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LETTER

Finite-strain analysis of relative compressibilities: Application to the high-pressure wadsleyite phase as an illustration

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ABSTRACT

Finite-strain analysis of recently published hydrostatic compression measurements shows that the isothermal bulk modulus of β-(Mg,Fe)$_2$SiO$_4$ wadsleyite is independent of composition [$1.00 \geq$ Mg/(Mg + Fe) ≥ 0.75] within $\pm 2.5\%$. The average bulk modulus over this composition range, $K_{0T} = 171.0$ ($\pm$ 0.6) GPa, agrees well with the value of 172.5 ($\pm$ 1.0) GPa obtained by Brillouin scattering. This offers a significant crosscheck between the elastic moduli determined by independent methods on an important mineral phase of the Earth's mantle.

INTRODUCTION

The application of single-crystal X-ray diffraction techniques to several specimens that are being compressed within a single, hydrostatic pressure chamber offers a precise method for determining the relative compressibilities of different crystals (Hazen, 1981; Hazen and Finger, 1982; McCormick et al., 1989; Hazen et al., 1990). In this way, it is possible to resolve the effects on the equation of state of varying composition, nonstoichiometry, site disordering, or other subtle factors. Hence, the finite-strain theory of equations of state has been extended to the analysis of such data (Jeanloz and Sato-Sorensen, 1986; Jeanloz, 1991).

The purpose of this note is to illustrate the finite-strain analysis of relative compressibilities by applying it to the recently published data for the high-pressure mineral phase, β-(Mg,Fe)$_2$SiO$_4$ wadsleyite (Hazen et al., 1990). The results turn out to be significant, not only as an illustrative example but also because they address two empirical conclusions that have been emerging from research in mineral physics: (1) that finite-compression and acoustic (infinitesimal-compression) elasticity data are internally consistent when reduced by the Eulerian finite-strain formalism (Birch, 1952, 1977, 1978; Jeanloz and Knittle, 1986; Jeanloz, 1989) and (2) that the bulk modulus is typically insensitive to composition across Mg-Fe solid solutions for oxides and silicates (Anderson, 1976, 1989; Jackson et al., 1978). In particular, the new data help validate the mutual reliability of Brillouin-scattering and single-crystal, static-compression measurements and are especially valuable in offering all of these crosschecks for a mineral phase that is thought to be abundant within the transition zone of the Earth's mantle (e.g., Jeanloz and Thompson, 1983; Gwanmesia et al., 1990b).

DISCUSSION

The Taylor expansion of enthalpy in the Eulerian measure of finite strain, $f = [(V/V_0)^{-2/3} - 1]/2$, results in the isothermal equation of state, or pressure-volume (P-V) relation

$$P = 3K_{0T}f(1 + 2f)^{2.5}(1 + af + \ldots) \quad (1)$$

in which K_{0T} is the bulk modulus and $a = 3(K'_{0T} - 4)/2$ (Birch, 1952, 1978). Here, subscripts zero and T denote ambient and isothermal conditions, respectively, and prime indicates differentiation with respect to pressure. Clearly, if $K'_{0T} = 4$ the third-order coefficient (of strain energy in strain) $a = 0$.

Birch (1978) has introduced the normalized stress, $F = P/[3f(1 + 2f)^{2.5}]$, in order to analyze compression data as a function of strain, f. A plot of F vs. f highlights the constraints that the data place on the terms in the equation of state because

$$F = K_{0T}(1 + af + \ldots) \quad (2)$$

from Equation 1. Thus, the intercept of such a plot yields K_{0T}, and if F is linear in f a third-order equation of state is adequate; that is, coefficients beyond a in the bracket of Equation 2 contribute insignificantly to the pressure over the compression range of the data.

The measurements of Hazen et al. (1990) for synthetic wadsleyite of compositions Mg/(Mg + Fe) = 100, 92, 84, and 75% are summarized in this manner in Figure 1. The average of the zero-pressure volumes, determined before and after compression, is used to calculate the strain, and the published uncertainties in the pressure ($\pm$ 0.05 GPa) and in the compressed volume are propagated to obtain the error bounds on f and F. Because the zero-pressure volumes were found to be reproducible to within much

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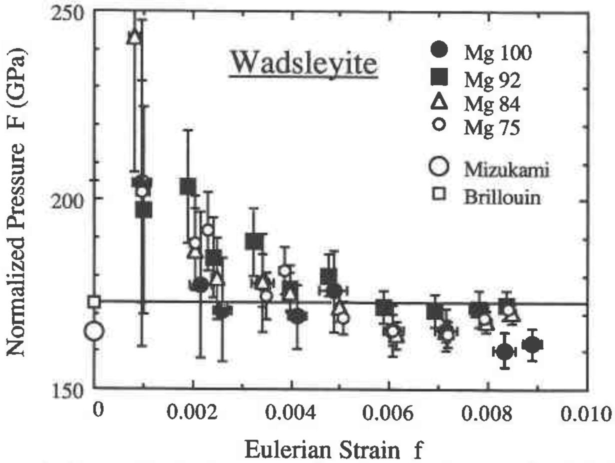

Fig. 1. Hydrostatic compression data of Hazen et al. (1990) plotted as Birch's (1978) normalized pressure F as a function of the Eulerian strain measure f. The bulk moduli of Mizukami et al. (1975) (large open circle) and Sawamoto et al. (1984) (open square), obtained from static-compression and Brillouin-scattering measurements on end-member β-Mg_2SiO_4, are shown at zero strain for comparison. A second-order Eulerian finite strain equation of state based on the Brillouin-scattering results is indicated by the horizontal line.

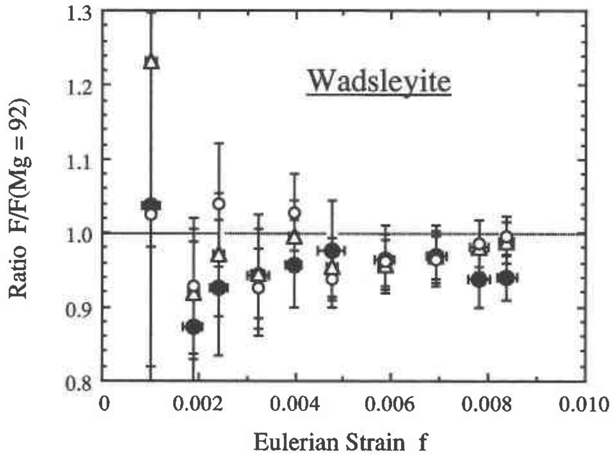

Fig. 2. Ratios of normalized pressures for wadsleyite compositions Mg_{100} (filled circles), Mg_{84} (open triangles), and Mg_{75} (open circles), relative to the Mg_{92} composition, are shown as a function of strain. The symbols are the same as in Figure 1, and a dashed line at $F(x)/F(92) = 1.0$ is shown for reference.

less than their estimated uncertainties (Hazen et al., 1990), the uncertainties in V_0 are not included in the error estimates for the strain and normalized pressure.

As is evident from Figure 1, the hydrostatic compression data are entirely compatible with the determination of Mizukami et al. (1975) by static compression of $K_{0T} = 165\ (\pm\ 40)$ GPa. Also, the new measurements are in good agreement with the value established by Sawamoto et al. (1984) of $K_{0T} = 172.5$ GPa: the adiabatic bulk modulus obtained from Brillouin scattering is converted to the isothermal value using the data listed in Jeanloz and Thompson (1983). Averaging of the elastic moduli probably contributes the largest ambiguity in this acoustic determination of K_{0T}, so ± 1.0 GPa is a reasonable estimate of its uncertainty. Finally, the hydrostatic compression measurement on the Mg100 sample (Fig. 1) is in agreement with the bulk modulus values $K_{0T} = 164.4$–166.8 ($\pm$ 0.8) GPa derived from the ultrasonic velocities variously reported by Gwanmesia et al. (1990a, 1990b) for polycrystalline β-Mg_2SiO_4.

The straight line shown in the figure is appropriate for a second-order equation of state ($a = 0$, $K'_{0T} = 4$). In fact, there is no statistical justification for incorporating any higher order terms when reducing this data set. Least-squares fits of the data of Hazen et al. (1990) in terms of F vs. f yield slopes that are indistinguishable from zero (although a slope may be apparent on casual observation, none is warranted when the data are properly weighted). This conclusion supports the assumption of Hazen et al. that $K'_{0T} = 4$ in their Birch-Murnaghan fit of the data.

In order to evaluate the relative compressibilities among samples of composition i and j, one simply forms the ratio of the normalized pressures

$$F(i)/F(j) = K_{0T}(i)/K_{0T}(j) \times [(1 + a_i f_i + \ldots)/(1 + a_j f_j + \ldots)]. \quad (3)$$

This is a measured quantity in the static-compression experiments, being completely determined by the volume strains of the two samples at a given pressure (Jeanloz and Sato-Sorensen, 1986; Jeanloz, 1991). That is, the pressure need not be measured, in principle, as long as it is known to be uniform across the samples i and j (for a given experiment). Hydrostatic conditions of stress are identical to a state of uniform, isotropic stress.

The ratio of normalized pressures is shown in Figure 2, in which the Mg_{92} composition is taken as the reference and the uncertainties quoted by Hazen et al. (1990) have been propagated through. Two immediate conclusions from this plot are that K_{0T} is constant to within ± 2.5 (± 1.5)% for all four compositions and that no variations are resolvable in K'_{0T} or higher order derivatives of the bulk modulus. The latter point is demonstrated by the fact that least-squares fits to the ratios in Figure 2 show no statistically resolvable dependence on strain. From Equation 3, this implies that the third-order (and higher) terms are insignificant in evaluating the relative compressibilities from these data.

Also, if one assumes that K_{0T} does not vary with composition and takes $a = 0$ ($K'_{0T} = 4$) for the Mg_{92} composition, which is a good approximation according to Figure 1, then a deviation of ± 0.03 from $F(x)/F(x = 92) = 1.00$ for strains $f \leq 0.0085$ requires variations in K'_{0T} as large as ± 4.7 from the value of 4. This is an implausibly large variation in K'_{0T} with composition since $2 \leq K'_{0T} \leq 6$ for most materials (e.g., Birch, 1977; Jeanloz, 1989). Thus, small-strain ($f < 0.01$) measurements are insensitive to reasonable variations or uncertainties in K'_{0T} (Jeanloz, 1991), and the present data must be analyzed assuming that K'_{0T} is independent of composition. As already implied, a second-order equation of state is adequate.

With these assumptions, the bulk modulus ratio $K_{0T}(x)/K_{0T}(x = 92)$ is simply given by the weighted average of $F(x)/F(x = 92)$, $\langle \zeta s^{-2} \rangle / \langle s^{-2} \rangle$ where $\langle\ \rangle$ denotes the average and s is the estimated uncertainty for each value of $\zeta = F(x)/F(x = 92)$. The results for the compositions Mg_{100}, Mg_{84}, and Mg_{75}, relative to the Mg_{92} value, are 0.950 (± 0.017), 0.972 (± 0.014), and 0.975 (± 0.013), with uncertainties given by $\langle s^{-2} \rangle^{-1/2}$. Because these values are obtained from different strain measurements that are collected simultaneously at each pressure, they should be free of most systematic biases that can influence the fitting of static-compression data for individual samples.

Except for the Mg_{100} value, the bulk moduli are indistinguishable from the Mg_{92} value at the 2σ level. Overall, the variation amounts to less than 5% for the different wadsleyite compositions, and factors other than composition, such as variations in intersite disordering, could be influencing the relative compressibilities within this range.

Considering that the unit-cell volume of wadsleyite increases by 1.5% as the Mg content decreases from 100 to 75% (Jeanloz and Thompson, 1983; Hazen et al., 1990), a decrease in bulk modulus of ~6 (± 3)% might be anticipated over the same composition range, assuming a logarithmic volume derivative of bulk modulus $(\partial K/K)/(\partial V/V)_{P=0} \sim -4$ (± 2). As noted above, the present data are consistent with pressure derivatives (for constant composition) $K'_{0T} = -(\partial \ln K_T/\partial \ln V)_{P=0} = 4$.

Instead, both the present analysis and that of Hazen et al. (1990) show that the bulk modulus of wadsleyite does not decrease as the Mg content decreases. If anything, there is a slight increase, as indicated by weighted fits of the normalized pressures, F, for each composition (Fig. 3): $K_{0T} = 164.8$ (± 2.3), 174.5 (± 1.8), 169.3 (± 1.4), and 170.1 (± 1.4) GPa for Mg_{100}, Mg_{92}, Mg_{84}, and Mg_{75} samples, respectively (1σ estimated uncertainties). This is in complete agreement with previous findings for other Mg-Fe oxide solid solutions; the bulk modulus is essentially constant or increases slightly (~2–12%) with increasing Fe substitution (Jackson et al., 1978).

As is evident from Figure 3, these values of bulk moduli differ in absolute magnitude from those quoted by Hazen et al. (1990). The main reason for this difference is that Hazen et al. did not use V_0 in their least-squares fits of the data to the Birch-Murnaghan equation of state. In the present analysis, we incorporate the observed values of V_0 in the data reduction, and as noted by Hazen et al., the resulting bulk moduli are systematically higher by ~5 GPa. This illustrates how elasticity parameters obtained from finite-compression measurements are sensitive, at the level of a few percent as is being considered here, to the detailed assumptions that are made in fitting the data (e.g., weighting of data, assumptions regarding fixed parameters). Specifically, it is important to include the constraint of V_0, when this value is well determined, in deriving equations of state from pressure-volume data.

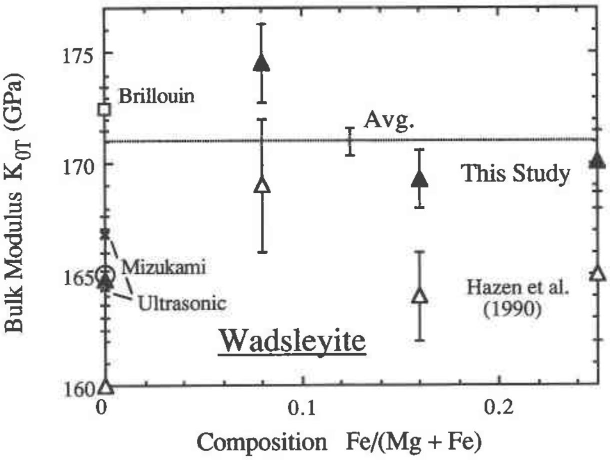

Fig. 3. Summary of the zero-pressure, isothermal bulk modulus of β-$(Mg,Fe)_2SiO_4$ wadsleyite as a function of composition. The triangles indicate the results obtained from the hydrostatic compression measurements according to the analysis of Hazen et al. (1990) (open) and the present analysis (filled). In both cases, $K'_{0T} = 4.0$ is assumed; taking $K'_{0T} = 4.7$ (Gwanmesia et al., 1990b) affects the derived K_{0T} values by <1.8 GPa over the strains of the measurements of Hazen et al. The average value (and uncertainty) obtained for all compositions in the present study is given by the horizontal dashed line. For comparison, the open circle, open square, and crosses show, respectively, values for the Mg end-member determined by Mizukami et al. (1975), Sawamoto et al. (1984), and Gwanmesia et al. (1990a, 1990b).

Because we have found that the bulk modulus of β-$(Mg,Fe)_2SiO_4$ is independent of Mg-Fe composition, an average value of $K_{0T} = 171.0$ (± 0.6) GPa can be derived from the hydrostatic compression data of Hazen et al. (1990). The quantitative agreement with $K_{0T} = 172.5$ (± 1.0) GPa obtained by Brillouin scattering (Sawamoto et al., 1984) is a significant validation of the reliability of the two methods.

In comparison, the recently reported ultrasonic measurements on polycrystalline wadsleyite yield bulk moduli ~2.5–3.9% lower in value. This difference exceeds the estimated uncertainty of the data (~0.5%, Gwanmesia et al., 1990a) and suggests that porosity still affects the polycrystalline measurements at pressures of 2–3 GPa. Indeed, $K'_{0T} \approx 4$ implies that the bulk modulus changes by an amount comparable to this discrepancy (2–4%) over 1–2 GPa. Therefore, the estimate by Gwanmesia et al. (1990b) of the pressure derivative of the bulk modulus may be somewhat high.

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