The elastic constants of MgSiO3 perovskite at pressures and temperatures of the Earth’s mantle

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The temperature anomalies in the Earth’s mantle associated with thermal convection1 can be inferred from seismic tomography, provided that the elastic properties of mantle minerals are known as a function of temperature at mantle pressures. At present, however, such information is difficult to obtain directly through laboratory experiments. We have therefore taken advantage of recent advances in computer technology, and have performed finite-temperature ab initio molecular dynamics simulations2 of the elastic properties of MgSiO3 perovskite, the major mineral of the lower mantle, at relevant thermodynamic conditions. When combined with the results from tomographic images of the mantle, our results indicate that the lower mantle is either significantly anelastic3 or compositionally heterogeneous on large scales4. We found the temperature contrast between the coldest and hottest regions of the mantle, at a given depth, to be about 800 K at 1,000 km, 1,500 K at 2,000 km, and possibly over 2,000 K at the core–mantle boundary.

Ab initio molecular dynamics, pioneered by Car and Parrinello5, has made a substantial impact on modern planetary and materials sciences6–8. Advantages of this approach—which is computationally expensive—include the explicit account of the quantum nature of electronic structure and interatomic interactions, and the description of the intrinsic anharmonicity of lattice vibrations. This is the method of choice for simulating high-temperature phenomena that are significantly anharmonic, such as melting9,10, ionic conductivity, displaceable phase transitions, thermal expansion10, and elastic properties. Calculations of elastic constants of materials using ab initio molecular dynamics can be done by one of two routes: (1) from fluctuations of stress or strain, or (2) from stress–strain relations, that is, from Hooke’s law. Both routes require enormous computational efforts; very long runs are required by the first method, and in the second method, it is necessary to perform several independent simulations for different lattice strains that include the nonlinearity of stress–strain relations. Recent advances in computer technology and increased accessibility of supercomputers have now made such simulations possible.

Orthorhombic MgSiO3 perovskite is an ideal subject for ab initio molecular dynamics simulations. When containing some Fe, it is the most abundant mineral in the Earth, comprising 60–100 vol.% of the lower mantle, and dominating many of its properties. The lower mantle comprises over 50% of the Earth’s volume; extending between the depths of 670 km and 2,891 km, it is characterized by very high pressures (24–136 GPa) and temperatures, roughly between 2,000 K and 3,000 K, possibly rising to about 4,000 K (ref. 11). At these temperatures atomic motion is essentially classical and possibly significantly anharmonic, making it appropriate to use the molecular dynamics approach. A hypothetical cubic phase with superionic conductivity has been proposed as an explanation of the observed high electrical conductivity of the lower mantle12,13; molecular dynamics is the only currently viable way to simulate fast ionic conduction phenomena in solids. Our previous work14 considered ‘static’ elastic constants (that is, the thermal motion of atoms was neglected), and used ab initio molecular dynamics to study the thermal expansivity and the thermal equation of state of MgSiO3 perovskite—which was found to stay orthorhombic at lower-mantle temperatures. Here we perform ab initio molecular dynamics simulations of elastic constants of MgSiO3 perovskite at lower-mantle conditions, taking full account of temperature. At this stage we consider only pure MgSiO3 perovskite. The effects of the moderate Fe content, while potentially important for certain properties (such as shear modulus), are expected to be negligible for others—especially for the thermal expansion, bulk modulus, and derivatives (with respect to pressure and temperature) of the elastic moduli and seismic wave velocities, which are the main subject of this work.

Seismic tomography gives insight into the three-dimensional structure and dynamics of the Earth, but its quantitative interpretation requires knowledge of temperature variations of seismic wave...
velocities. Seismology gives $R_T = (\partial \ln v_s/\partial \ln P)_T$, the ratio of variation of the shear ($v_s$) and compressional ($v_p$) velocities due to pressure alone, as 0.7 (ref. 1). A similarly defined parameter, $R_P = (\partial \ln v_p/\partial \ln P)_T$, measuring the same ratio, but due to temperature effects alone, is much larger: it increases from 1.7 to 2.6 between the depths of 1,000 km and 2,000 km according to seismic tomography data\cite{15}. The large difference between $R_T$ and $R_P$ has been a puzzle for geophysicists over past 15 years; Anderson\cite{1} suggested that the difference is entirely due to intrinsic anharmonicity, the simulation of which needs molecular dynamics or Monte Carlo methods, rather than the quasiharmonic approximation.

Our ab initio molecular dynamics simulations (Figs 1 and 2) were performed with the VASP code\cite{3} run on 128 nodes of the CRAY T3E supercomputer at Manchester Computer Centre. The calculated equilibrium lattice parameters, isothermal and adiabatic elastic constants, and thermal expansion coefficients are presented in Table 1. One of the calculated points, 38 GPa and 3,500 K, is close to the melting point of MgSiO$_3$ perovskite\cite{16} (results of this study indicated that melting would occur at ~3,800 K under a pressure of 38 GPa; however, there is still controversy about the melting curve of MgSiO$_3$ perovskite). Although we observed very large displacements of atoms, all atoms vibrated about their ideal crystallographic locations and did not diffuse, and shear elastic constants were large and positive. It is remarkable that even at these conditions orthorhombic MgSiO$_3$ perovskite does not transform to a cubic or tetragonal phase. Anomalous elastic constants obtained at these critical conditions were not used in the further analysis.

We calculate $R_T = 0.61$–0.81 (our static simulations\cite{17} give 0.59–0.74), in keeping with geophysical observations. The value of $R_P$ increases from 1.5 at a depth of 1,000 km to 1.9 at 2,000 km. These

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**Table 1 Properties of MgSiO$_3$ perovskite at high pressures and temperatures**

| Property | 38 GPa, 1,500 K | 38 GPa, 2,500 K | 38 GPa, 3,500 K | 88 GPa, 1,500 K | 88 GPa, 3,500 K |
|----------|----------------|----------------|----------------|----------------|----------------|
| $V$      | 147.63         | 150.83         | 154.08         | 132.55         | 136.48         |
| $a$      | 4.628          | 4.675          | 4.723          | 4.435          | 4.499          |
| $b$      | 4.792          | 4.814          | 4.836          | 4.674          | 4.674          |
| $c$      | 6.668          | 6.703          | 6.747          | 6.420          | 6.492          |
| $\alpha$ | 37.9           | 38.0           | 38.0           | 88.1           | 87.6           |
| $P$      | 37.9           | 37.6           | 37.6           | 88.1           | 87.6           |
| $C_{11}^{\text{TS}}$ | 601/616 | 593/679 | 525/564 | 813/826 | 749/783 |
| $C_{12}^{\text{TS}}$ | 697/711 | 629/654 | 545/578 | 978/991 | 847/878 |
| $C_{44}^{\text{TS}}$ | 649/663 | 591/815 | 545/580 | 933/845 | 821/850 |
| $C_{55}^{\text{TS}}$ | 266/250 | 233/258 | 222/258 | 464/477 | 398/451 |
| $C_{66}^{\text{TS}}$ | 235/249 | 218/243 | 218/256 | 348/362 | 324/356 |
| $g_{23}$ | 251/264 | 240/265 | 251/286 | 383/396 | 364/395 |
| $G$     | 262            | 232            | 202            | 336            | 270            |
| $C_{12}$ | 219            | 210            | 190            | 266            | 234            |
| $C_{44}$ | 199            | 178            | 147            | 264            | 195            |
| $K_{23}$ | 382.7/396.8   | 349.9/375.8   | 332.7/389.5   | 565.7/579.4   | 508.6/542.5   |
| $\gamma$ | 0.60          | 0.51          | 0.51          | 0.51          | 0.51          |
| $\alpha$ | 2.15          | 2.15          | 2.26          | 1.34          | 1.51          |

Here $V$, $a$, $b$, and $c$ are unit cell volume and lattice parameters, in $\text{Å}^3$ and $\text{Å}$, respectively; $\alpha$, $\beta$, $\gamma$ are stress tensor components, showing that non-hydrostatic deviations from the average pressure $P$ are very small; $C_{ij}$ are elastic constants (7; isothermal; $S$, adiabatic) in GPa (errors of a few per cent); $K$ and $G$ are Voigt-Reuss-Hill bulk and shear moduli in GPa (errors within 2%); $\gamma$ is the Grüneisen parameter and $\alpha$ a thermal expansion in $10^{-4}$ K$^{-1}$ (errors within 1%). Important derivatives: $\partial \ln v_s/\partial \ln P)_T = 2.49 \times 10^{-4}$ K$^{-1}$ (88 GPa), $-2.49 \times 10^{-4}$ K$^{-1}$ (88 GPa), $-2.49 \times 10^{-4}$ K$^{-1}$ (88 GPa); $-1.98 \times 10^{-4}$ K$^{-1}$ (88 GPa); $-1.98 \times 10^{-4}$ K$^{-1}$ (88 GPa); $-1.98 \times 10^{-4}$ K$^{-1}$ (88 GPa); $-1.98 \times 10^{-4}$ K$^{-1}$ (88 GPa); $-1.98 \times 10^{-4}$ K$^{-1}$ (88 GPa).
values, obtained taking full account of anharmonic effects, are still lower than the observed values. Karki et al., using the quasiharmonic approximation, found $R_0$ of MgO to increase from 1.4 to 1.9 from the top to the bottom of the lower mantle. This agrees well with our results for MgSiO$_3$; the remaining deficit of $R_0$ can only be explained by either significant anelasticity or large-scale compositional heterogeneity of the lower mantle.

Seismic tomography is a quickly developing technique; the most recent tomography maps have similar qualitative features (locations of cold slabs and hot plumes), and give the absolute velocity perturbations within $\sim$25% uncertainty. For interpreting seismic tomography in terms of temperature, it is most convenient to use the bulk sound velocity $v_p$, whose seismological determination is unaffected by anelastic effects. The bulk velocity maps can be accurately determined by the joint inversion of the shear and compressional velocities. Perhaps the most reliable global seismic tomography maps currently available are those of Masters et al. Older higher-resolution maps of Kennett et al. realistically give much narrower cold (high-velocity) zones, but strongly underestimate the amplitudes of the velocity variations.

We find the temperature derivative of the bulk velocity, $\phi = (\delta v_p/\delta T)_s$, to vary from $1.7 \times 10^{-4}$ K$^{-1}$ at 1,000 km to $-0.9 \times 10^{-5}$ K$^{-1}$ (errors $\pm 20\%$) at 2,000 km depth. Temperature variations can be obtained from the relative velocity perturbations: $\delta T = (\delta v_p/\delta v_p)\phi$. Combined with bulk sound velocity maps of Masters et al. (maximum velocity contrast $\delta v_p/v_p = 1.4\%$ at 1,225 km and 2,195 km), this gives the temperature contrast between the hot plumes and cold slabs increasing from 800 K to 1,500 K between 1,000 and 2,000 km depth. Linear extrapolation gives $\sim 550$ K at the top of the lower mantle, and 2,150 K at the bottom. The root-mean-square temperature variations are $\sim 150$–250 K across the lower mantle. Our temperature contrasts are $\sim 2$–4 times smaller than estimates obtained using extremely uncertain extrapolations of $\Delta \phi = (\delta v_p/\delta T)_s$ and which would suggest partial melting of the lower mantle. Our results can support partial melting only in the lowermost part of the lower mantle. Castle et al., using their shear velocity maps for the bottom of the lower mantle (maximum $\Delta v_p/v_p = 7.4\%$) and a reasonable guess for $\phi$, obtained an estimate of the temperature contrast at the core–mantle boundary similar to ours, $\sim 1,600$ K. Using the $v_p$-maps of Kennett et al. (maximum $\Delta v_p/v_p = 1.0\%$ at 1,225 km and 2,195 km), we get much smaller temperature contrasts, rising from $\sim 500$ K to $\sim 1,000$ K between the depths of 1,000 km and 2,000 km.

It is becoming increasingly clear that temperature variations are the main factor determining the perturbations of seismic wave velocities in the lower mantle. Anelasticity can be important for the shear velocities, but is negligible for the bulk velocities. Compositional heterogeneity is significant only near the core–mantle boundary; it can occur due to the chemical reaction between core and mantle, driving Fe from the silicate mantle into the metallic core. Hot plumes, rising from the core–mantle boundary, would then be depleted in Fe. When substituting for Mg, Fe dramatically decreases shear moduli of many silicates and oxides, while the effect on bulk moduli is very small. Hence, even minor regional variations of the Fe content can have a major effect on the shear velocities, being less important for the bulk velocity. For example, very hot, slightly Fe-depleted mantle rocks can have the same shear velocities as very cold, slightly Fe-enriched mantle rocks. Consistent with the depletion of plumes in Fe, we find the temperature contrasts at 2,000 km determined for the shear velocities (1,000 K from maps) to be smaller than those determined from the corresponding bulk velocities (1,500 K from maps). This effect can even produce an anticorrelation between the bulk and shear velocities, but not its observed pattern: it remains a mystery why it is the bulk (not shear) velocity anomalies that undergo a reversal near the core–mantle boundary (that is, low-velocity zones at the core–mantle boundary underlay high-velocity anomalies of the rest of the lower mantle). In any case, the temperature contrasts obtained from the bulk velocities must be the most reliable, at least outside the anomalous core–mantle boundary region, in which compositional effects seem to be significant for all types of seismic waves. The temperature contrasts that we have found could be used as important constraints in numerical modelling of mantle convection.

Kesson et al. estimated that lithospheric slabs should be at least $\sim 650$ K colder than surrounding mantle if they are to sink to the core–mantle boundary, and at least 250 K colder to reach the depth of 1,100 km. Our maximum cold temperature anomalies (roughly half of the total temperature contrasts) are similar to these estimates, and suggest that some lithospheric slabs might stop sinking before reaching the core–mantle boundary. Neutrally buoyant slabs would be dissolved by the convecting mantle; some tomographic maps show most slabs disappearing in the middle of the lower mantle, while others’ show that most slabs do reach the core–mantle boundary.

The next step is to estimate the extent of chemical heterogeneity and anelasticity in the lower mantle, and construct a three-dimensional compositional model of the Earth’s mantle. With improved seismic tomography models and mineral physics data, this could be achieved in the foreseeable future. We believe that ab initio molecular dynamics simulations will be important in solving this and many other geologically important problems.

1. Anderson, D. L. Theory of the Earth (Blackwell Scientific Publications, Boston, 1989).
2. Car, R. & Perrillen, M. Unified approach for molecular dynamics and density-functional theory. Phys. Rev. Lett. 55, 2471–2474 (1985).
3. Kresse, G. & Furthmuller, J. Efficiency of ab initio total-energy calculations for metals and semiconductors using a plane-wave basis set. Comp. Mater. Sc. 6, 15–50 (1996).
4. Karato, S.-i. Importance of anelasticity in the interpretation of seismic tomography. Geophys. Res. Lett. 20, 1623–1626 (1993).
5. Masters, G., Loske, G., Bolton, H. & Dziembowski, A. In Earth’s Deep Interior: Mineral Physics and Tomography. From the Atomic to the Global Scale (eds Karato, S.-i. et al.) 61–87 (AGU Geophys. Monogr. 113, American Geophysical Union, Washington DC, 2000).
6. Andriolo, F., Ciardelli, G. L., Scandalò, S. & Tossati, E. Dissociation of methane into hydrocarbons at extreme (planetary) pressure and temperature. Science 275, 1288–1290 (1997).
7. Cavazzoni, C. et al. Superionic and metallic states of water and ammonia at giant planet conditions. Science 283, 44–46 (1999).
8. Alff, D., Gillian, M. J. & Price, G. D. The melting curve of iron at the pressures of the Earth’s core from ab initio calculations. Nature 401, 462–464 (1999).
9. Sago, O. & Car, R. Ab initio molecular dynamics study of first-order phase transitions: melting of silicon. Phys. Rev. Lett. 74, 1823–1826 (1995).
10. Buda, F., Car, R. & Perrillen, M. Thermal expansion of c-Si via ab initio molecular dynamics. Phys. Rev. B 74, 16180–16183 (2009).
11. da Silva, C., Wentzcovitch, R. M., Patel, A., Price, G. D. & Karato, S.-i. The composition and geotherm of the lower mantle: constraints from the elasticity of silicate perovskite. Phys. Earth Planet. Inter. 118, 103–109 (2000).
12. O’Keeffe, M. & Bovin, J. O. Solid electrolyte behaviour of NaMgF$_3$: geophysical implications. Science 266, 599–600 (1979).
13. Matsui, M. & Price, G. D. Simulation of the pre-melting behaviour of MgSiO$_3$ perovskite at high pressures and temperatures. Nature 353, 735–737 (1991).
14. Ogawa, A. K., Brodholt, J. P. & Price, G. D. Ab initio electronic and thermal elasticity of state of MgSiO$_3$ perovskite. Earth Planet. Sci. Lett. 184, 555–560 (2001).
15. Robertson, G. S. & Woodhouse, J. H. Constraints on lower mantle properties from seismology and mineral physics. Earth Planet. Sci. Lett. 143, 197–205 (1996).
16. Shen, G. & Lazor, P. Measurement of melting temperatures of some minerals under lower-mantle pressure. J. Geophys. Res. 100, 17699–17713 (1995).
17. Karki, B. B., Wentzcovitch, R. M., de Gironcoli, S. & Baroni, S. The composition and geotherm of the lower mantle: constraints from the elasticity of silicate perovskite. J. Geophys. Res. 105, 140,113–140,118 (2000).
18. O’Keeffe, M. & Bovin, J. O. Solid electrolyte behaviour of NaMgF$_3$: geophysical implications. Science 266, 599–600 (1979).
Phylogenetic comparative investigations typically rely on a single phylogenetic tree and reconstruct ancestral states on the basis of the method of parsimony. However, phylogenetic trees are rarely known without error and different tree topologies can give different estimates of ancestral states. In addition, ancestral states reconstructed by parsimony do not account for the statistical uncertainty of ancestral inferences. Both of these problems are acute when reconstructing the evolution of the lichen symbiosis. All previous broad phylogenetic studies of the Ascomycota had low bootstrap support and unstable relationships in critical portions of the trees. Furthermore, parsimony methods may perform poorly when rates of character evolution are high.

We used a Bayesian statistical procedure based on Markov chain Monte Carlo (MCMC) sampling methods to account for phylogenetic uncertainty. This sampling procedure allows us to draw a random sample from the universe of possible phylogenetic trees. The frequency distribution of the sample estimates the posterior probability distribution of trees (see Methods). From the distribution of sampled trees we calculated the posterior probability of ancestral nodes and focused our data interpretation on those nodes with the highest statistical certainty.

We used a statistical model of trait evolution to estimate on each tree the evolutionary rate of gains and losses of lichenization, and the most probable ancestral states (lichen-forming/non-lichen-forming) at specified nodes. Rates of evolution between states are calculated over all possible states at each node of a given tree and are therefore independent of any particular reconstruction of the ancestral states. The model of trait evolution takes into account the lengths of the branches of the phylogenetic tree, does not constrain the rates of gains and losses a priori, and expresses the statistical uncertainty associated with estimates of ancestral states at each node. To derive an overall estimate of the rates of evolution or the probability of an ancestral state, the estimates from each tree are averaged (see Methods). Our inferences about the nature of the evolutionary processes underlying lichen evolution thereby take account of uncertainty inherent to the phylogenetic hypothesis, and are not conditional on any particular tree.

We sampled 19,900 phylogenetic trees using the MCMC procedure, and estimated by maximum likelihood the rates of gains and losses of lichenization on each (Fig. 1). Larger rate values correspond to a higher expected number of transformations (losses or gains), and the loss/gain ratio (dots in Fig. 1) directly estimates the ratio of expected losses to expected gains of lichenization during evolution.

In contrast with previous work on the evolution of the lichen symbiosis, our results show that rates of loss of lichenization exceed rates of gain in the Ascomycota. In 18,029 of the 19,900 sampled trees (90.6%) the estimated rate of loss exceeds the rate of gain (that is, the loss/gain ratio is greater than one, and therefore is above the

**Figure 1** The rate of loss of lichenization exceeds the rate of gain of lichenization, independently of tree topology. Data are for 19,900 MCMC trees. The 1:1 relationship is indicated by the solid line.

**Major fungal lineages are derived from lichen symbiotic ancestors**

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About one-fifth of all known extant fungal species form obligate symbiotic associations with green algae, cyanobacteria or with both photobionts. These symbioses, known as lichens, are one way for fungi to meet their requirement for carbohydrates. Lichens are widely believed to have arisen independently on several occasions, accounting for the high diversity and mixed lineages within the Ascomycota. Ascomycota include lichen-forming taxa, and 8–11 of these lineages are derived from lichen-symbiotic ancestors. Aspergillus is a genus exclusively non-lichen-forming species are derived from lichen-forming ancestors. These species include taxa with important benefits and detriments to humans, such as *Penicillium* and *Aspergillus*.

To investigate the evolution of the lichen symbiosis it is necessary to account for the phylogenetic relationships within the Ascomycota, and to infer the rates and likely pattern of gains and losses of the symbiotic state. We reduced the high level of uncertainty associated with small subunit nuclear ribosomal RNA gene (SSU nuclear rDNA) phylogenies of the Ascomycota by obtaining sequences from the small and large subunit (LSU) of the nuclear rRNA genes for 52 species of the Ascomycota. Our sample includes representatives from 24 of 46 orders, representing 27% of the Ascomycota species diversity.

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