Elastic Moduli of Wadsleyite (β-Mg_2SiO_4) to 7 Gigapascals and 873 Kelvin

Baosheng Li,* Robert C. Liebermann, Donald J. Weidner

Simultaneous sound velocity measurements and x-ray diffraction studies were made on wadsleyite (β-Mg_2SiO_4) to 7 gigapascals and 873 kelvin. The calculated adiabatic bulk (*K*) and shear (*G*) moduli yield *K* (at room conditions) = 172(2) gigapascals, dK/dP = 4.2(1), and dK/dT = −0.012(1) gigapascals per kelvin, and *G* (at room conditions) = 113(1) gigapascals, dG/dP = 1.5(1), and dG/dT = −0.017(1) gigapascals per kelvin, respectively. The data imply that the *P* and *S* wave velocity contrasts between olivine and wadsleyite require an olivine amount of 38 to 39 percent in the upper mantle to satisfy the observed 410-kilometer discontinuity, but 55 to 60 percent to account for the velocity increase through the transition zone.

The velocity increases associated with the phase transformation of olivine to wadsleyite (β phase) can be used to infer the proportion of olivine in Earth's upper mantle by comparison with the measured 410-km seismic discontinuity in the mantle. However, because of the lack of experimental data for the elastic properties of these phases at the pressure and temperature conditions of the transition zone, the olivine content in the upper mantle has been in debate (*1–7*).

Acoustic measurements for olivine are available for temperatures up to 1700 K at room pressure (*8*) and for transition zone pressures above 10 GPa at room temperature for both olivine (*9–11*) and wadsleyite (*12, 13*). Elasticity studies at high temperatures for wadsleyite had only been possible through static compression experiments that provide indirect determinations of the bulk modulus (*14, 15*); no data have been available for the temperature dependence of the wadsleyite shear modulus. Consequently, estimates of the olivine content of the upper mantle based on analysis of the seismic discontinuity at 410-km depth have ranged from 27 to 65% (*3–6, 10, 11*). Here we report data obtained for pressures up to 7 GPa and temperatures up to 873 K.

We incorporated ultrasonic techniques for use in a DIA-type, cubic-anvil apparatus (SAM 85) installed on the superconducting wiggler beamline (X17B) at the National Synchrotron Light Source (NSLS) of the Brookhaven National Laboratory (*16*). We conducted travel time measurements of *P* and *S* waves for a polycrystalline wadsleyite specimen (bulk density ρ = 3.470 g/cm^3, 0.2% porosity). Benchtop velocity measurements yielded V_P = 9.63(3) km/s and V_S = 5.67(2) km/s (the value in parentheses is the standard error in the last digit), which are within 1% of the Hashin-Shtrikman average from the single-crystal data (*17*). The experiments were conducted along a series of heating and cooling cycles at different pressures, thereby providing a dense coverage to a pressure of 7 GPa and a temperature of 873 K (Fig. 1, A and B). At the same pressure and temperature conditions, energy-dispersive x-ray diffraction spectra were collected for both the sample and NaCl, yielding direct determinations of the sample volume and the cell pressure (*16*). The density and length of the sample are obtained from the observed sample volume (*18*). The *P* and *S* wave velocities and the associated elastic moduli were calculated for all pressure and temperature conditions (Fig. 2, A and B).

We treated the longitudinal (*L*) and shear (*G*) moduli data as linear functions of both pressure and temperature with three adjustable parameters: L_0 and G_0, the elastic moduli at room conditions; dL/dP and dG/dP, the pressure derivatives at constant temperature; and dL/dT and dG/dT, the temperature derivatives at constant pressure. Data collected under cold compression and during heating at low temperatures (<573 K) were not used because nonhydrostatic stresses were generated by the NaCl pressure medium under these conditions. When we fit the longitudinal and shear moduli data above 573 K we obtain L_0 = 322(4) GPa, dL/dP = 6.3(2), and dL/dT = −0.034(1) GPa/K, and G_0 = 113(1) GPa, dG/dP = 1.5(1), and dG/dT = −0.017(1) GPa/K, respectively (Fig. 2, A and B). The corresponding results for the bulk modulus are K_0 = 172(1) GPa, dK/dP = 4.2(1), and dK/dT = −0.012(1) GPa/K. The values of K_0 and G_0 are within 2% of the Hashin-Shtrikman average of the single-crystal elastic moduli (*17*), whereas dK/dP and dG/dP are in good agreement with those measured by the same ultrasonic techniques to 12 GPa at room temperature on a comparable sample (*12*) and single-crystal data from Brillouin scattering spectroscopy (*13*).

Our experimental measurements of dK/dT and dG/dT for wadsleyite, together with previous data for olivine $(MgFe)_2SiO_4$, allowed us to calculate the elastic wave velocities of olivine and wadsleyite at the pressure and temperature conditions of the 410-km discontinuity. The calculation was performed along a 1673 K adiabat with the Eulerian finite strain approach (*4*). The velocity contrast between these two phases, $(V_\beta - V_\alpha)/V_\alpha$, reaches 11.7 and 12.1% at 410-km depth for *P* and *S* waves, respectively. If other mineral phases make no contribution to this discontinuity, we infer an olivine content of 38 to 39% for the upper mantle to satisfy seismic jumps of 4.6% (*19, 20*).

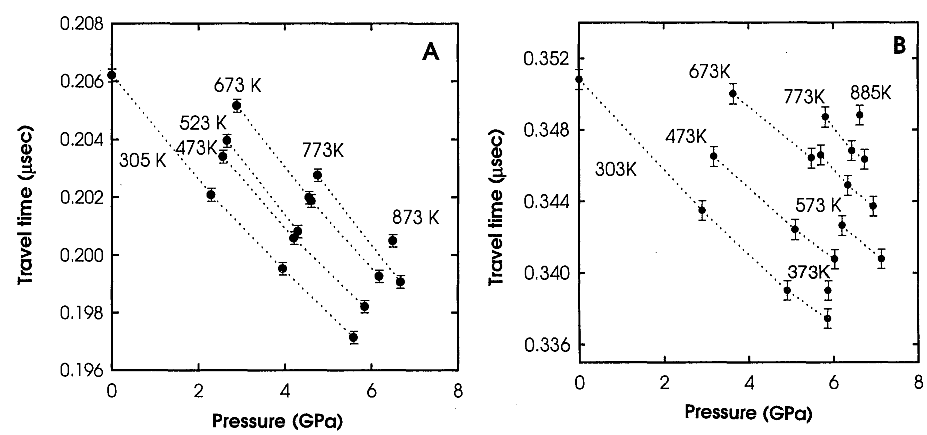

Fig. 1. Travel times of the *P* and *S* waves. (**A**) In the *P* wave experiment, the cell was heated to 573 K at 2 GPa before compression to peak pressure to optimize the acoustic signal. (**B**) In the *S* wave experiment, the data were collected in sequence by compression to peak pressure at room temperature, heating to a peak temperature of 873 K, and subsequent heating and cooling cycles.

B. Li, Center for High Pressure Research and Mineral Physics Institute, State University of New York, Stony Brook, NY 11794–2100, USA. R. C. Liebermann and D. J. Weidner, Center for High Pressure Research and Department of Geosciences, State University of New York, Stony Brook, NY 11794–2100, USA.

*To whom correspondence should be addressed.

In Fig. 3, we compare the velocity-depth profiles to 660-km depth for a pyrolite compositional model with seismic results using our data for wadsleyite and published data for the olivine, pyroxene, majoritic garnet, and ringwoodite phases (*4, 8, 10, 15, 21–23*). For depths in the upper mantle below 200 km (for which an adiabatic geotherm applies), the pyrolite model velocities agree with the seismic data both in absolute values and gradients. In the transition zone, the pyrolite model has larger jumps at 410 km but smaller gradients between 410 and 660 km than the body-wave models from synthetic waveform analyses (*24*). Consequently, the pyrolite model and the seismic profiles converge at the bottom of the transition zone just above the 660-km discontinuity. Compositional models with less olivine than pyrolite might satisfy the 410-km discontinuity [see, for example, (*10*)], but they will predict velocities that are too slow at the base of the transition zone.

Seismic impedance contrast also gives a direct measure of the magnitude of the velocity jump across the 410-km discontinuity (*25*). Gaherty and co-workers have constructed velocity models for the olivine plus wadsleyite mixed phase and calculated the associated impedance contrast, concluding that a pyrolite olivine content matches the seismic observations very well (*26*).

Thus, there is a dilemma in attempting to draw compositional inferences about Earth's upper mantle and transition zone from comparison of mineral physics and seismic models. Could the apparent mismatch of pyrolite and the seismic models in the transition zone be due to incorrect parameterization of the seismic waveform inversions (*27*)? Are there unknown high-pressure phases not accounted for in the mineral physics modeling? What is the effect of Fe partitioning on the elasticity calculations? These questions must be answered before we can conclude the Mg/Si ratio on the basis of the magnitude of the 410-km discontinuity.

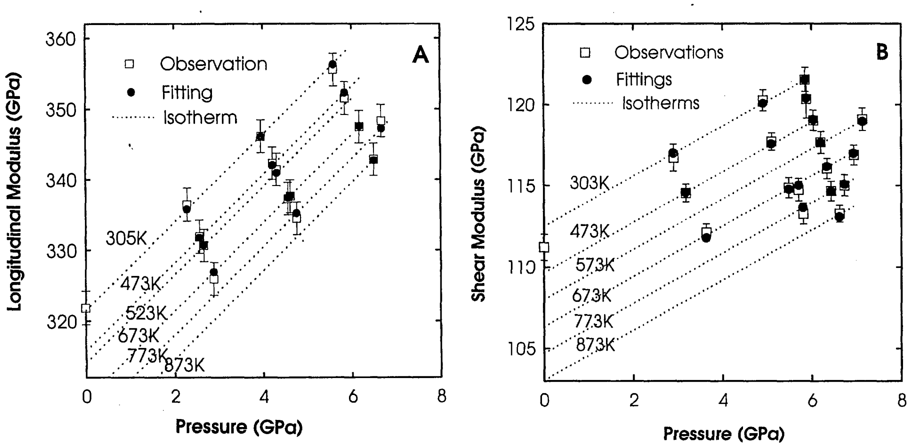

Fig. 2. Comparison of the experimental measurements (open squares) and the calculated values of the longitudinal modulus L (**A**) and the shear modulus G (**B**) of wadsleyite by fitting G and L as linear functions of both pressure and temperature. The fitted L_0 value agrees well with the measurement at zero pressure and room temperature, but the fitted G_0 value is slightly higher than the measured one. It might be a result of oriented microcracks that give rise to low S wave velocity at room conditions, but that are closed at high pressures.

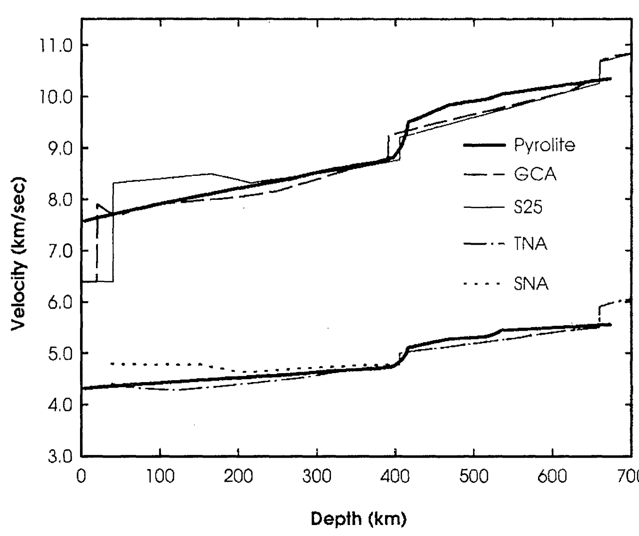

Fig. 3. Comparison of the P and S wave velocities for a pyrolite model with seismic velocity–depth profiles GCA, S25, TNA, and SNA given in (*25*). The velocities for olivine, orthopyroxene, clinopyroxene, and pyrope were calculated along a 1673 K adiabat by using a Eulerian finite strain approach (*4*). We obtained the velocities of a pyrolite model using the Hashin-Shtrikman average for a mineralogical assemblage of olivine (57%), orthopyroxene (17%), clinopyroxene (12%), and pyrope (14%) and using elasticity data of this study and previously published data (*4, 12, 23, 24*).

References and Notes

1. J. D. Bass and D. L. Anderson, *Geophys. Res. Lett.* **11**, 237 (1984).
2. C. R. Bina and B. J. Wood, *J. Geophys. Res.* **92**, 4853 (1987).
3. D. J. Weidner and E. Ito, in *High Pressure Research in Minerals Physics*, M. H. Manghnani and Y. Syono, Eds. (Terra Scientific, Tokyo, 1987), pp. 439–446.
4. T. Duffy and D. L. Anderson, *J. Geophys. Res.* **94**, 1895 (1984).
5. G. D. Gwanmesia, S. Rigden, I. Jackson, R. C. Liebermann, *Science* **250**, 794 (1990).
6. S. M. Rigden, G. D. Gwanmesia, I. Jackson, R. C. Liebermann, in *High Pressure Research: Application to Earth and Planetary Sciences*, Y. Syono and M. Manghnani, Eds. (American Geophysical Union, Washington, DC, 1992), pp. 167–182.
7. J. Ita and L. Stixrude, *J. Geophys. Res.* **97**, 6894 (1992).
8. D. G. Isaak, O. L. Anderson, T. Goto, *ibid.* **94**, 5895 (1989).
9. J. M. Zaug, E. H. Abramson, J. M. Brown, L. J. Slutsky, *Science* **260**, 1487 (1993).
10. T. S. Duffy, C. S. Zha, R. T. Downs, H. K. Mao, R. J. Hemley, *Nature* **378**, 170 (1995).
11. C. S. Zha, T. S. Duffy, R. T. Downs, H. K. Mao, R. J. Hemley, *J. Geophys. Res.* **101**, 17535 (1996).
12. B. Li, G. D. Gwanmesia, R. C. Liebermann, *Geophys. Res. Lett.* **23**, 2259 (1996).
13. C. Zha *et al.*, *Earth. Planet. Sci. Lett.* **147**, E9 (1997).
14. Y. Fei *et al.*, *J. Geophys. Res.* **97**, 4489 (1992).
15. Y. Meng *et al.*, *ibid.* **98**, 22199 (1993).
16. R. C. Liebermann *et al.*, *Eos* **78**, F753 (1997). The ultrasonic measurements were implemented by mounting an acoustic transducer (3.2-mm diameter, 40-MHz $LiNbO_3$, 41° X-cut for S wave and 36° Y-cut for P wave) on the back of a WC anvil. A glass buffer rod was inserted between the WC anvil and the specimen. Precompressed boron-epoxy (4:1 weight % ratio) cubes were used as the pressure medium. The specimen was surrounded by a mixture of NaCl and BN (10:1 weight % ratio) inside a BN sleeve. Outside the BN sleeve was a cylindrical graphite furnace with graphite rings on both ends. Gold foils (2-μm thickness) were inserted between the WC anvil and the glass buffer rod and between the glass buffer rod and the sample to enhance the mechanical coupling. The perturbation to the travel times introduced by the gold foil between the buffer rod and the sample was corrected following the procedures of Niesler and Jackson [H. Niesler and I. Jackson, *J. Acoust. Soc. Am.* **86**, 1573 (1989)]. The uncertainties in the corrected travel times are less than 0.4% at all pressures and temperatures. The sample pressures were calculated from x-ray spectra of NaCl with the Decker scale [D. L. Decker, *J. Appl. Phy.* **42**, 3239 (1971)]. The uncertainties in calculated pressures are about 0.7%. The low shear strength of NaCl also provides a pseudo-hydrostatic stress environment for the sample at low temperatures, which becomes progressively more hydrostatic at elevated temperatures (*28*). The sample temperatures were measured from the thermocouple adjacent to the center of the sample.
17. H. Sawamoto, D. J. Weidner, S. Sasaki, M. Kumazawa, *Science* **224**, 749 (1984).
18. According to (*28*), the yield strength of NaCl is less than 0.05 GPa above 300°C, which is about the error in pressure in our measurement. Beyond 300°C in heating as well as on subsequent cooling, the sample is under a hydrostatic stress environment; therefore, the length change at these pressure and temperature conditions can be obtained from the cube root of the volume change. The propagated errors in the lengths are about 0.4%.
19. H. M. Benz and J. E. Vidale, *Nature* **365**, 147 (1993).

20. G. Nolet, S. P. Grand, B. L. N. Kennett, *J. Geophys. Res.* **99**, 23753 (1994).
21. S. M. Rigden, G. D. Gwanmesia, R. C. Liebermann, *Phys. Earth Planet. Inter.* **86**, 35 (1994).
22. L. Flesch, B. Li, R. C. Liebermann, *Am. Mineral.* **83**, 444 (1998).
23. S. M. Rigden, G. D. Gwanmesia, J. D. FitzGerald, I. Jackson, R. C. Liebermann, *Nature* **354**, 143 (1991).
24. The seismic velocity-depth profiles we used for comparison are in the following references. GCA: M. C. Walck, *Geophys. J. R. Astron. Soc.* **76**, 697 (1984); SNA and TNA: S. Grand, and D. Helmberger, *ibid.*, p. 399; and S25: L. V. LeFevre and D. Helmberger, *J. Geophy. Res.* **94**, 17749 (1989).
25. J. Revenaugh and T. H. Jordan, *J. Geophys. Res.* **96**, 19781 (1991).
26. J. B. Gaherty, P. Puster, T. H. Jordan, Y. Wang, D. J. Weidner, *Eos* **78**, F486 (1997).
27. L. Stixrude, *J. Geophy. Res.* **102**, 14835 (1997).
28. D. J. Weidner *et al.*, in (*6*), pp. 13–17.
29. We thank all those who contributed to the implementation of these ultrasonic experiments in SAM 85 on the X17B1 beamline of the NSLS at Brookhaven National Laboratory and J. B. Hastings and D. P. Siddons at the NSLS for their technical support. Support was from the State University of New York at Stony Brook and from the NSF Science and Technology Center for High Pressure Research (grant EAR89-20239 and NSF grants EAR93-04502 and EAR96-14612 to R.C.L.). This is Mineral Physics Institute contribution number 229.

18 March 1998; accepted 1 June 1998

Ultrasonic Shear Wave Velocities of $MgSiO_3$ Perovskite at 8 GPa and 800 K and Lower Mantle Composition

Yegor D. Sinelnikov,* Ganglin Chen, Daniel R. Neuville, Michael T. Vaughan, Robert C. Liebermann

Ultrasonic interferometric measurements of the shear elastic properties of $MgSiO_3$ perovskite were conducted on three polycrystalline specimens at conditions up to pressures of 8 gigapascals and temperatures of 800 kelvin. The acoustic measurements produced the pressure (P) and temperature (T) derivatives of the shear modulus (G), namely $(\partial G/\partial P)_T = 1.8 \pm 0.4$ and $(\partial G/\partial T)_P = -2.9 \pm 0.3 \times 10^{-2}$ gigapascals per kelvin. Combining these derivatives with the derivatives that were measured for the bulk modulus and thermal expansion of $MgSiO_3$ perovskite provided data that suggest lower mantle compositions between pyrolite and C1 carbonaceous chondrite and a lower mantle potential temperature of 1500 ± 200 kelvin.

Experimental and theoretical efforts have focused on determining the elastic behavior of $(Mg,Fe)SiO_3$ perovskite, the most abundant mineral in Earth's lower mantle, because its physical properties constrain the chemical composition and rheology of the lower mantle (*1–4*). Experimental and theoretical studies of the ambient elastic moduli indicate that $MgSiO_3$ perovskite has an anomalously high shear modulus G, which requires a large temperature derivative of G to satisfy seismic velocities in the lower mantle with reasonable petrological models (*5, 6*).

In the absence of sufficiently large specimens for acoustic techniques, static compression studies have been employed to determine the isothermal bulk modulus K_T, the pressure and temperature derivatives of K_T, and thermal expansion α for silicate perovskite. Discrepancies in α and $(\partial K_T/\partial T)_P$ resulted in different lower mantle bulk compositions. The lower values of α and $|(\partial K_T/\partial T)_P|$ (*7*) favor a chemically uniform mantle with a composition similar to pyrolite (*8*) [Si/(Mg + Fe) = 0.69], whereas analyses based on the higher values of α and $|(\partial K_T/\partial T)_P|$ (*9*) favor a hotter, heterogeneous lower mantle that is enriched in silica [Si/(Mg + Fe) ~ 1]. To determine which model might be more realistic, we measured the pressure and temperature dependence of G of $MgSiO_3$ perovskite, which allows us to constrain the possible temperature and chemical composition of the lower mantle more precisely.

Polycrystalline samples of $MgSiO_3$ perovskite were synthesized in a uniaxial split-sphere apparatus at pressures above 24 GPa and at temperatures around 1700 K, for run durations between 0.5 and 3 hours. By modifying the existing 10-mm octahedral cell assembly (*10*) to maximize the sample volume and to produce minimal temperature gradients, we were able to recover cylindrical specimens that were ~1.5 mm in diameter and thickness, suitable for ultrasonic experiments with bulk densities within 2% of the single-crystal x-ray values (Table 1).

Monochromatic x-ray diffraction spectra from the polished tops and bottoms of the cylinders contained only perovskite peaks (*11*). Each sample was thoroughly examined from the ends and sides of the cylinders with microfocus Raman spectroscopy (*12*), and the best three samples of structurally pure, polycrystalline perovskites were chosen for subsequent high-pressure acoustic experiments. After polishing the cylinders under liquid nitrogen cooling, we performed acoustic tests at high pressures to confirm that the propagation of 20- to 70-MHz signals was possible through the samples.

With a recently developed technique (*13*), ultrasonic interferometric measurements of the shear elastic properties of the three samples were performed over a range of pressure and temperature (Fig. 1). The experimental paths consisted of initial compression at room temperature followed by a series of heating and cooling cycles as pressure was slowly decreased. The in situ acoustic and x-ray diffraction measurements were performed simultaneously at high pressure and at high temperature.

At each pressure and temperature for which travel times (*14*) were measured, energy-dispersive x-ray diffraction patterns from the sample and from the NaCl-confining media were col-

Table 1. Density ρ, G, and the derivatives of G from ultrasonic measurements of polycrystalline samples of $MgSiO_3$ perovskite.

Data source	ρ (10^3 kg/m^3)	G (GPa)	$(\partial G/\partial P)_T$	$-(\partial G/\partial T)_P$ (10^{-2} GPa/K)
Sample 2997	4.03(2)	175(12)	1.8(1)	3.0(1)
Sample 3020	4.06(2)	176(5)	1.9(3)	2.9(2)
Sample 3081	4.10(2)	174(7)	1.8(4)	2.8(3)
Other studies	4.107*	177(4)†	1.6–2.2‡	2.0–3.5§

*$MgSiO_3$ x-ray density from Joint Commission on Powder Diffraction Standards card 341216. †$MgSiO_3$ single-crystal Brillouin-scattering measurements (*6*). ‡Elasticity systematics of $\partial G/\partial P$ versus K_S/G for $MgSiO_3$ perovskite (*15*). §Temperature-averaged $\partial G/\partial T$ values of the lower mantle (*5*).

Y. D. Sinelnikov and R. C. Liebermann, Center for High Pressure Research and Department of Geosciences, State University of New York at Stony Brook, Stony Brook, NY 11794–2100, USA. G. Chen and M. T. Vaughan, Center for High Pressure Research and Mineral Physics Institute, State University of New York at Stony Brook, Stony Brook, NY 11794–2100, USA. D. R. Neuville, Laboratoire de Physique des Geomateriaux, Institut de Physique du Globe, 4 Place Jussieu, 75252 Paris Cedex 05, France.

*To whom correspondence should be addressed.