

Revised Shock-Wave Equations of State for High-Pressure Phases of Rocks and Minerals¹

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Shock-wave data for the high-pressure phases of a number of rocks and minerals have been reanalyzed using a revised seismic equation of state to constrain the zero-pressure properties of the high-pressure phases. The anomalously low values of dK/dP resulting from a previous analysis are thereby removed. The inferred zero-pressure densities of the high-pressure phases are reduced by an average of 4%, and the values of the zero-pressure seismic parameter Φ_0 are reduced by up to 30%, bringing them into approximate agreement with the hypothesis of the molar additivity of Φ . For most of the materials considered, the derived pressure trajectories of density versus the seismic parameter Φ are consistent with shock-wave data on such materials as MgO , Al_2O_3 , and SiO_2 (stishovite) where no zero-pressure assumptions are required. Iron-rich compounds may require further revision. It is demonstrated that in poorly constrained cases the Birch-Murnaghan equation can produce a singularity in dK/dP at high pressure. Possible crystal structures of the high-pressure phases are considered using the revised zero-pressure densities. It seems likely that olivines with less than about 10-mole % FeO content can transform to a phase significantly denser than the isochemical mixture of oxides, in contrast to olivines with higher iron content. The possibility that electron spin transitions occur in iron-rich compounds is considered, but no strong evidence has been obtained. The derived zero-pressure densities of the high-pressure phases are usually not of sufficient accuracy to distinguish between all alternative structures, but in some cases an alternative structure to that previously chosen is preferred here.

Our knowledge of the properties of rocks and minerals at the temperatures and pressures of the lower mantle depends heavily on the results of shock-wave experiments. The reduction of shock-wave results to quantities that can be compared to known properties of the lower mantle is complicated because most of the minerals likely to be important constituents of the mantle undergo phase transformations under high pressure. In most cases the crystal structure of the high-pressure phase is unknown. Several recent papers have employed various assumptions about the zero-pressure properties of the high-pressure phases in order to derive appropriate pressure-density relations for these phases [e.g., Wang, 1968; D. L. Anderson and Kanamori, 1968; Ahrens *et al.*, 1969]. In this paper we have used for this purpose a revised form of the seismic equation

of state [D. L. Anderson, 1967, 1969] that is more appropriate to the close-packed crystal structures to be expected at high pressures. Other forms of this equation were used by D. L. Anderson and Kanamori [1968] and Ahrens *et al.* [1969]. We will show that the revised seismic equation of state yields high-pressure behavior that is physically more reasonable than that yielded by previous forms.

Specifically, use of the revised seismic equation of state removes anomalously low values of $K'_S = (dK_S/dP)_S$ at high pressures that resulted from the analysis by Ahrens *et al.* [1969]. (Here K is the bulk modulus, P is pressure, and subscript S denotes constant entropy.) It also reduces the inferred zero-pressure densities of the high-pressure phases by a few percent, and reduces by 20% or more the zero-pressure value Φ_0 of the seismic parameter $\Phi = K/\rho$, where ρ is density. The resulting values of Φ_0 are shown to agree approximately with values predicted by the hypothesis of the molar additivity of Φ of the component oxides proposed by D. L. Anderson [1969].

It is demonstrated that in extreme cases the

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Birch-Murnaghan equation can cause a singularity in dK/dP at high pressure, and that it must therefore be applied with caution when there is a lot of uncertainty in the parameters of the equation, or when extrapolation to very high pressures is desired.

Possible crystal structures of the high-pressure phases of shocked minerals and rocks were discussed by *Ahrens et al.* [1969] on the basis of the derived zero-pressure densities. These are reconsidered here using the new zero-pressure densities. In many cases the same structure still seems appropriate. The possibility that, in some of the iron-rich compounds, the Fe ions have undergone high-spin to low-spin transitions is investigated, but no clear evidence of this transition is obtained.

We have considered shock-wave data of the 17 rocks and minerals previously studied by *Ahrens et al.* [1970], and the 2 diabases discussed by *D. L. Anderson and Kanamori* [1968]. The original data are from McQueen, Marsh, and Fritz (unpublished), *Wackerle* [1962], *Altshuler et al.* [1965], and *Trunin et al.* [1965]. Some of the data of McQueen et al. have been published by *McQueen et al.* [1967] and by Birch in *Clark* [1966].

METHOD OF ANALYSIS OF SHOCK-WAVE DATA

The procedure used here for the reduction of shock-wave hughoniot data to appropriate adiabats is essentially the same as that described by *Ahrens et al.* [1969]. All pressure-density curves (Hugoniot and adiabats) have been approximated by the Birch-Murnaghan equation

$$P = 1.5K_0(x^7 - x^5)[1 - \xi(x^2 - 1)] \quad (1)$$

where $x = (\rho/\rho_0)^{1/3}$, ρ_0 is the zero-pressure density, K_0 is the zero-pressure bulk modulus, and ξ is a parameter related to the pressure derivative of the bulk modulus at zero pressure by

$$(\partial K/\partial P)_{P=0} = K_0' = 4 - (4/3)\xi \quad (2)$$

It has been argued recently [*Thomsen*, 1970] that alternative equations to the Birch-Murnaghan equation can be derived either by including higher order terms, or by using alternative definitions of strain. An indication of the effect of changing the form of the pressure-density

relation can be obtained from the results of *D. L. Anderson and Kanamori* [1968], who reduced the raw Hugoniot data of a number of materials using both the Birch-Murnaghan equation and the Murnaghan equation. Their results indicate that use of the Murnaghan equation would increase the zero-pressure densities obtained here by less than 1%, that Φ_0 would change by less than about 4%, and that Φ at a pressure of 1 mb would be changed by less than 10%. These effects would not change the conclusions of this paper.

The Grüneisen ratio γ has been calculated from the Dugdale-Macdonald formula

$$\gamma = -\frac{V}{2} \frac{d^2(PV^{2/3})/dV^2}{d(PV^{2/3})/dV} - \frac{1}{3} \quad (3)$$

where $V = 1/\rho$ is the specific volume, and the derivatives are taken at 0°K. If the 0°K isotherm is assumed to have the Birch-Murnaghan form (1), then

$$\gamma = \frac{(5x^2 - 2) - (1/3)\xi_r(28x^4 - 30x^2 + 6)}{(5x^2 - 3) - \xi_r(7x^2 - 3)(x^2 - 1)} \quad (4)$$

where ξ_r is the parameter of the 0°K isotherm. An excellent approximation to ξ_r is ξ_s , the parameter of the adiabat centered at 300°K and $P = 0$, so it is therefore not necessary to calculate the 0°K isotherm. Nevertheless, an iterative scheme must be used to simultaneously calculate γ and the 'room temperature' adiabat from the shock-wave data, since they are interdependent.

Fortunately, the rather crude assumptions that we are forced to make about γ do not materially affect the conclusions about the zero-pressure densities of the high-pressure phases. The main constraints on the present problem are the shock-wave data and the choice of the seismic equation of state parameters. For example, *Ahrens et al.* [1969, Table 9] assumed various zero-pressure values of γ , and tested both $\gamma = \text{constant}$ and $\gamma/V = \text{constant}$. For the present study, the additional laws $\gamma/V^2 = \text{constant}$ and $\gamma/V^4 = \text{constant}$ were tested. Through all of these cases the variation of ρ_0 was less than 1%, the variation of Φ_0 about 2%, and the variation of Φ at 1-mb pressure about 10%. These variations are significantly less than the effects of the revision of the seismic equation of state to be presented here.