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The effect of cation order on the elasticity of omphacite from atomistic calculations

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Abstract

Omphacite, a clinopyroxene mineral with two distinct crystallographic sites, M1 and M2, and composition intermediate between diopside and jadeite, is abundant throughout the Earth's upper mantle, and is the dominant mineral in subducted oceanic crust. Unlike the end-members, omphacite exists in two distinct phases, a P2/n ordered phase at low temperature and a high-temperature C2/c disordered phase. The crystal structure and full elastic constants tensor of ordered P2/n omphacite have been calculated to 15 GPa using plane-wave density functional theory. Our results show that several of the elastic constants, notably $C_{11}$, $C_{12}$, and $C_{13}$ deviate from linear-mixing between diopside and jadeite. The anisotropy of omphacite decreases with increasing pressure and, at 10 GPa, is lower than that of either diopside or jadeite. The effect of cation disorder is investigated through force-field calculations of the elastic constants of Special Quasirandom...
Structures supercells with simulated disorder over the M2 sites only, and over both cation sites. These show that cation order influences the elasticity, with some components displaying particular sensitivity to order on a specific cation site. C\textsubscript{11}, C\textsubscript{12}, and C\textsubscript{66} are sensitive to disorder on M1, while C\textsubscript{22} is softened substantially by disorder on M2, but insensitive to disorder on M1. This shows that the elasticity of omphacite is sensitive to the degree of disorder, and hence the temperature. We expect these results to be relevant to other minerals with order-disorder phase transitions, implying that care must be taken when considering the effects of composition on seismic anisotropy.

**Keywords**

Elasticity; Omphacite; Cation Order; Special Quasirandom Structures; Density functional theory

1. Introduction

Diopside-rich clinopyroxenes are a major component of the Earth's upper mantle, comprising ~20% of the region's total volume (Herzberg 1995). The proportion of clinopyroxene in eclogite, the principal component of subducted oceanic crust, is even higher, reaching up to ~65% by volume, although this proportion drops rapidly above 10 GPa, where clinopyroxene dissolves into garnet, the other major component of eclogite (Irifune et al. 1986; Irifune and Ringwood 1987; Irifune and Ringwood 1993). In natural eclogites, such as those that occur in the mantle and subducted oceanic crust, garnet exhibits weak crystallographic preferred orientation (CPO) and is essentially elastically isotropic (Bascou et al. 2001; Mainprice et al. 2004). In contrast, omphacite has pronounced shear-induced CPO, with the [001] axis parallel to the direction of greatest elongation (Mauler et al. 2001; Bascou et al. 2002). Consequently, seismic anisotropy in eclogitic rocks is dominated by the behaviour of omphacite (Mauler et al. 2000; Bascou et al. 2001; Zhang and Green 2007). It has
been suggested that cation order affects the development of CPO in omphacite (Brenker et al. 2002), although this conclusion has been disputed (Ulrich and Mainprice 2005). It is possible that cation order influences the elastic properties of omphacite.

Like other clinopyroxenes, omphacite (shown in Fig. 1) is a monoclinic silicate mineral with four formula units per unit cell and the general composition \( \text{M1M2Si}_2\text{O}_6 \), where M1 and M2 are metallic cations occupying crystallographically distinct sites. The M2 site is occupied by either Ca\(^{2+}\) or Na\(^+\), while the M1 site is occupied by Mg\(^{2+}\) or Al\(^{3+}\), with the amount of each cation determined by charge balance considerations. The primary structural features of omphacite are chains of corner-linked SiO\(_4\) tetrahedra and edge-sharing M1O\(_6\) octahedra, both of which lie parallel to the c-axis. As in jadeite and diopside, the M2 cations occupy irregular eight-fold coordinated sites, which are more compressible than either the M1 or Si sites (Levién and Prewitt 1981). Naturally occurring omphacite has two distinct phases: a low temperature, ordered phase with space group P2/n and a high temperature, disordered phase with space group C2/c (Carpenter 1980).

In the P2/n structure, cation ordering causes the M1 and M2 sites to split into two sub-sites each, labelled M11 and M12, and M21 and M22, respectively. Mg\(^{2+}\) preferentially occupies the M11 sub-site, while Ca preferentially occupies the M22 sub-site. At all temperatures where the P2/n phase is stable, the M11 and M22 sub-sites are more ordered than the M21 and M22 sub-sites. It has been observed in both experimental (Boffa Ballaran et al. 1998) and computational (Vinograd et al. 2007) studies that, at moderate temperatures, the relationship between cation order on the two sites closely follows \( Q_{M1} = 2 Q_{M2} \), where \( Q_{M1} \) and \( Q_{M2} \) are the long range order parameters of the M1 and M2 sites, respectively.
While it has been suggested that this ordering scheme is required for local charge balance (Rossi et al. 1983), recent calculations predict that the stable structure at zero Kelvin should be completely ordered (Burton and Davidson 1988; Vinograd 2002a; Vinograd 2002b). However, the slow kinetics of cation diffusion in omphacite at low temperature inhibits the ordering process, and natural omphacite always possess some cation disorder (Carpenter 1978). Vinograd et al. (2007) compared order parameters calculated using Monte Carlo simulations with values obtained for a natural omphacite (Boffa Ballaran et al. 1998), and concluded that cation ordering is kinetically ineffective below 600 °C. The order parameters decrease systematically to ~850 °C, where both order parameters are effectively zero.

Despite their abundance, the elastic properties of the clinopyroxene minerals remain poorly understood, due primarily to the low symmetry of the clinopyroxenes, and their correspondingly large number of independent elastic constants, which makes experimental measurements difficult at mantle pressures (Mainprice 2007). Consequently, existing studies have primarily focused on the elastic properties of clinopyroxenes at ambient pressure. Brillouin scattering has been used to measure the elastic constants of jadeite at ambient temperature and pressure (Kandelin and Weidner 1988), and of diopside at room pressure and ambient (Levien et al. 1979) and high temperature (Isaak et al. 2006). Brillouin scattering has recently been used to measure the individual elastic constants of single-crystal diopside to 14 GPa (Sang and Bass 2014), and were found to be consistent with earlier measurements of polycrystal bulk and shear moduli (Li and Neuville 2010). Measurements of the elastic constants of omphacite are even more limited in number, essentially restricted to the Brillouin scattering study of Bhagat et al. (1992), who measured elastic constants of a single-crystal of disordered omphacite at ambient temperature and pressure. Comparing their results with data for jadeite and diopside, they concluded that the elastic constants were not
significantly different from those predicted by linear mixing (between diopside and jadeite), except for $C_{22}$, which was softer by $\sim$9 GPa. Linear mixing was also found for a diopside rich natural clinopyroxene solid solution although, once again, the cation sites were completely disordered (Collins and Brown 1998). While the effect of order on the elasticity of omphacite has not been measured, resonant ultrasound spectroscopic measurements on spodumene ($LiAlSi_2O_6$) through an ordering transition (from spacegroup $C2/c$ to $P2_1/c$) demonstrate that its elastic constants are discontinuous across the phase transition (Sondergeld et al. 2006). It was suggested by Sondergeld et al. that similar discontinuities may be observed across order-disorder phase boundaries in mantle clinopyroxenes.

Computational methods do not have the same limitations, and have been used to calculate the high-pressure elastic constants of clinopyroxenes, particularly jadeite and diopside. The first such study was due to Matsui and Busing (1984), who used a simple set of interatomic potentials to calculate the elastic constants of diopside to 5 GPa. More recently, density functional theory (DFT; Hohenberg and Kohn 1964; Kohn and Sham 1965) has been used to calculate the structure and elastic constants of diopside ($CaMgSi_2O_6$) and jadeite ($NaAlSi_2O_6$) to 20 GPa (Walker 2012). However, these studies have focused exclusively on clinopyroxenes with end-member compositions, while mantle clinopyroxenes invariably occur as solid solutions.

Substitutional systems, including alloys and solid solutions, are typically disordered, and lack translational symmetry, making them difficult to model using computational methods such as DFT, which use periodic boundary conditions. Many techniques have been developed to calculate the properties of substitutional systems but, due to the large number of possible configurations of an alloy, these techniques invariably involve significant trade-off between accuracy and computational
cost. Some methods, including the virtual crystal approximation (Bellaiche and Vanderbilt 2000) and the coherent-potential approximation (Faulkner and Stocks 1980) treat the crystal as an average over all possible configurations. Consequently these methods can use small simulation cells, at the cost of neglecting the effects of local strain on the energy of a specific configuration, which may be significant for substitutional systems in which mixing is accommodated by local relaxation. A recently developed method, based on averages over symmetry-irreducible classes of atomic configurations (Mustapha et al. 2013; D’Arco et al. 2013; Lacivita et al. 2014), permits the inclusion of local relaxation, although at the cost of a greater number of calculations relative to the virtual crystal or coherent potential approximations. Cluster expansion calculations, in which the properties of a solid solution are expanded in terms of the properties of “clusters” of atomic sites, incorporate the effects of local relaxation (Laks et al. 1992). Although originally developed to model scalar properties, the cluster expansion formalism can be extended to tensor-valued quantities, including the elasticity tensor (van de Walle 2008), although at significant computational cost. Another approach to modelling alloys and solid solutions is the Special Quasirandom Structures method (SQS; Zunger et al. 1990), in which the atoms in a supercell are arranged such that the correlations between the occupancies of different sites in a cluster are as close as possible to those of a truly random alloy. In practice, only a finite number of clusters are used, as the properties of the alloy are assumed to be controlled by short-ranged few-body correlations. By looking for the cell that most closely approximates the statistical properties of a disordered material, the properties of the random alloy can be computed by considering only a single simulation cell of finite size, with periodic boundary conditions. This permits calculations to be carried out at relatively low computational cost without neglecting the contribution of local relaxation to the structure and energetics of the configuration.
In this study, the effect of cation disorder on the elastic constants of omphacite at mantle pressure is investigated using *ab initio* density functional theory calculations and parameterized interatomic potentials. The effect of pressure on the elastic constants of the ordered phase of omphacite is established using plane-wave DFT calculations at a range of upper mantle pressures. To investigate the effect of cation disorder on the elastic constants, disordered supercells are prepared using the SQS method. As these supercells are necessarily much larger than the unit cell, the computational cost of DFT is prohibitive. We thus turn to a parameterised interatomic potential model, developed by Vinograd et al. (2007) to study the energetics and thermodynamics of cation ordering in omphacite, to calculate the elastic constants of the SQS supercells. Two disordering scenarios are considered: disorder on M2 but not M1, corresponding to the intermediate temperature case, and a fully disordered structure, corresponding to the high-temperature C2/c phase. As both experiments (eg. Rossi et al. 1983; Boffa Ballaran et al. 1998) and simulations (Vinograd et al. 2007) have shown that the M2 site is always more disordered than the M1 site, we do not here consider the effect of disorder on M1 in the absence of disorder on M2. As we are concerned specifically with the effect of cation disorder on the elasticity of omphacite, we neglect all thermo-elastic effects when calculating elastic constants.

2. Methodology

*Ab initio* Calculations

The elastic constants of the P2/n structure were calculated using plane-wave DFT with the pseudopotential approximation, as implemented in the Quantum Espresso software package (Giannozzi et al. 2009). The PW91 GGA exchange-correlation (xc) functional (Perdew 1991;
Perdew et al. 1992) was used in all calculations. For all calculations, we used a 2 x 2 x 4 Monkhorst-Pack grid (Monkhorst and Pack 1976) and a cutoff for the plane wave basis of 60 Ry (~815 eV), giving well-converged values for the total energy and structure of the unit cell, as well as the forces on individual atoms. Core electrons were treated using Vanderbilt ultrasoft pseudopotentials (Vanderbilt 1990), with the $3s3p4s$, $2s2p$, $3s3p$, $2p3s$, $3s3p$, and $2s2p3s$ electrons treated as valence for Ca, O, Si, Mg, Al and Na, respectively. Cell parameters and atomic coordinates were relaxed in variable-cell calculations using the damped Wentzcovitch algorithm (Wentzcovitch et al. 1993; Wentzcovitch et al. 1995).

The full elastic constants matrix was calculated by applying a strain to the unit cell and calculating the resulting stress, from which the elastic constants could be found using the Hooke's Law linear stress-strain relationship (eg. Wentzcovitch et al. 1995; Karki et al. 1999; Stackhouse et al. 2005; Perger et al. 2009). For monoclinic crystals, symmetry constraints reduce the number of independent elastic constants to just 13, rather than the full set of 21 for a triclinic crystal. These can be calculated using just four distinct strain patterns (Walker 2012). As Hooke's Law breaks down at large strain amplitudes, the magnitude $\delta$ of the applied strain must be relatively small so that stress and strain are linearly related. Conversely, if $\delta$ is too small, the errors introduced by the finite convergence criteria used in the DFT calculation will be of the same order of magnitude as the induced stress, leading to poorly constrained values of the elastic constants. In this study, strains were applied at the six magnitudes $\pm 0.03333$ a.u., $\pm 0.06666$ a.u and $\pm 0.1$ a.u.

**Special Quasirandom Structures**

In this study, the SQS method was used to simulate the effects of disordering of the M1 and M2
cation sites on the elasticity of omphacite. For calculations performed with periodic boundary conditions, the finite size of the simulation cell introduces artificial intersite correlations. The SQS method arranges atoms in a supercell such that intersite occupation correlations are as close as possible to those of a random alloy. For small supercell size, SQS supercells can be generated through exhaustive enumeration of all possible supercell configurations, but this scales factorially with the number of interchangeable sites, and is computationally prohibitively expensive for large supercell sizes. SQS supercells of various sizes were generated using \textit{mcsqs} program (van de Walle et al. 2013), part of the Alloy Theoretic Automated Toolkit (van de Walle et al. 2002; van de Walle 2009). The \textit{mcsqs} algorithm finds the supercell of the specified size which is most similar to a random alloy, in the sense that a specified set of intersite correlation functions are close to those of a random alloy. This minimises the error associated with correlated occupancies caused by the use of periodic boundary conditions, and allows us to find the properties of a random alloy by performing calculations on a single structure of finite size. For fitting of the SQS structure, we used all two-body clusters with diameter less than 9.0 Å, along with all three-body clusters with diameter less than 5.0 Å. These are precisely the diameters at which the effective cluster interactions calculated by Vinograd et al. (2007) for the diopside-omphacite-jadeite system are effectively zero, suggesting no coupling between sites.

Having generated an SQS supercell, its elastic constants can be calculated using any of the standard methods used in computational materials science. In this study, due to the large size of the SQS supercell required to converge the elastic constants and the poor (N^3) scaling of DFT with system size, calculations were performed using molecular mechanics force-fields, as implemented in GULP (Gale 1997; Gale and Rohl 2003), with the interatomic potentials of Vinograd et al. (2007), which has previously been used to study order-disorder phenomena in the diopside-jadeite system. This
model uses the shell model to simulate oxygen polarizability (Dick and Overhauser 1958), Buckingham potentials for the interactions between oxygen shells and cations, and three body potentials to constrain bond angles in the SiO$_4$ tetrahedra and the AlO$_6$ and MgO$_6$ octahedra. Ionic charges are set equal to 0.85 times the formal charge, which has been shown to improve the transferability of these potentials for oxides and silicates (Vinograd et al. 2004; Vinograd et al. 2006).

Due to the finite size of the simulation cells used, generated SQS supercells typically belong to a lower symmetry class than would an ideal disordered crystal of the same composition (Tasnádi et al. 2012), with a corresponding increase in the number of non-zero elastic constants. To obtain approximate values for the elastic constants in the true symmetry class of the disordered crystal, the calculated elasticity tensor must be projected into a tensor with the desired symmetry properties (Moakher and Norris 2006). This may be done by mapping the elastic constants matrix into the 21 dimensional vector

\[ \mathbf{C} = (C_{11}, C_{22}, C_{33}, \sqrt{2}C_{23}, \sqrt{2}C_{13}, \sqrt{2}C_{12}, 2C_{44}, 2C_{55}, 2C_{66}, 2C_{14}, 2C_{25}, 2C_{36}, 2C_{34}, \\
2C_{15}, 2C_{26}, 2C_{24}, 2C_{35}, 2C_{16}, 2\sqrt{2}C_{56}, 2\sqrt{2}C_{46}, 2\sqrt{2}C_{45}) \]  \hspace{1cm} (1)

Where the constant factors are there to ensure invariance of the Euclidean norm. The closest elastic tensor with a high point group symmetry, in the sense that $\| \mathbf{C} - \mathbf{C}^{\text{sym}} \|$ is minimized, is found by applying a 21 x 21 projection matrix $P^{\text{sym}}$ to the elastic constants vector $\mathbf{C}$, giving
For crystals with monoclinic symmetry, $P^{\text{sym}}$ is quite simple, with all off-diagonal terms equal to zero, $P_{ij}^{\text{sym}} = 0$ if $i=10, 11, 13, 14, 16, 17, 19$ or $20$, and all other diagonal entries equal to 1 (Browaeys and Chevrot 2004). This method has previously been used to model the elastic constants of several random alloys, including $\text{Cr}_{1-x}\text{Al}_x\text{N}$ (Zhou et al. 2013), $\text{In}_x\text{Al}_{1-x}\text{N}$ (Xie et al. 2012), and $(\text{Al}_x\text{Mg}_{1-x})\text{Sc}$ (Saha and Zwanziger 2014).

3. Results and Discussion

High pressure elasticity

Before considering the effects of cation disorder on the elastic properties of omphacite, we calculate the elastic of the fully ordered structure using DFT. The elastic constants of $\text{P2/n}$ omphacite at zero applied pressure calculated in this study are listed in Table 1, together with the zero-pressure elastic constants of diopside and jadeite calculated by Walker (2012), also using plane-wave DFT. All reported uncertainties are fitting errors, and larger, systematic errors are likely to be present, in particular those due to the underbinding of the GGA xc-functional. The underbinding of GGA can be corrected through the application of an Empirical Energy Correction (eg. Otero-de-la-Roza and Luaña 2011a; Otero-de-la-Roza and Luaña 2011b; Luo et al. 2013). The simplest such correction is the PSHIFT EEC, in which an additional term $E_{\text{correction}} = P_{\text{shift}}V$ is added to the energy of the cell (Otero-de-la-Roza et al. 2011). In the case of GGA functionals, $P_{\text{shift}} > 0$, reducing the unit cell...
volume at constant pressure. This correction works because the energy derivatives as a function of volume are reproduced more accurately than the cell volume as function of pressure (Vanderbilt 1998), and has seen wide application in the computational mineral physics (eg. Oganov et al. 2001; Walker et al. 2008; Li et al. 2014). In the absence of low-temperature cell-volume data for P2/n omphacite, we have calculated the empirical pressure correction by comparing the calculated cell volumes with those obtained using X-ray powder diffraction for a natural ordered omphacite at room temperature (Pavese et al. 2001), corrected to 0 K using the volumetric thermal expansion coefficient of $\alpha_V = 2.58 \times 10^{-5} \text{ K}^{-1}$ found for P2/n omphacite in a recent study (Pandolfo et al. 2014).

Note that since the volumetric thermal expansion vanishes as the temperature approaches 0 K, the cell volumes used here are slightly too small, resulting in marginal overestimation of the pressure correction. Comparing the calculated and experimental cell volumes (Fig. 2), the necessary pressure correction is found to be 4.47 GPa, very close to the average of the pressure corrections of 4.30 GPa for jadeite and 4.66 GPa for diopside found by Walker (2012) using the PBE exchange correlation functional (Perdew et al. 1996), consistent with previous findings that the PSHIFT EEC for a material of intermediate composition can be obtained as a composition weighted average of EECs for end-member compositions (van de Walle and Ceder 1999). The applied pressure minus the calculated pressure correction will be referred to throughout the rest of this paper as the ‘nominal pressure,’ and it is this value that is most relevant for comparisons with experimental data.

As can be seen from the final column of Table 2, the isotropic bulk and shear moduli of P2/n omphacite are broadly consistent with linear mixing between diopside and jadeite, as are many of the individual elastic constants. However, several of the elastic constants deviate measurably from linear mixing, in particular $C_{23}$ which is softer than predicted from linear mixing by 5.0 GPa, and $C_{11}, C_{12},$ and $C_{13}$, which are 7.6, 7.7, and 10.6 GPa stiffer than predicted, respectively. In fact, not
only do the calculated values for $C_{12}$ and $C_{13}$ exceed the linear mixing predictions, they are greater than the corresponding values calculated for either diopside or jadeite.

The pressure evolution of the calculated elastic constants of P2/n omphacite is presented in Fig. 3. At all nominal pressures greater than 0 GPa, $C_{11}$ is the stiffest of the longitudinal constants, while $C_{22}$ is the softest. While the majority of the elastic constants stiffen as the pressure increases, the pressure derivatives of $C_{15}$, $C_{25}$, $C_{35}$, and $C_{46}$ are negative, with the values of $C_{15}$ and $C_{46}$ converging on zero at high pressure. This is broadly similar to the reported high pressure behaviour of diopside (Walker 2012; Sang and Bass 2014) although, in the case of P2/n omphacite, the value of $C_{25}$ remains positive even at high pressure.

Clinopyroxenes are of particular interest in seismological studies because of their high degree of anisotropy. There are a number of ways to measure the elastic anisotropy of a low-symmetry crystal, including the Universal Anisotropy Index (Ranganathan and Ostoja-Starzewski 2008), defined as

$$\quad A^U = 5 \frac{G^R}{G^V} + \frac{K^R}{K^V} - 6$$

where $G$ is the shear modulus, $K$ is the bulk modulus and the superscripts $R$ and $V$ refer to the Reuss (homogeneous stress) and Voigt (homogeneous strain) bounds, respectively. Using the elastic constants calculated in this study (Fig. 3), we find that the anisotropy of P2/n omphacite, as
measured by $A^U$, decreases monotonically with increasing pressure, from 0.421 at 0.526 GPa nominal pressure to 0.297 at 10.526 GPa. By way of comparison, a previous DFT study found that $A^U$ equals 0.495 and 0.334 at 0 GPa nominal pressure for diopside and jadeite, respectively, decreasing to 0.383 and 0.382 at 10 GPa (Walker 2012), while the elastic constants of diopside found in a Brillouin scattering study using a single crystal of diopside (Sang and Bass 2014) give $A^U = 0.343$ at 0 GPa, decreasing to 0.21 at 10.5 GPa. The significant differences between the elastic constants of diopside found using DFT (Walker 2012) and Brillouin scattering (Sang and Bass 2014), seemingly due to disagreement between the values of the off-diagonal components of the elastic constants matrix, make determining the relative anisotropy of P2/n omphacite and the two end-member clinopyroxenes difficult, and lead to different conclusions about their relative anisotropy at high pressure. However, given that this study has used plane-wave DFT to calculate the elastic constants, we suggest that the most appropriate comparison is with the calculations of Walker (2012), indicating that, at low pressure, P2/n omphacite is more anisotropic than jadeite but less anisotropic than diopside, but is less anisotropic than either end-member at high pressure. This conclusion is supported by the maximum $S$-wave anisotropy $\Delta V_S = (V_{S1} - V_{S2}) / \sqrt{2} (V_{S1} + V_{S2})$, where $V_{S1}$ and $V_{S2}$ are the fast and slow $S$-wave velocities, which, at high pressure, is lower for P2/n omphacite than for either end-member, although the $P$-wave anisotropy differs little among the three clinopyroxenes.

Effect of cation disorder

Omphacite has two distinct cation sites over which cation mixing can occur (M1 and M2). Since the two sites have measurably different properties, with the M1 octahedra being more rigid and incompressible than the M2 polyhedra, disordering over each site might be expected to impact the
elastic constants differently. To determine the relative influence of ordering of the M1 site versus
the M2 site on the elasticity, we calculated the elastic constants for supercells with simulated
disorder over the M2 site only, and compared these with the elastic constants for a supercell with
both sites fully disordered. This is also a physically relevant comparison, as the M2 site disorders at
lower temperatures than the M1 site, and so there is a wide range of temperatures at which the
cation distribution over M2 sub-sites is substantially disordered, while M1 remains largely ordered.
Consequently, the first model can be thought of as approximating the situation at moderate
temperatures, where the M2 site is disordered, but the M1 site is still largely ordered, while the
second simulates full disorder over both cation sites, as would be expected at temperatures above
the P2/n → C2/c phase transition. As M1 is always more ordered than M2, we do not calculate the
elastic constants of an SQS supercell with full order on M2 and disorder on M1.

While Vinograd et al. (2007) showed that the cell parameters and atomic coordinates of
clinopyroxenes were well reproduced by their interatomic potentials, a more rigorous test of the
potentials is to compare calculated elastic constants with those obtained from the ab initio
calculations described in the previous section. As expected, since the elastic constants depend on
the second derivative of the internal energy and are consequently more sensitive to model
deficiencies, some of the elastic constants calculated in GULP (Table 2) deviate significantly from
the DFT calculations presented in Table 1. One of the most obvious differences is the anomalously
high values of $C_{13}$ and $C_{33}$ found for all three minerals, Given that the stiffness of the c-axis is
controlled by chains of SiO$_4$ tetrahedra (Pavese et al. 2000), this suggests that the charge of the Si
atoms (+3.4) may be somewhat too large. Conversely, the diagonal shear constants $C_{44}$, $C_{55}$, and $C_{66}$
are all somewhat underestimated, particularly for jadeite and P2/n omphacite. $C_{11}$ and $C_{22}$ are
overestimated by ~5% for diopside, but are well reproduced for both jadeite and P2/n omphacite.
The isotropic bulk modulus of P2/n omphacite calculated using GULP is 7% greater than the DFT value. However, if the bulk modulus is recalculated using the values of $C_{13}$ and $C_{33}$ from the DFT calculations (Table 1) and values for all other constants from Table 2, we obtain a value of $K_{\text{vih}} = 116.3$ GPa, comparable to the value for DFT reported in Table 1. In Table 2, we also report the calculated difference between the elastic constants of P2/n omphacite and those obtained from linear mixing between diopside and jadeite. There are a number of differences between these values and those obtained using DFT, with the most notable being that GULP predicts $C_{11}$ to follow linear mixing, and $C_{15}$ to deviate substantially from it. However, aside from these discrepancies, the two methods generally agree on the qualitative difference between the elasticity of P2/n omphacite and a linear mixture of diopside and jadeite.

A comparison between the pressure evolution of the elastic constants calculated using interatomic potentials (Fig. 4) and the pressure evolution calculated using plane-wave DFT (Fig. 3) shows that the pressure derivatives of the elastic constants of omphacite are reasonably well reproduced by the interatomic potentials. Computing the average values of the pressure derivatives for each elastic constant over the pressure range 0-5 GPa using GULP and DFT. We find that both methods give the same sign for each of the $dC_{ij}/dP$ over this range, with the difference between average pressure derivatives calculated using DFT and GULP being -0.7 for $C_{11}$, 1.2 for $C_{12}$, and 0.7 for $C_{23}$. The magnitudes of all other differences are < 0.5. Additionally, GULP was able to correctly reproduce the relative ordering of $dC_{ij}/dP$ found with DFT for 74 of the 78 possible unique pairs of elastic constants, with the only exceptions being $C_{33}$ and $C_{12}$, $C_{44}$ and $C_{55}$, $C_{15}$ and $C_{25}$, and $C_{15}$ and $C_{46}$. Consequently, given the degree of approximation inherent to molecular mechanics, and the fact that construction of SQS supercells involves changes in the distributions of cations relative to the ordered structure, but not the number of each species present (or their coordination environment), it
was judged that the interatomic potentials of Vinograd et al. (2007) should be sufficiently accurate to provide a useful guide to the qualitative effect of cation order on the elastic constants of omphacite.

Since the SQS method was not originally developed to calculate tensor-valued properties, it is necessary to test the convergence of the elastic constants with increasing SQS supercell size, as insufficiently large supercells can be artificially anisotropic (Tasnádi et al. 2012). This is done for the two different disordering cases by calculating the normalized Euclidean distance

$$\frac{\|C - C^{4\times 4\times 4}\|}{\|C^{4\times 4\times 4}\|}$$  \hspace{1cm} (4)

between the calculated elastic constants of each generated SQS supercell and a 4x4x4 SQS supercell. Examining these distances as function of supercell size (Fig. 5), it can be seen that, in both cases (disorder on M2 and full disorder), the distance decreases markedly with increasing supercell size. The elasticity tensor of the supercell with disorder over M2 only converges more rapidly than that with disorder over both sites, with the absolute difference falling below 1% when a 2x2x2 supercell is used, while the difference remains above 1% for supercells smaller than 3x3x3 in the case of full disorder over both sites. The convergence of individual elastic constants is more mixed, with some constants (eg. $C_{11}$ and $C_{55}$) converging much faster than the full elasticity tensor while others, such as $C_{66}$, converging quite slowly. Nevertheless, the majority of the elastic constants were converged to within 1% by the 3x3x3 supercell. As such, all further calculations were performed using a 3x3x3 supercell containing 1080 atoms, including 108 M1 and M2 sites.
In Table 2, the calculated 0 GPa elastic constants are tabulated for the two different SQS supercells. For comparison, we have also calculated the elastic constants for each disordering scenario using a mean-field approach, in which mixing sites are treated as having multiple atoms with fractional occupation present simultaneously, and the interatomic potentials are scaled according to

$$U_{ij\ldots m}^{m-f} = o_i o_j \ldots o_m U_{ij\ldots m}$$ \hspace{1cm} (5)$$

where $o_i \in [0,1]$ is the average occupancy factor of species $i$ and $U_{ij\ldots m}$ is an n-body interatomic potential (Gale and Rohl 2003). These are listed in Table 2, alongside the corresponding SQS results. For both disordering scenarios, the mean-field bulk and shear moduli are greater than the values obtained using SQS, as are the majority of the individual elastic constants. Looking now at the SQS results, it is seen the bulk modulus is relatively unchanged by disorder, while the shear modulus softens moderately, particularly for the fully disordered supercell.

While the isotropic bulk and shear moduli are, at most, moderately sensitive to cation order, the individual elastic constants of omphacite can be highly sensitive to cation order. Comparing the elastic constants for P2/n omphacite calculated using GULP with the SQS results for the two disordering scenarios (Table 2), it is clear that, while the elastic constants are generally softened slightly as overall cation disorder increases, individual constants change significantly more than others, often with a marked dependence on the order parameter of a specific cation site. To cite specific examples, $C_{11}$, $C_{12}$, and $C_{66}$ are essentially unchanged by disorder on M2 only, but soften
significantly when the M1 site is allowed to disorder as well. Other elastic constants soften upon
disorder of M2, but are unaffected by any further disorder on M1. This is true particularly of $C_{22}$,
whose value at 0 GPa declines from 198.3 to 189.5 GPa going from complete order to disorder on
M2 only, but is only an additional 1.3 GPa softer (i.e. effectively unchanged) when both cation sites
are fully disordered. Several of the elastic constants, such as $C_{33}$ and $C_{13}$, do not seem to have any
particular dependence on the degree of disorder at either site.

To demonstrate that these results hold at mantle pressures, we extend these calculations to 10 GPa
and calculate the difference between the elastic constants of the P2/n phase displayed in Fig. 4 and
the elastic constants to the SQS supercells for the two disordering cases. Examining these values
(displayed in Fig. 6), it is immediately apparent that the differences at ambient pressure persist
across the entire pressure stability field for omphacite in the mantle. Moreover, the differences
between the elastic constants for the ordered and disordered structures change by less than ~1 GPa
over the pressure range studied, with few exceptions. The most obvious of these is $C_{11}$ (the filled
squares in Fig. 6ac), whose sensitivity to cation order increases substantially over this range, with
the magnitude of its deviation from the value calculated for the P2/n structure tripling between 0
and 10 GPa when disorder occurs on M2 only, and increasing by a factor of ~2 for mixing over both
sites. $C_{22}$ (filled diamonds) also exhibits anomalously high pressure sensitivity although, in its case,
the effect of increasing pressure is to reduce the difference between the ordered and disordered
values of this elastic constant.

Although relating changes in individual elastic constants to structural features is often difficult,
some of the differences noted above are due to the particular structural motifs of the clinopyroxene
structure. In particular, the fact that $C_{11}$, $C_{12}$, and $C_{66}$ depend on the order parameter of the M1 site,
but not that of the M2 site is likely due to the moderate sensitivity of the \(a\) cell parameter to the occupancy of the M1 sites (Pavese et al. 2000). Conversely, since the stiffness of the \(c\) axis is controlled by the chains of SiO\(_4\) tetrahedra (Pavese et al. 2000), \(C_{33}\) should have little direct dependence on the occupancies of either the M1 or M2 cation sites. This is in accord with the results presented in Table 2 and Fig. 6, where it can be seen that \(C_{33}\) is softened equally by disorder on each cation site, with the observed softening due exclusively to the dilation of the unit cell that accompanies cation disorder.

To demonstrate the effect that changing cation order can have on seismic wave-speeds and anisotropy, we calculate phase velocities for the quasi-\(P\), and fast (\(V_{S1}\)) and slow (\(V_{S2}\)) quasi-\(S\) waves as a function of propagation direction for ordered, partially disordered, and fully disordered omphacite. The elastic constants for P2/n omphacite calculated using plane-wave DFT from Table 1 and, for each disordering case, add the difference between the elastic constants of the associated SQS supercell and P2/n omphacite calculated using interatomic potentials (Table 2). Pole figures of the quasi-\(P\) wave velocities, \(S\)-wave anisotropy \(aV_S\), and fast quasi-\(S\) wave polarisation, calculated using the Matlab Seismic Anisotropy Toolkit (MSAT; Walker and Wookey, 2012), are plotted in Fig. 7. The effect of increasing cation disorder on the isotropic wave-speeds is negligible, with both \(P\)- and \(S\)-wave velocities varying by <2\% between the P2/n and C2/c structures. In contrast, the magnitude and pattern of anisotropy appears to vary significantly with changing cation order. In particular, the \(P\)-wave anisotropy decreases by ~15 \% going from the P2/n structure to full disorder over both cation sites. There is also a general reduction in \(aV_S\), particularly in the equatorial plane containing the \(b\) and \(c\) lattice vectors.

These results are of direct relevance to the elasticity of mantle omphacites as the P2/n \(\rightarrow\) C2/c
order-disorder phase transition has been found to occur at ~850 °C (Carpenter 1980), a conclusion that is supported by Monte Carlo simulations using a cluster-expansion approach (Vinograd et al. 2007). At pressures sufficiently great for eclogite to form, temperatures in the interiors of old subducted slabs, such as those beneath the Izu-Bonin or Tonga-Kermadec subduction zones, can be as low as 400 °C (Peacock and Wang 1999; Abers et al. 2006; Syracuse et al. 2010). Indeed, thermal modeling of the Nicaragua-Costa Rica subduction zone shows that, even at pressures in excess of 6 GPa, temperatures at the center of a subducting slab may be <600 °C (Peacock et al. 2005). These temperatures lie well below the P2/n → C2/c order-disorder phase transition, and suggest that omphacite is subducted slabs may be partially ordered to great depths, enhancing the sensitivity of the pattern of anisotropy to the temperature of the slab interior.

Cation order has previously been found to affect the bulk and shear moduli of several major minerals, including ringwoodite (Panero 2008) and MgAl$_2$O$_4$ spinel (eg. Cynn et al. 1993; Hazen and Yang 1999; Li et al. 2007a). Sensitivity of the elastic constants to cation order has also been documented for several garnets, including majorite (Li et al. 2007b) and grossular-andradite solid solutions (eg. Babuška et al. 1978; O’Neill et al. 1989; Erba et al. 2014). In this last case, however, a recent ab initio investigation has used averages over symmetry-independent classes of nuclear configurations to determine the elastic behavior of solid solutions along the grossular-andradite join, finding that the isotropic bulk and shear moduli follow a linear-mixing trend between the two end-members (Lacivita et al. 2014).

In many of these studies, both the isotropic and anisotropic elastic moduli were sensitive to the degree of cation order. For example, GGA-DFT calculations found that, for ringwoodite, a disorder fraction of 0.125 is sufficient to reduce $C_{11}$ from 323.4 GPa (ordered) to 301.5 GPa (disordered),
and to reduce the bulk modulus from 180 GPa to 166.8 GPa (Panero 2008). In some cases, however, the responses of the isotropic and anisotropic elastic moduli may diverge. Li et al. (2007b) found that many of the elastic constants of majorite, especially $C_{66}$, were sensitive to disordering of the Mg and Si cations, while the isotropic bulk and shear moduli were effectively independent of cation order. Similarly, the results presented here for omphacite show a limited dependence of the isotropic bulk and shear moduli on cation order (beyond the softening due to unit-cell dilation), but several of the individual elastic constants harden substantially as cation order increases. This illustrates a general point that, even in cases when the effect of cation order on the isotropic bulk and shear moduli is negligible, the individual elastic constants may be occupation-dependent, causing the anisotropy (and related phenomena such as S-wave splitting) to vary with changing cation order.

4. Conclusions

In this study, we have calculated the elastic constants of fully ordered omphacite using plane-wave DFT. It was found that many of the elastic constants are broadly consistent with linear mixing between diopside and jadeite, with several notable exceptions, including $C_{11}$, $C_{12}$, and $C_{13}$. While the anisotropy of omphacite was intermediate between that of diopside and jadeite at 0 GPa, it decreased rapidly with increasing temperature and, at 10 GPa, P2/n omphacite may be less anisotropic than either diopside or jadeite. Using the SQS method, we demonstrated that the elastic constants of omphacite depend on the degree of cation disorder present at both the M1 and M2 sites. However, the relationship between the elasticity tensor and the total cation order was found to be non-trivial, with some elastic
constants (e.g., $C_{11}$, $C_{12}$, and $C_{66}$) displaying particular sensitivity to the order parameter of the M1 site, while others (e.g., $C_{22}$) are affected primarily by order on M2. Numerical simulations have suggested that temperatures in subducted oceanic crust at depths > 100 km can be as low as 400-600 °C (e.g., Peacock and Wang 1999; Peacock et al. 2005), well below the temperature at which the P2/n $\rightarrow$ C2/e phase transition occurs. Indeed, an earlier computational study indicated that at these temperatures, although the M2 site is significantly disordered ($Q_{M2} < 0.6$), the M1 site should still be essentially fully ordered ($Q_{M1} > 0.9$) (Vinograd et al. 2007). Consequently, we expect that cation order in omphacite should affect the pattern and magnitude of seismic anisotropy in subducting slabs. Moreover, given that increasing cation disorder softens the elastic constants omphacite (with $C_{23}$ the lone exception), we suggest that the seismic anisotropy of omphacite should more strongly temperature-dependent than a simple mechanical mixture of diopside and jadeite.

Acknowledgements

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Figure captions

Fig. 1 (a) Unit cell of omphacite, with the M11, M12, M21, and M22 cation sub-sites labeled. In
fully ordered P2/n omphacite, M11 is fully occupied by Mg$^{2+}$, M12 by Al$^{3+}$, M21 by Na$^+$, and M22 by Ca$^{2+}$. (b) The crystal structure viewed down the b-axis, which clearly shows the corner-linked chains of SiO$_4$ tetrahedra parallel to the c-axis. The crystal structure has been visualized using the program Vesta 3 (Momma and Izumi 2011)

**Fig. 2** Uncorrected (triangles) and pressure-corrected (inverted triangles) cell volumes of P2/n omphacite calculated using DFT, compared with experimental cell volume data (circles) taken from (Pavese et al. 2001), corrected to 0 K using the volumetric thermal expansion coefficient from (Pandolfo et al. 2014)

**Fig. 3** The elastic constants of P2/n omphacite as a function of pressure, calculated using plane-wave DFT. (a) Longitudinal (Symbols: $C_{11}$, filled squares; $C_{22}$, filled diamonds; $C_{33}$, filled triangles) and diagonal shear components of the elastic constants matrix $C_{ij}$ ($C_{44}$, empty diamonds; $C_{55}$, empty squares; $C_{66}$, empty inverted triangles). (b) Off-diagonal components of $C_{ij}$ (Symbols: $C_{12}$, filled squares; $C_{13}$, filled diamonds; $C_{23}$, filled triangles; $C_{15}$, empty diamonds; $C_{25}$, empty squares; $C_{35}$, empty inverted triangles; $C_{46}$, filled inverted triangles). Calculated uncertainties are smaller than the symbol size. Lines are a guide for the eye

**Fig. 4** (a) Bulk and diagonal shear components, and (b) off-diagonal shear components of the elastic constants matrix of P2/n omphacite as a function of pressure, calculated in GULP using the force-field model of Vinograd et al. (2007). The symbols are the same as those in Fig. 3. Lines are a guide for the eye

**Fig. 5** Euclidean distance deviations between a 4x4x4 SQS supercell and smaller SQS supercells,
calculated using equation (4) for disorder over M2 only (hollow) and disorder over both sites (filled).

Fig. 6 Calculated difference between the elastic constants of the 3x3x3 SQS supercells with those of the ordered P2/n phase. (a) and (c) show results for the diagonal components of the elastic constants matrices in the case of disorder on M2 only and disorder on both sites, respectively. (b) and (d) show the off-diagonal components, for disorder on M2 only and disorder on both sites. The symbols are the same as those in Fig. 3. Lines are a guide for the eye.

Fig. 7 Wave velocities and anisotropy pole figures for (a) fully ordered omphacite (space group P2/n) (b) omphacite with disorder on M2 only, and (c) fully disordered omphacite (space group C2/c). Pole figures were calculated in MSAT (Walker and Wookey 2012) using the ab initio elastic constants for P2/n omphacite presented in Table 1, with the effect of cation disorder simulated by taking the difference between the elastic constants of ordered and disordered omphacite calculated with SQS (Table 2). Cartesian coordinate system is shown in the inset, with $b$ and $c$ parallel to $X_2$ and $X_3$, respectively. The lines on the pole figures in the second column show the direction of fast-shear wave polarization.

References


Faulkner J, Stocks G (1980) Calculating properties with the coherent-potential approximation. Phys


Table 1 Elastic constants (in GPa) of P2/n omphacite at 0 GPa applied pressure calculated using plane-wave DFT, compared with values for jadeite and diopside taken from Walker (2012). Bulk and shear moduli are the Voigt-Reuss-Hill averages (Hill 1952)

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- $a$: Compositionally weighted linear mixing of elastic constants of diopside and jadeite
- $b$: Difference between the elastic constants of omphacite predicted from linear mixing and those calculated using DFT
Table 2 Elastic constants (in GPa) of P2/n omphacite, diopside, and jadeite calculated in GULP using the interatomic potential from Vinograd et al. (2007), as well as for the 4x4x4 SQS supercells of omphacite for the two cation disorder cases considered: mixing over M2 only, and mixing over both cation sites. The elastic constants calculated using the mean field method (Gale and Rohl 2003) have also been included, and the often substantial difference between these and the elastic constants calculated for the SQS supercells illustrate the importance of local structural relaxation in solid solutions.

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Figure

Euclidean distance deviation (%) vs. Supercell size.

- M2 disordered
- M1 and M2 disordered
Figure

(a) $V_p$ (km/s)

Ordered

Min. $V_p = 6.83$, max. $V_p = 9.54$
Anisotropy = 33.1%

(b) $V_p$ (km/s)

M2 disordered

Min. $V_p = 6.88$, max. $V_p = 9.33$
Anisotropy = 30.8%

(c) $V_p$ (km/s)

M1 and M2 disordered

Min. $V_p = 6.95$, max. $V_p = 9.22$
Anisotropy = 28.55%