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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.