1.67	3390	1.75	1.67	3374	1.71	1.72
$MgAl_2O_4$-Spinel	4.1[illegible]	3641	0.537	3.28	4.19	0.79	3819	1.06	2.49	3869	1.01	2.66	3805	0.991	2.68
Al_2SiO_5-Sillimanite	3.93	2972	0.603	2.93	4.00	0.[illegible]7	3187	1.40	2.33	2781	1.57	1.90	3179	1.37	2.17
Al_2SiO_5-Andalusite	3.90	2870	0.636	3.1[illegible]	3.9[illegible]	0.73	304[illegible]	1.16	2.46	2910	1.25	2.33	3037	1.10	2.[illegible]3
Fe_3O_4-Magnetite	6.27	4411	1.4[illegible]	2.06	6.30	0.39	4488	1.66	1.79	4483	1.66	1.79	4487	1.64	1.81
Fe_2O_3-Hematite	[illegible].94	3963	1.41	2.13	[illegible].96	0.49	3991	1.52	1.98	3814	1.59	1.88	3993	1.50	2.00
Mg_2SiO_4-Forsterite	4.24	4195	1.19	2.41	4.31	1.0	4425	2.22	1.05	4307	2.20	1.07	4427	2.20	1.06
$MgSiO_3$-Enstatite	4.07	3491	3.11	2.86	4.20	0.15	4031	4.23	-1.64	3953	4.25	-1.66	4027	4.31	-1.75
Bronzitite (Mont.)	3.79	2335	1.13	2.49	3.74	0.74	2117	1.14	2.48	2109	1.14	2.48	2113	1.09	2.55
Twin Sisters Dunite (Wash.)	4.11	3245	0.564	3.25	4.12	0.62	2367	1.01	2.65	3253	1.01	2.65	3257	0.940	2.75
Olivenite 1	4.40	4111	0.201	3.73	4.48	0.93	4540	0.861	2.65	4853	0.924	2.90	4757	0.741	3.01
Hortonolite Dunite (S. Africa)	4.69	3163	0.854	2.86	4.7[illegible]	0.69	3319	1.22	2.37	3361	1.16	2.45	3311	1.17	2.44
Fayalite (Rockport)	4.17	2962	1.35	2.19	4.31	1.0[e]	3319	1.87	1.50	3277	1.87	1.50	3325	1.86	1.52
Eclogite (Healdsburg)	3.69	1701	0.646	3.13	3.61	1.00	1555	0.755	2.99	1499	0.69	3.09	1542	0.627	3.16
Anorthosite (N.Y.)	3.68	2013	0.685	3.09	3.71	0.70	2084	1.20	2.40	2086	1.20	2.40	2092	1.14	2.48
Oligoclase (Muskrat Lake)	3.6[illegible]	2074	0.6[illegible]3	3.11	3.69	1.0[e]	2198	1.60	1.87	2177	1.62	1.85	2193	1.[illegible]	1.93
Albite (Pa.)	3.58	2[illegible]16	0.606	3.15	3.[illegible]	1.0[e]	2[illegible]0	1.53	1.82	2[illegible]24	1.[illegible]	1.80	2542	1.[illegible]6	1.69
Microcline (Ontario)	3.[illegible]2	1[illegible]67	0.8[illegible]	2.86	3.[illegible]0	1.0[e]	1[illegible]3	1.47	2.04	13[illegible]	1.43	2.[illegible]13	1[illegible]1	1.4[illegible]	2.11
Westerly Granite (Mass.)	3.91	2727	0.[illegible]46	3.2[illegible]	3.96	0.62	2907	1.32	2.24	2[illegible]14	1.5[illegible]	1.90	2869	1.41	2.26

[a] Data sources given in Table 1.

[b] Preferred value given in Table 6.

[c] McQueen and Marsh (1966).

[d] Altschuler et al. (1965).

[e] Grüneisen ratio set to value 1.0.

Table 3

Comparison of release adiabat zero-pressure and ultrasonic measurements of bulk modulus K_s and $(\partial K_s/\partial P)_s$, P = 0 for various values of initial strength correction $\Delta\sigma$ and pressure coefficient α for MgO.

	Ultrasonic[a]		$\Delta\sigma_o$ = 15 kb, α = 0		$\Delta\sigma_o$ = 15 kb, α = 0.04		$\Delta\sigma_o$ = 28 kb, α = 0	
T (°K)	K_s (Mb)	$\left(\frac{\partial K_s}{\partial P}\right)_s$	K_s (Mb)	$\left(\frac{\partial K_s}{\partial P}\right)_s$	K_s (Mb)	$\left(\frac{\partial K_s}{\partial P}\right)_s$	K_s (Mb)	$\left(\frac{\partial K_s}{\partial P}\right)_s$
300	1.628	3.85	1.693	3.913	1.626	3.913	1.620	4.056
400	1.612	3.83	1.677	3.926	1.612	3.922	1.608	4.059
500	1.595	3.81	1.659	3.939	1.596	3.931	1.595	4.063
600	1.576	3.78	1.640	3.952	1.579	3.941	1.580	4.067
700	1.556	3.76	1.619	3.966	1.562	3.950	1.564	4.071
800	1.536	3.74	1.600	3.979	1.544	3.959	1.549	4.074
900	1.516	3.72	1.581	3.988	1.529	3.964	1.536	4.073
1000	1.496	3.71	1.564	3.993	1.514	3.966	1.524	4.070
1100	1.476	3.70	1.549	3.998			1.512	4.066
1200	1.456	3.69						

Table 4

Comparison of the pressure dependence of shear strength obtained from shock wave analysis, with that inferred from ultrasonic data according to the hypothesis of Towle and Riecker (1968).

Substance	ε_s (shock)	ε_u (ultrasonic)
MgO (crystal)	2.0	2.0
Al_2O_3 (crystal)	1.9	1.1
Al_2O_3 (ceramic)	0.4	1.1

Table 5

Equation of State Parameters for Stishovite

Solution	γ_o	A	C_o (km/sec)	K_{os} (kbar)	$\left(\frac{dK_{os}}{dP}\right)_s$	K_{ot} (kbar)	$\left(\frac{\partial K_{oT}}{\partial P}\right)_T$	$\left(\frac{\partial K_{os}}{\partial T}\right)_P$ (kbar/°K)	$\alpha \times 10^6$ [a] (°K^{-1})
I	1.875	10	8.47	3075	7.67	3043	7.98	-0.85	18.7
II	1.875	8	8.21	2890	7.82	2858	8.08	-0.74	19.9
III	1.780	8	8.32	2969	7.59	2940	7.82	-0.70	18.4
IV	1.580	8	8.55	3135	7.14	3102	7.32	-0.61	15.5
V	1.58	6	8.37	3000	6.86	2977	7.02	-0.50	16.2
--	--	--	--	4272 [b]	4.66 [c]	--	--	--	--

[a] Calculated from $\gamma_o C_p \rho_o / K_{os}$

[b] Apparent zero-pressure bulk modulus along α-quartz Hugoniot (K_{oh}) for apparent density of 4.26 g/cm^3

[c] $(dK_{oh}/dp)_h$, subscript h indicates along the Hugoniot

FIGURE CAPTIONS

Figure 1. Pressure-density relations for material undergoing a shock-induced phase change. Low pressure regime represents Hugoniot of material with zero-pressure density, ρ_o^{ℓ}. High pressure regime represents Hugoniot of material which has been completely converted to high pressure phase with zero-pressure density, ρ_o. Metastable Hugoniot, adiabat, and isotherm for high pressure phase are centered at state P = 0, T = 25°C.

Figure 2. Pressure-density Hugoniot curves for solid and porous (sandstone) α-quartz and fused quartz in the stishovite regime. Calculated adiabat centered at standard conditions and 25°C isotherm for stishovite are calculatd from solid α-quartz data. Isothermal X-ray data for stishovite compares closely with calculated 25°C isotherm.

Figure 3. Gruneisen ratio versus density for stishovite.

Figure 4. Lines of constant thermodynamic gamma in the pressure-volume plane. Adiabats, calculated from the data of Spetzler (1969b), centered at ambient pressure, and temperature ranging from 300°K to 1200°K are indicated.

Figure 1. Pressure-density relations for material undergoing a shock-induced phase change. Low pressure regime represents Hugoniot of material with zero-pressure density, ρ_o^l. High pressure regime represents Hugoniot of material which has been completely converted to high pressure phase with zero-pressure density, ρ_o. Metastable Hugoniot, adiabat, and isotherm for high pressure phase are centered at state P = 0, T = 25°C.

2000
1800
1600
1400
1200
1000
800
600
400
200
0
Pressure, kbar
4.2
4.6
5.0
5.4
5.8
Density, g/cm³
HUGONIOT, α-QUARTZ
o Wackerle (1962)
• Altshuler et al., (1965)
HUGONIOT
FUSED
QUARTZ
ADIABAT
STISHOVITE
25 °C ISOTHERM,
STISHOVITE
HUGONIOT,
COCONINO
SANDSTONE
(Jones et al., 1968)
X-RAY ISOTHERMS,
STISHOVITE
Liu et al., (1969)
(Bassett & Barnett (1969)

Figure 2

THERMODYNAMIC VALUE
SANDSTONE (JONES et al., 1968) - α QUARTZ
SANDSTONE - METHOD II
FUSED QUARTZ (SHIPMAN, 1969) - α QUARTZ
FUSED QUARTZ - α QUARTZ (McQUEEN, 1968)
FUSED QUARTZ (WACKERLE, 1962 AND SHIPMAN, 1969) - SANDSTONE
$\gamma = 1.58(\rho_0/\rho)^6$
γ
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
4.0
4.2
4.4
4.6
4.8
5.0
ρ, g/cm³

Figure 3