



High-pressure, temperature elasticity of Fe- and Al-bearing MgSiO₃: Implications for the Earth's lower mantle



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ABSTRACT

Fe and Al are two of the most important rock-forming elements other than Mg, Si, and O. Their presence in the lower mantle's most abundant minerals, MgSiO₃ bridgmanite, MgSiO₃ post-perovskite and MgO periclase, alters their elastic properties. However, knowledge on the thermoelasticity of Fe- and Al-bearing MgSiO₃ bridgmanite, and post-perovskite is scarce. In this study, we perform *ab initio* molecular dynamics to calculate the elastic and seismic properties of pure, Fe³⁺- and Fe²⁺-, and Al³⁺-bearing MgSiO₃ perovskite and post-perovskite, over a wide range of pressures, temperatures, and Fe/Al compositions. Our results show that a mineral assemblage resembling pyrolite fits a 1D seismological model well, down to, at least, a few hundred kilometers above the core–mantle boundary, i.e. the top of the D'' region. In D'', a similar composition is still an excellent fit to the average velocities and fairly approximate to the density. We also implement polycrystal plasticity with a geodynamic model to predict resulting seismic anisotropy, and find post-perovskite with predominant (001) slip across all compositions agrees best with seismic observations in the D''.

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1. Introduction

Fe-bearing perovskite (Pv, a.k.a. bridgmanite) and post-perovskite (pPv) are the most abundant minerals in the Earth's lower mantle. A good knowledge of their elastic properties under relevant high-pressure (P) and temperature (T) conditions is of fundamental importance for understanding the structure and dynamics of the Earth's interior. Experiments have suggested that Pv hosts ~10 mol.% iron and a slightly lower amount of Al in the pyrolitic model composition, expected from the top to, at least, the mid-lower mantle (Irifune et al., 2010). It is also known that the amount of Fe in different ionic states can be controlled by oxidation, charge disproportionation and the existence of Al (Xu et al., 2015). Despite this, it is still debated how much iron remains in Pv, how it is distributed between Pv and pPv, and whether Fe²⁺ disproportionates to form Fe³⁺ + Fe⁰ metal, or partitions into magnesio-wüstite or melt, in the lowermost mantle (e.g., Mao et al., 2004; Irifune et al., 2010). Currently, there is scarce experimental data available on the elastic properties of these systems (Murakami et al., 2012), and the uncertainty could be huge, due to the interplay

between the above factors and technical issues relating to the extreme conditions. This necessitates theoretical methods, which are not limited by the same constraints as experiments and have been proven to be a powerful tool in determining the elastic properties of minerals at lower mantle conditions.

There have been several reports on the elastic properties of these Pv and pPv systems using first-principle calculations. However, these have mainly focused on pure MgSiO₃ for high- T conditions (Oganov et al., 2001; Wentzcovitch et al., 2004, 2006; Stackhouse et al., 2005; Stackhouse and Brodholt, 2007; Zhang et al., 2013), or Fe/Al-bearing systems at 0 K (Kiefer et al., 2002; Caracas and Cohen, 2005; Li et al., 2005a; Stackhouse et al., 2005, 2006, 2007; Tsuchiya and Tsuchiya, 2006), because of the high computational cost and the complex structural and electronic properties of Fe/Al-bearing systems at high P and T .

Examples on this complexity include the pressure-induced high-spin (HS) to low-spin (LS) transition in iron (Badro et al., 2004) and challenges arising from the large number of mechanisms that iron can enter the Pv and pPv structures. Ferrous iron substitutes for Mg in the pseudo-dodecahedral A (Mg-) site, but for ferric iron charge balance requires the coupled substitution of Fe–Al or Fe–Fe pairs (Zhang and Oganov, 2006a), with one cation at the A site and the other at the octahedral B (Si-) site. Incorporation

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of ferric iron via the oxygen vacancy mechanism is not expected in Pv and pPv at lower mantle conditions (Brodholt, 2000).

Ferrous iron, in the A site, is expected to remain in the HS state, in Pv and pPv, at all mantle conditions (Hsu et al., 2011b; Yu et al., 2012). In contrast, ferric iron undergoes a spin transition at lower-mantle pressures, as the crystal field splitting surpasses the spin pairing energy, which breaks the Hund's rule that predicts all five *d* electrons in Fe³⁺ have the same spin (HS state) and stabilizes the LS state (3 electrons spin up, 2 down). The spin transition of ferric iron is expected to start at about 75 GPa at the A site, and at much lower pressures at the B site (Zhang and Oganov, 2006b; Li et al., 2005b; Hsu et al., 2011a, 2012).

In recent years, there have been several studies on the effects of ferrous and ferric iron on the thermoelastic properties of Pv and pPv (Metsue and Tsuchiya, 2011; Tsuchiya and Wang, 2013; Shukla et al., 2015). To date, agreement with seismological models of the lower mantle has not been reached. One potential reason is that the influence of Al³⁺ has not yet been included, and another could be related to the possible inadequacy of using the quasi-harmonic approximation (QHA) in computing thermoelasticity at high-*P* and *T*. There has been one study that used density functional molecular dynamics (DFT-MD) to calculate the properties of Pv and pPv enriched with ferrous iron (Muir and Brodholt, 2015), but this only reports values at one pressure.

In this letter, we apply DFT-MD to determine the elastic properties of ferrous and ferric iron-bearing Pv and pPv over a wide range of pressure and temperature conditions relevant to the Earth's lower mantle. In the case of ferric iron, Fe–Al and Fe–Fe substitution are considered. DFT-MD naturally accounts the anharmonicity of lattice dynamics, which is important for describing the elastic behavior of minerals at high *T* (above the Debye temperature) and has been used in several previous studies (Stackhouse et al., 2005; Zhang et al., 2013). In the case of ferrous iron only the HS state is considered, whereas for ferric iron different Fe–Fe or Fe–Al compositions in various possible spin states are considered. The structures are included in the supplementary material. High-*T* lattice parameters are obtained by performing DFT-MD simulations at constant pressures (NPT ensemble), which is followed by fixed-cell (NVT) calculations on strained structures to calculate the elastic coefficients and other elastic properties. Based on these calculations, we derive the seismic properties of a mineral assemblage to compare with a 1D seismological model, with the aim of constraining the mineral composition of the lower mantle. We further exemplify shear wave anisotropic properties resulting from deformation within a deep subducting slab and discuss the implications for seismic observations of shear wave anisotropy.

2. Theory

2.1. Computational methods

Our calculations are performed using the Vienna *ab initio* simulation package (VASP) (Kresse and Furthmüller, 1996). The local density approximation (LDA)-based (Ceperley and Alder, 1980) exchange–correlation functional is used. It has been shown that in some cases, standard DFT functionals can fail to predict the correct electronic properties of iron-bearing minerals, and inclusion of a Hubbard *U* term leads to improved predictions of their electronic, structural and elastic properties (Stackhouse et al., 2010). However, a recent study suggests that provided standard DFT functionals produce the correct insulating ground states and correct orbital occupancy, the structural and elastic properties predicted with them should be similar to those with a *U* term (Hsu et al., 2011b). We confirmed this conclusion by comparing the results of calculations with and without a *U* term, for a select number of

iron-bearing Pv structures (Table S4, supplementary material), and performed the remainder without a *U* term.

The supercell sizes $2 \times 2 \times 1$ (80-atom) for Pv, and $3 \times 1 \times 1$ (60-atom) or $4 \times 1 \times 1$ (80-atom) for pPv are used. We employ projector augmented wave pseudopotentials with core radii equaling 2.2, 1.9, 2.0, 1.9, and 1.52 Bohr for Fe, Al, Mg, Si, and O, respectively. In static calculations, the plane wave energy cutoff is set to 800 eV, and *k*-mesh of $2 \times 2 \times 4$ (for Pv supercell) or $6 \times 6 \times 6$ (for pPv supercell) are chosen for Brillouin zone sampling. The enthalpy is evaluated based on structures that are all relaxed until all forces are smaller than 10^{-4} eV/Å. In MD simulations, we follow previous studies (Stackhouse and Brodholt, 2007; Zhang et al., 2013) and use time step of 1 fs, energy cutoff of 500 eV and only the Γ point to sample the Brillouin zone. Tests show that using these settings the elastic properties are converged to within statistical error. We use the Nosé thermostat to control the temperature (Nosé, 1984). The lattice constants are obtained by averaging over NPT trajectories. These are then used in the NVT simulations. For calculating the elastic constants from linear stress–strain relations, three axial and one triclinic strain are applied to the cell. During NPT, we fix the cell to be orthorhombic to avoid unnecessary fluctuations. The same averaging scheme is applied to NVT trajectories to retrieve stress components and energies. The NPT and NVT trajectories are typically over 3 ps and 5 ps, respectively. The convergence is shown in the supplementary material.

For ferrous iron we include four Fe²⁺ in 80-atom unit cells of Pv and pPv to construct (Mg_{1-x}Fe_x)SiO₃ structures with an atomic percent *x* equal to 25%. For ferric iron we include one or two Fe³⁺–M³⁺ (M representing Fe or Al) pairs in MgSiO₃ by charge-coupled substitution Fe_{Mg} + M_{Si} in order to construct (Mg_{1-x}Fe_x)(Si_{1-x}M_x)O₃ structures with atomic percent *x* equal to 6.25% or 12.5% for Pv, and 8.33% or 16.7% for pPv. Such iron or aluminum compositions are relevant to the lower mantle (Irfune et al., 2010). For Fe²⁺ in these models, we consider only the HS (spin momentum $S = 4/2$) ferromagnetic state, whereas for Fe³⁺ we consider both the HS ($S = 5/2$) and LS ($S = 1/2$) states. Intermediate-spin states are not considered because they have been found to be energetically disfavored in previous studies (Hsu et al., 2011a). For systems with multiple ferric iron cations, we take into account all possible spin configurations, including pure HS, pure LS, or HS–LS mixtures in the ferromagnetic (FM) or antiferromagnetic (AFM) states. Our results confirm conclusions reached in several previous DFT calculations on the site-dependence and values of the transition pressure, i.e., Fe³⁺ has higher transition pressure at the A-site than at B-site. This enables us to disregard unlikely configurations, for example, B-site Fe³⁺ in HS at 100 GPa. In spite of this, there are still an ample amount of configurations to consider.

For ferric iron-bearing structures, we first perform a structural relaxation at 0 K by fixing the spin state of each iron in the system. For the different compositions, we compare the enthalpies of the different spin states at each pressure, in order to determine the most stable configurations. The magnetic entropy is the same for Fe³⁺ at either A or B site whether it is HS or LS ($S_{\text{mag}} = k_B \ln 6$, see supplementary material). If we assume the vibrational entropy of the different spin configurations to be similar, then the enthalpies provide a good approximation to the most stable spin states at high temperature without having to calculate the Gibbs free energy. We limit our studies of high temperature elasticity mainly to the most stable configurations at 0 K. In spite of this, because there does not exist a perfect way of describing the correlation effects of 3*d* electrons of iron and temperature could potentially stabilize the HS state, at high temperature we selectively carry out additional calculations on configurations other than the most stable ones at 0 K, in order to get a more complete picture on the effect of different magnetic states on the elastic properties.

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