

Ab initio study of the elastic behavior of MgSiO₃ ilmenite at high pressure

Cesar R. S. Da Silva,¹ Bijaya B. Karki,¹ Lars Stixrude,²
Renata M. Wentzcovitch¹

Abstract. We investigate the athermal high pressure behavior of the elastic properties of MgSiO₃ ilmenite up to 30 GPa using the *ab initio* pseudopotential method. Our results at zero pressure are in good agreement with single-crystal elasticity measurements. The elastic anisotropy is shown to decrease slightly under compression and hence to remain substantial (25 to 20% shear wave anisotropy and 16 to 10% longitudinal wave anisotropy) over the pressure regime studied. The directions of fastest and slowest wave propagation are found to change slightly with pressure as determined by the pressure dependence of c_{14} and c_{25} . Comparisons with the elastic behavior of other deep transition zone phases such as ringwoodite and garnet show that ilmenite is likely to be the fastest and most anisotropic mineral in this region. Large contrasts ($\approx 10\%$) in velocities and densities between ilmenite and garnet are suggested to be significant for the interpretation of lateral structure in the transition zone.

1. Introduction

MgSiO₃ ilmenite is a high pressure polymorph of enstatite that is stable to temperatures as high as 2100 K in the Mg-metasilicate system [Gasparik, 1990]. In the mantle, the stability field of this phase is restricted to lower temperatures by the presence of Al which tends to stabilize garnet at the expense of ilmenite. Because of its limited stability in the earth, ilmenite is expected to occur only in cold subduction environments near the bottom of the transition zone. Here its unusual elastic properties may play an important role in the interpretation of three-dimensional seismic structure, especially of subducted slabs.

The MgSiO₃ end-member is expected to provide a good approximation to the elasticity of this phase in the mantle, where it will also contain secondary amounts of Fe-silicate and alumina components. At ambient conditions, single-crystal X-ray diffraction [Horiuchi *et al.*, 1982] and elasticity [Weidner and Ito, 1985] data for MgSiO₃ ilmenite are available. At higher pressures, only its equation of state and phase stability have been studied via theory and experiment [Matsui and Price, 1992; D'Arco *et al.*, 1994; Reynard *et al.*, 1996]; its elastic constants or seismic wave velocities are unknown. In this paper, we report first-principles determinations of the elastic parameters of MgSiO₃ ilmenite

as a function of pressure up to 30 GPa. The predicted elastic constants are used to study the pressure dependence of elastic anisotropy and wave velocities, and their geophysical implications.

2. Calculations and Results

Computations are performed using first principles variable cell shape (VCS) molecular dynamics [Wentzcovitch *et al.*, 1993] with the local density approximation (LDA) and pseudopotential theory. The soft and separable Troullier-Martins pseudopotentials [Troullier and Martins, 1991] are used. A plane wave basis set with cutoff of 70 Ry is used to expand the valence electronic wave functions. The Brillouin zone is sampled on a $3 \times 3 \times 3$ regular grid which produces 2 special k-points for the equilibrium structure and up to 4 points for strained lattices. The elastic constants are obtained from stress-strain relations as in the previous work [*e.g.*, Karki *et al.*, 1997]. The differences in energies and stresses are well converged so that computational uncertainties in the elastic constants are within 1-2 %.

MgSiO₃ ilmenite is a trigonal structure with space group $R\bar{3}$ and is characterized by seven independent elastic constants which we determine as a function of pressure up to 30 GPa (Figure 1). Our results at zero pressure compare favorably with ambient condition single-crystal measurements [Weidner and Ito, 1985] (Table 1). As expected, the first principles results show better agreement with experiment than do previous semi-empirical calculations [Matsui *et al.*, 1987]. Much of the differences between our results and experiment can be attributed to the temperature difference of 300 K (since our computations are static) and the overbinding effects of the local density approximation of our method. The elastic constant c_{11} remains much larger than c_{33} throughout the pressure regime studied indicating that the *c*-axis is more compressible than the *a*-axis, consistent with the high pressure x-ray powder diffraction data [Reynard *et al.*, 1996].

In order to study the elastic anisotropy in ilmenite, we calculate the single-crystal elastic wave velocities as a function of propagation direction by solving the Christoffel equation [Musgrave, 1970]. The trigonal ilmenite structure represents a slightly distorted hexagonal close-packing of O atoms with Mg and Si atoms in interstices. Relatively small values of c_{14} and c_{25} also indicate a slight deviation from hexagonal symmetry which shows transverse isotropy about the zonal (*z*) axis and finite anisotropy in the *yz* and *zx* planes [Musgrave, 1970]. Figure 2 depicts the azimuthal dependence of the compressional (P) and shear (S) wave velocities in ilmenite in the *xy*, *yz* and *zx* planes at zero pressure. The velocity curves in the basal plane show nearly circular symmetry about the *z*-axis, and this weak azimuthal anisotropy comes entirely from the small values of two off-diagonal elas-

¹Department of Chemical Engineering and Materials Science, Minnesota Supercomputing Institute, University of Minnesota, Minneapolis.

²Department of Geological Sciences, University of Minnesota, Ann Arbor, Michigan.

Copyright 1999 by the American Geophysical Union.

Paper number 1999GL900149.
0094-8276/99/1999GL900149\$05.00

Table 1. Zero pressure elastic moduli (M) in GPa and their pressure derivatives of MgSiO₃ ilmenite (from third-order finite strain fits), compared with experimental data [Weidner and Ito, 1985] and previous calculations [Matsui et al., 1987]

	c_{11}	c_{33}	c_{44}	c_{12}	c_{13}	c_{14}	c_{25}	K	G
Calc									
M	477	392	121	153	89	-28	-16	222	144
$\partial M/\partial P$	6.0	5.7	2.2	3.5	3.9	-0.4	0.3	4.5	1.6
Semi-empirical Calc									
M	444	383	90	173	122	-24	-28	234	120
Expt									
M	472	382	106	168	70	-27	-24	212	132

tic constants c_{14} and c_{25} . However, all elastic constants contribute to the anisotropy in other planes. The yz plane is found to show a stronger wave velocity anisotropy than the zx plane; and this slight difference in the anisotropy is associated with the condition that $c_{14} > c_{25}$.

We calculate the pressure variations of the total azimuthal anisotropy and maximum polarization anisotropy (for S-waves) [e.g., Karki et al., 1997], as shown in Figure 3. The azimuthal anisotropy is equal to the polarization anisotropy for S-waves at all pressures. The calculated anisotropy shows a slight monotonic decrease with increasing pressure. The S-wave anisotropy is much stronger than the P-wave anisotropy: The anisotropy is 25% for S-waves and 16% for P-waves at zero pressure whereas it is 20% for S-waves and 10% for P-waves at 30 GPa. The fastest

and slowest S-waves propagate in a direction close to [100], whereas P-waves are fastest and slowest for propagation directions close to [010] and [011] respectively, as marked in Figure 2. These directions change slightly under compression, and this behavior can be traced back to the pressure variations of c_{14} and c_{25} .

We determine the isotropically averaged velocities for P- and S-waves using the Voigt-Ruess-Hill averaging scheme [Hill, 1952] over the pressure range studied. The calculated athermal densities and wave velocities at zero pressure are 2-3 % larger than the measured values at ambient conditions [Weidner and Ito, 1985], partly as a result of the difference in temperature. The difference between upper (Voigt) and lower (Ruess) bounds is significant for this highly anisotropic mineral (up to 5%), and decreases with increasing pressure.

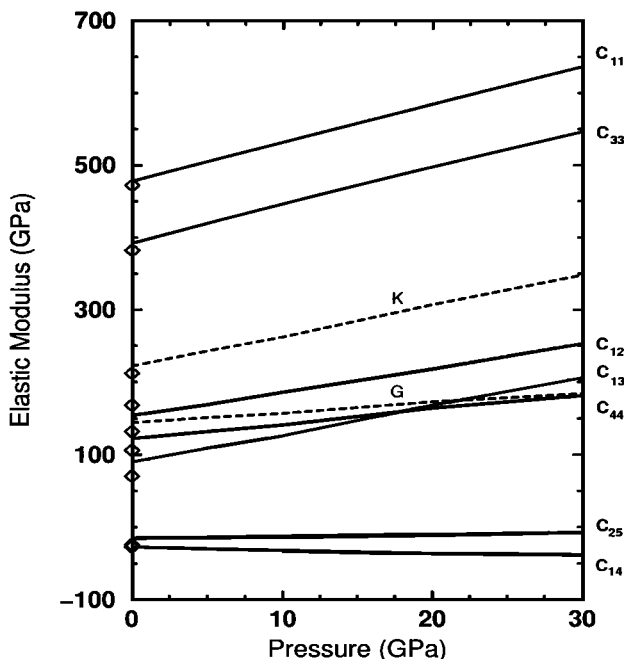


Figure 1. Pressure dependence of the elastic moduli (c_{ij} , K and G) of MgSiO₃ ilmenite. Symbols are the experimental data [Weidner and Ito, 1985].

3. Discussion

A comparison of the seismic wave velocities of ilmenite with those of other expected deep transition zone phases shows that ilmenite is the fastest mineral in the upper mantle (Figure 4). Its shear wave velocity is a few percent faster than that of ringwoodite [Kiefer et al., 1997], and 10 % faster than that of garnet-majorite [Liu et al., 1998]. This result is not likely to be substantially altered by the effects of more complex bulk composition and temperature. We estimate, based on the parameters given by [Duffy and Anderson, 1989], that addition of iron in the amount $X_{Fe} = 0.10$ may decrease the velocity difference between ilmenite and garnet-majorite to 8 %, and increasing the temperature to 1800 K has a similar, small effect, also reducing the difference to 8 %. Moreover, we note that addition of small amounts of alumina to MgSiO₃ ilmenite is likely to make this phase still faster compared with other upper mantle phases: corundum is 6 % faster than MgSiO₃ ilmenite [Duan et al., 1998].

The large contrast in V_S between ilmenite and garnet may be important for the interpretation of the three-dimensional structure of the transition zone as revealed by seismology [e.g. van der Hilst et al., 1991]. In general, lateral variations in seismic wave velocities may be caused by lateral variations in temperature, phase assemblage, or bulk composition. In the transition zone, lateral variations in tem-

perature and phase assemblage will be closely linked: one expects an isobaric phase transition from garnet to ilmenite as one moves from normal mantle into a cold subduction environment [Anderson, 1987]. The large velocity contrast

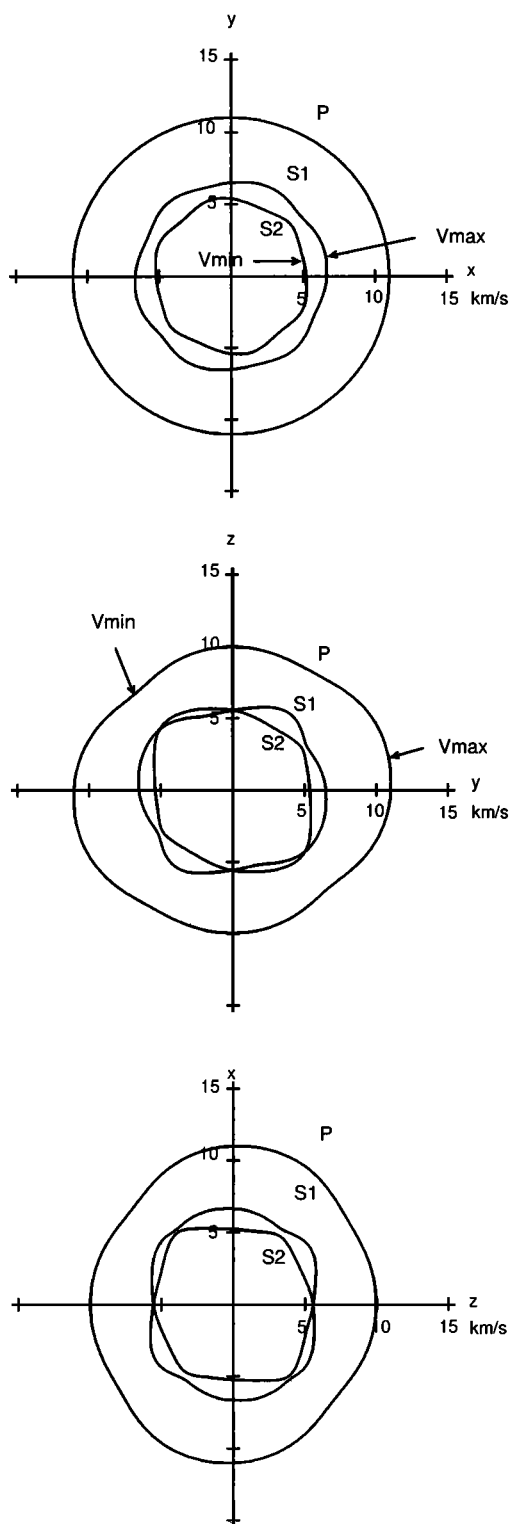


Figure 2. Angular variations of P- and S-wave velocities in the xy , yz and zx planes of MgSiO₃ ilmenite at zero pressure.

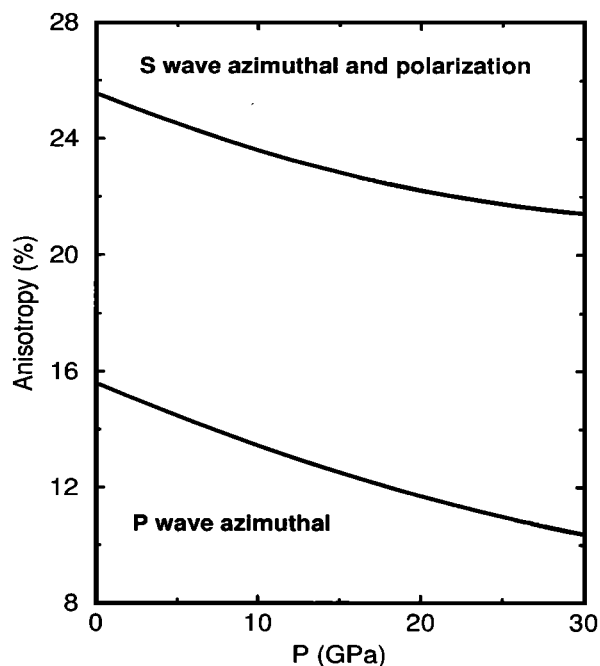


Figure 3. Pressure dependence of P- and S-wave velocity anisotropy of MgSiO₃ ilmenite.

between these two phases will magnify lateral heterogeneity compared to what would be expected on the basis of thermal effects alone. Our results indicate that at the bottom of the transition zone in a pyrolite mantle, a temperature decrease of 500 K will increase V_S by approximately 6 % if the effects of temperature and the isobaric phase change are included, or twice the effect of temperature alone.

The combined effects of temperature and isobaric phase transitions may also be significant for dynamical models that are based on conversion of seismic structure to lateral variations in density [Hager *et al.*, 1985]. The reason is that the garnet to ilmenite phase transition entails a density contrast (10 %) that is as large as the velocity contrast (Figure 4). Whereas dynamical calculations typically convert lateral variations in seismic wave velocities to variations in density by using a model value of $\partial \ln \rho / \partial \ln V_S < 0.4$ that is assumed to be independent of depth [Ricard *et al.*, 1993], our results indicate that this underestimates lateral density variations in the deep transition zone. A value closer to unity may be more appropriate for a pyrolite-like mantle composition in this region.

The structure of the transition zone and the interpretation of tomographic results may be further complicated by the very large anisotropy of ilmenite. We predict that the single-crystal S-wave anisotropy of ilmenite is comparable to that of olivine (greater than 20 %) and substantially greater than that of other deep transition zone phases such as ringwoodite and garnet-majorite [Kiefer *et al.*, 1997; Pacalo and Weidner, 1997; Chai *et al.*, 1997]. Moreover, some degree of alignment of ilmenite crystals in the non-hydrostatic environment of the slab may be expected. This is significant because it indicates that our results place an approximate upper bound on the anisotropy of cold portions of the deep transition zone: the maximum expected anisotropy (7 % in S, 4 % in P) is that of single crystal ilmenite reduced by its volume fraction [≈ 30 % in a pyrolite mantle, Ita and Stürzrude, 1992]. More precise statements regarding the

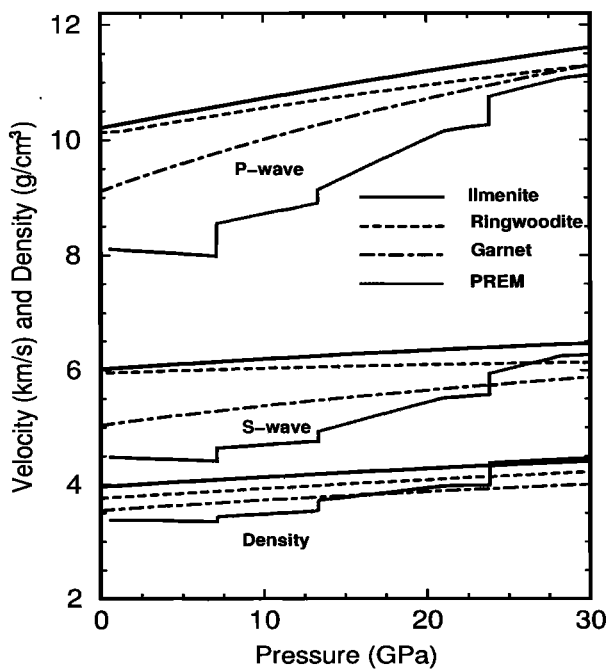


Figure 4. Density and isotropic P- and S-wave velocities of MgSiO₃ ilmenite as a function of pressure (solid lines). These results are compared with the properties of the mantle as represented by PREM [Dziewonski and Anderson, 1981] and other deep transition zone phases including ringwoodite [Kiefer et al., 1997] and garnet (62% pyrope + 38% majorite) [Liu et al., 1998].

likely anisotropy of this region will depend in detail on the texture of the polycrystalline aggregate, which is currently unknown.

Acknowledgments. This research was supported by the Minnesota Supercomputer Institute and the National Science Foundation under grants EAR-9628199 and EAR-9628042.

References

- Anderson, D. L., Thermally induced phase changes, lateral heterogeneity of the mantle, continental roots, and deep slab anomalies, *J. Geophys. Res.*, **92**, 13968-13980, 1987.
- Chai, M., J. M. Brown, and L. J. Slutsky, The elastic constants of a pyrope-grossular-almandine garnet to 20 GPa, *Geophys. Res. Lett.*, **24**, 523-526, 1997.
- D'Arco, P., G. Sandrone, R. Dovesi, E. Apra, and V. R. Saunders, A quantum-mechanical study of the relative stability under pressure of MgSiO₃ ilmenite, MgSiO₃ perovskite, and MgO-periclase+SiO₂ stishovite assemblage, *Phys. Chem. Miner.*, **21**, 285-293, 1994.
- Duan W., B. B. Karki, and R. M. Wentzcovitch, Elasticity of alumina by first-principles, *Am. Miner.*, 1998 (submitted).
- Duffy, T. and D. L. Anderson Seismic velocities in mantle minerals and the mineralogy of the upper mantle, *J. Geophys. Res.*, **94**, 1895-1912, 1989.
- Dziewonski, A. M., and D. L. Anderson, Preliminary reference Earth model, *Phys. Earth Planet. Inter.*, **25**, 297-356, 1981.
- Gasparik, T., Phase relations in the transition zone, *J. Geophys. Res.*, **95**, 15751-15769, 1990.
- Hager, B. H., R. W. Clayton, M. A. Richards, R. P. Comer, and A. M. Dziewonski, Lower mantle heterogeneity, dynamic topography and the geoid, *Nature*, **313**, 541-545, 1985.
- Hill, R., The elastic behavior of a crystalline aggregate, *Proc. Phys. Soc.*, **65A**, London, 349-354, 1952.
- Horiuchi, H., M. Horano, E. Ito, and Y. Matsui, MgSiO₃ (ilmenite-type): single crystal X-ray diffraction study, *Am. Mineral.*, **67**, 788-793, 1982.
- Ita, J. J. and L. Stixrude, Petrology, elasticity, and composition of the mantle transition zone, *J. Geophys. Res.*, **97**, 6849-6866, 1992.
- Karki, B. B., L. Stixrude, S. J. Clark, M. C. Warren, G. J. Ackland, and J. Crain, Elastic properties of orthorhombic MgSiO₃ perovskite at lower mantle pressures, *Am. Mineral.*, **82**, 635-638, 1997.
- Kiefer, B., L. Stixrude, and R. M. Wentzcovitch, Elastic constants and anisotropy of Mg₂SiO₄ spinel at high pressure, *Geophys. Res. Lett.*, **24**, 2841-2844, 1997.
- Liu, J., G. Chen, G. D. Gwanmesia, and R. C. Liebermann, Elastic wave velocities of a pyrope-majorite (Py₆₂Mj₃₈) garnet to 9 GPa, *Phys. Earth Planet. Int.*, in press.
- Matsui, M., M. Akaogi, and T. Matsumoto, Computational model of the structural and elastic properties of the ilmenite and perovskite phases of MgSiO₃, *Phys. Chem. Miner.*, **14**, 101-106.
- Matsui, M., and G. D. Price, Computer simulation of the MgSiO₃ polymorphs, *Phys. Chem. Miner.*, **18**, 365-372, 1992.
- Musgrave, M. J. P., *Crystal Acoustics*, Holden-Day, San Francisco, 1970.
- Pacalo, R. E. G. and D. J. Weidner, Elasticity of majorite, MgSiO₃ tetragonal garnet *Phys. Earth Planet. Int.*, **99**, 145-154, 1997.
- Reynard, B., G. Fiquet, J. -P. Itie, and D. C. Rubie, High-pressure X-ray diffraction study and equation of state of MgSiO₃ ilmenite, *Am. Mineral.*, **81**, 45-50, 1996.
- Ricard, Y., M. Richards, C. Lithgow-Bertelloni, and Y. Lestunff, A geodynamic model of mantle density heterogeneity, *J. Geophys. Res.*, **98**, 21895-21909, 1993.
- Troullier, N., and J. L. Martins, Efficient pseudopotentials for plane-wave calculations, *Phys. Rev. B*, **43**, 1993-2003 (1991).
- van der Hilst, R., R. Engdahl, W. Spakman, and G. Nolet, Tomographic imaging of subducted lithosphere below northwest pacific island arcs, *Nature*, **353**, 37-43, 1991.
- Wentzcovitch, R. M., J. L. Martins and G. D. Price, *Ab initio* molecular dynamics with variable cell shape: application to MgSiO₃ perovskite, *Phys. Rev. Lett.*, **70**, 3947-3950, 1993.
- Weidner, D. J., and E. Ito, Elasticity of MgSiO₃ in the ilmenite phase, *Phys. Earth Planet. Int.*, **40**, 65-70, 1985.
- C. R. S. Da Silva, B. B. Karki, and R. M. Wentzcovitch, Department of Chemical Engineering and Materials Science, Minnesota Supercomputing Institute, University of Minnesota, 421 Washington Ave., SE, Minneapolis, MN 55455. (e-mail: karki@cems.umn.edu)
- Lars Stixrude, Department of Geological Sciences, University of Michigan, 425 E. University Ave., Ann Arbor, MI 48109-1063. (e-mail: stixrude@umich.edu)

(Received December 18, 1998; revised February 18, 1999; accepted February 23, 1999.)