Abstract

Due to their widespread occurrence in several geological settings, omphacite inclusions could be used for elastic Raman geothermobarometry. However, the Raman scattering of complex silicate minerals entrapped in a host depends on both the chemical composition and elastic strain developed during the metamorphic pathway, which makes the task very challenging. Here, as a very first step to probe the potential of omphacite to be used as a mineral inclusion in elastic geothermobarometry, we report the pressure dependence of the Raman spectra of omphacite crystals with the same composition, approximately Jd$_{45}$Di$_{55}$, but having different symmetry because of the existence ($P2/n$) or absence ($C2/c$) of chemical order at the six- and eight-coordinated cation sites. The experimental results are complemented by ab initio quantum
mechanical simulations on fully ordered omphacite (Jd0.50Di0.50). We demonstrate that the position of the well-resolved Raman peak near 688 cm⁻¹, arising from Si-O-Si bond bending, is very sensitive to pressure but independent of the state of chemical order, which makes it promising to be utilized in Raman geobarometry. The width of this peak varies with chemical order but not with pressure and therefore can be used to constrain the temperature of inclusion entrapment, because the chemical order is indicative of the closure temperature of the cation-exchange reaction. However, further detailed analyses on the compositional variation of the Raman spectra of omphacite is required before considering omphacite-in-garnet systems as suitable for Raman elastic geothermobarometry.

**Keywords:** Omphacite, site-occupancy order, Raman spectroscopy, high pressure, ab initio calculation

**Introduction**

Clinopyroxenes (general formula M2M1T₂O₆) are key minerals, due to their widespread occurrence in the Earth’s crust and upper mantle (Skelton and Walker 2015), to characterize various geological settings and processes. They can be found as both rock-forming and accessory minerals in several terrestrial rock types from diverse geological contexts, including mantle xenoliths, magmatic rocks (e.g., Lentz et al. 2011; Murri et al. 2016, 2019b; Gianola et al. 2023) and high-pressure/temperature metamorphic rocks (Philpotts and Ague 2009; Gilio et al. 2020). Clinopyroxenes also occur as inclusions in diamonds (Meyer and Boyd 1972; Nestola et al. 2016; Pasqualetto et al. 2022) and as rock-forming minerals in meteorites (e.g., Papike 1980; Alvaro et al. 2015; Carli et al. 2023). Among clinopyroxenes, omphacite, a solid solution of jadeite (NaAlSi₂O₆) (20-80%), augite [Ca(Mg,Fe²⁺)Si₂O₆] (20-80%), and aegirine (NaFe³⁺Si₂O₆) (0-50%)
(Morimoto 1988) with the general formula \((\text{Ca,Na})(\text{Mg,Fe}^{2+},\text{Al})\text{Si}_2\text{O}_6\), is extremely important for constraining pressure and temperature conditions in eclogitic metabasites where quartz is not present as an equilibrium phase at peak conditions. It is well known that omphacites may exhibit site-occupancy cation order, which leads to a splitting of both M1 and M2 sites into (M1, M11) and (M2, M21), respectively (Figure 1). Consequently, the chemical order reduces the space group symmetry from \(C2/c\) to \(P2/n\) (e.g., Carpenter et al. 1990a, b; Boffa Ballaran et al. 1998a, b). Thus, the determination of the state of chemically ordered omphacite can constrain the closure temperature and cooling rate experienced by the host rock. The degree of cation order of omphacite is commonly determined by means of single-crystal X-ray diffraction (XRD) measurements followed by structural refinements, but this analysis generally requires large (~50-150 \(\mu\)m) good-quality single crystals. Moreover, chemically ordered regions form antiphase domains that are detectable by transmission electron microscopy, therefore their size variation has been proposed to serve as a geothermometer (Phakey and Ghose 1973; Carpenter 1980, 1981a, b). However, the dimensions of chemically ordered regions depend also on the chemical composition as well (Cámara et al. 1998) and they can be further affected by post-crystallization deformation processes (Van Roermund and Lardeaux 1991). Raman spectroscopy can verify the existence of M-site cation order in omphacite by the splitting of the \(\text{SiO}_4\)-stretching Raman peak near 1017 cm\(^{-1}\), due to the doubling of the primitive unit cell (Katerinopoulou et al. 2008). Besides, Raman spectroscopy has the advantage to probe micrometer-size spatial regions without the necessity to extract the crystal from the host. Consequently, this analytical method is among the most popular experimental techniques used in elastic geothermobarometry (Korsakov et al. 2009; Anzolini et al. 2018; Nestola et al. 2018; Zhong et al. 2019; Campomenosi et al. 2021). By using this technique, it is possible to estimate the equilibration pressure and temperature of a mineral. The pressure and temperature conditions of the inclusion entrapment \((P-T_{\text{trap}})\) can be estimated
knowing the inclusion pressure ($P_{\text{inc}}$) at the conditions at which it is exhumed to the surface ($P_{T_{\text{end}}}$) and the elastic properties of the host and the inclusion, that allow to calculate isomekes (Gilio et al. 2021). An isomeke is a line in the pressure-temperature space along which the volume strain of the inclusion and the surrounding host are the same (Campomenosi et al. 2022). Then, isomekes are used to determine the over- or under-pressure conditions developed in the inclusion, and, therefore, the final inclusion pressure. Thus, to utilize omphacite inclusions as geothermobarometry markers in metamorphic rocks, detailed analyses of the atomic dynamics of omphacite as a function of chemical composition, temperature and pressure is required. However, Raman-scattering data on omphacite are available only at ambient conditions, mainly in comparison with other chain silicates (Buzatu and Buzgar 2010; Andò and Garzanti 2014; Franz et al. 2014).

Here, as a very first step to probe the potential of omphacite to be used as a mineral inclusion in elastic geothermobarometry, we report the Raman spectra of omphacite crystals with and without $M$-site cation order, while having the same composition $\sim Jd_{45}Di_{55}$, at pressures up to $\sim 10$ GPa, along with Hartree-Fock/Density-Functional-Theory (HF/DFT) simulations on fully ordered $Jd_{50}Di_{50}$ omphacite in the same pressure range.

**Materials and methods**

**Sample description**

We used omphacite crystals from Münchberg Mass, Bavaria (Matthes and Schmidt 1974; O’Brien 1993), which belong to the same omphacite sample that has been previously analyzed with infrared spectroscopy by Boffa Ballaran et al. (1998a, b) (sample 74AM41) and by high-pressure single-crystal XRD by Pandolfo et al. (2012a, b). We selected single crystals with low iron content to avoid further chemical effects on the Raman spectra (Katerinopoulou et al. 2008). For
in situ high-pressure Raman spectroscopic measurements, we used two natural samples (natural-8 and natural-11), which exhibited a high degree of cation order (Boffa Ballaran et al. 1998a), and two samples annealed at 1173 K for 168 h (annealed-3 and annealed-7) to achieve a state of long-range cation disorder. The size of samples natural-8, natural-11 and annealed-3 was approximately 90×150×200 μm³, whereas size of sample annealed-7 was ~50×50×60 μm³.

Chemical composition

Wavelength-dispersive electron microprobe analyses (EMPA) were performed on the very same specimens used in the high-pressure Raman-scattering experiments. After conducting the Raman experiments, the omphacite crystals were embedded into epoxy resin, polished, and carbon coated for electron microprobe analyses. The chemical composition was determined with a Jeol 8200 Super Probe electron microprobe at the Department of Earth Sciences of the University of Milan, operating at an acceleration voltage of 15 kV and beam current of 5 nA (beam size = 3 μm). A ZAF correction (Z = atomic number, A = absorption coefficient, F = fluorescence coefficient), using the PAP routine (Pouchou and Pichoir 1985) was applied. Standards, spectral lines, and analytical crystals used were: grossular (Si, AlKα, TAP; CaKα, PET), ilmenite (TiKα, PET), metallic Cr (CrKα, LIF), fayalite (FeKα, LIF), rhodonite (MnKα, LIF), forsterite (MgKα, TAP), omphacite (NaKα, TAP) and K-feldspar (Kα, PET).

Single-crystal X-ray diffraction

Single-crystal XRD experiments were performed at the Department of Earth Sciences of the University of Milan to determine the degree of long-range M-site cation ordering in the crystals selected for high-pressure Raman spectroscopy. Samples natural-8, natural-11, annealed-3 were analyzed with a Xcalibur-1-Oxford diffractometer equipped with a MoKα sealed tube source and a
charge-coupled device (CCD) detector. Due to its smaller size (see above), sample annealed-7 was analyzed with a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE HPC area detector, using a monochromatic X-ray incident beam with an energy of 17.4 keV (\(\lambda=0.71073 \text{ Å},\) i.e., MoK\(\alpha\)), which is characterized by a higher brilliance. Structure refinements were performed using the program SHELXL (Sheldrick 2015). The structure of ordered and disordered omphacite was refined in \(P2_1/n\) and \(C2/c\) space groups, respectively, starting from the models provided by Pavese et al. (2000) and McCormick (1986). Scattering curves were taken from the International Tables for Crystallography (Wilson 1995). Neutral vs. ionized scattering factors were used to refine the occupancy for all sites that are not involved in chemical substitutions (i.e. O sites and \(^{T1}\)Si in \(P2_1/n\)) (Hawthorne et al. 1995), while scattering factors of ionized atoms were used for \(^{T2}\)Si and the six-coordinated M1 and M11 sites alongside the eight-coordinated M2 and M21 sites. The site partitioning was obtained using the refinement model proposed by Boffa Ballaran et al. (1998a) and the chemical constraints from our EMPA data. Crystallographic information files (CIFs) are available as Online Materials.

**High-pressure Raman spectroscopy**

Raman spectra of the four selected crystals were collected using a Horiba Jobin-Yvon S.A.S. T64000 triple monochromator spectrometer at the Mineralogisch-Petrographisches Institut, Universität Hamburg, equipped with an Olympus BX41 confocal microscope and a Symphony liquid-N\(2\)-cooled CCD detector. Raman scattering was excited with the 514.532-nm or the 488.0-nm lines of a Coherent Innova 90C Fred Ar\(^+\) laser, using an Olympus LM Plan FLN 50× long-working distance objective with a numerical aperture of 0.5. The spectrometer was calibrated to the \(T_{2g}\) mode at 520.5 cm\(^{-1}\) of a Si wafer. The spectral resolution was \(\sim 2\) cm\(^{-1}\), while the instrumental accuracy in determining the peak position was \(\sim 0.35\) cm\(^{-1}\).
In situ high-pressure Raman experiments were conducted with Boehler-Almax diamond anvil cells equipped with diamonds with a culet diameter of 600 μm. The sample chamber was made by a stainless-steel gasket with a thickness of 0.25 mm, which was initially indented to ~ 95 μm and then drilled with an Almax-easyLab spark eroder with tungsten carbide tips, to obtain a hole with a diameter of 300 μm. A 16:3:1 methanol–ethanol–water mixture was used as a pressure-transmitting medium, which remains hydrostatic up to 10.5 GPa (Angel et al. 2007). The pressure P was determined via the ruby photoluminescence R1 line (Munro et al. 1985) with a precision of ~ 0.1 GPa.

Parallel polarized Raman spectra (polarization of incident light $E_i$ parallel to the polarization of the scattered light $E_s$) were collected in the range 50-1250 cm$^{-1}$ with acquisition times of 60 or 180 s averaged over three accumulations. The variations in the relative intensities indicated that the samples were oriented with the crystallographic c axis approximately parallel (natural-8 and annealed-3) or perpendicular (natural-11 and annealed-7) to $E_i$; the orientational dependence of the Raman intensities was established by measuring an omphacite grain for which single-crystal XRD showed that the prism axis coincides with the crystallographic c axis. In both cases, the direction of the propagation of the incident light $k_i$ was $\perp$ to c. Therefore, in ($c \parallel E_i \parallel E_s$) scattering geometry the Raman scattering is dominated by the (zz)-component of the Raman polarizability tensor, whereas in ($c \perp E_i \parallel E_s$) scattering geometry the Raman spectrum is determined by (xx)- and/or (yy)-components of the polarizability tensor, depending on the orientation of the b axis with respect to $k_i$. At each pressure step, the Raman scattering from the diamond anvils was collected to estimate the degree of depolarization of Raman scattering due to stress-induced changes in the optical properties of the diamond anvils (Mihailova et al. 2019). In addition, a background spectrum was measured aside from the sample while keeping the same focus, and subsequently subtracted from the sample spectrum to eliminate the contribution from
the pressure-transmitting medium. Then the spectra were reduced by the Bose-Einstein population factor to account for the temperature dependence of the Raman intensities, using the relation: 
\[ I_{\text{reduced}} = \frac{I_{\text{measured}}}{\left( e^{\frac{\hbar \omega}{k_B T}} - 1 \right)^{-1} + 1} \]
where \( \hbar \), \( k_B \), \( \omega \), and \( T \) are the reduced Planck’s constant, Boltzmann’s constant, phonon angular frequency (in \( \text{s}^{-1} \)) and temperature (in K), respectively. The peak positions, full widths at half maximum (FWHMs) and integrated intensities were determined by fitting the temperature-reduced spectra with pseudo-Voigt peak-shape functions \( PV=qL+(1-q)G \), where \( L \) and \( G \) are Lorentzian and Gaussian functions and \( q \) is a variable weighting coefficient. The OriginLab 2022 software package was used for data evaluation.

**Computational methods**

Ab initio hybrid HF/DFT simulations have been conducted with the CRYSTAL17 software (Dovesi et al. 2018) by using the WC1LYP functional. This functional has been shown to correctly reproduce the elastic and vibrational properties of crystals (e.g. Prencipe et al. 2011, 2012; Prencipe 2012, 2018; Stangarone et al. 2016). The WC1LYP functional is based on the generalized gradient approximation (GGA) exchange functional WC (Wu and Cohen 2006), mixed with 16% of the exact non-local Hartree-Fock exchange, and the Lee-Yan-Parr (LYP) correlation functional (Lee et al. 1988). The grid for the numerical evaluation of the DFT exchange-correlation functionals was chosen by the keyword XLGRID of CRYSTAL17 (Dovesi et al. 2018) and corresponds to a total of 900,780 points in the unit cell. A measure of the numerical accuracy provided by such a grid is the evaluation of the total number of electrons in the unit cell, by the numerical integration of the electron density over the cell volume. For omphacite, we obtained 415.99999 electrons out of 416 for the reference volume at the static limit (no zero-point and thermal pressures due to vibrational effects included, see Prencipe et al. 2011) and at a static pressure of 0 GPa. The localized contracted atomic basis sets used were: Na 8-511(1d)G; Al 85-11(1d)G; Ca 865-11(3d)G; Mg 85-
CRYSTAL code, the accuracy in evaluating the Coulomb and Hartree-Fock exchange series is controlled by the keyword TOLINTEG, for which we set the four T1, T2, T3 and T4 parameters to 9 and T5 to 22 (Dovesi et al. 2018). The diagonalization of the Hamiltonian matrix was performed at 30 independent \( k \) vectors in the reciprocal space (Monkhorst net; Monkhorst and Pack 1976) by setting the shrinking factor IS to 4 (Dovesi et al. 2018). Unit-cell parameters and fractional coordinates were optimized by analytical gradient methods, as implemented in CRYSTAL17 (Civalleri et al. 2001; Dovesi et al. 2018). Geometry optimization was considered converged when each component of the gradient (TOLDEG parameter in CRYSTAL17) was smaller than 0.00003 Hartree/Bohr and displacements (TOLDEX) were smaller than 0.00012 Bohr with respect to the previous step. Simulations of the Raman spectra of omphacite at the static limit have been performed at pressures ranging from 0 to 6 GPa (with step of 2 GPa from 0 to 4 GPa and then a step of 1 GPa from 4 to 6 GPa) by using the keyword EXTPRESS. The wavenumbers of all normal modes were calculated at the \( \Gamma \) point within the limit of the harmonic approximation, by diagonalizing a mass-weighted Hessian matrix, whose elements are the second derivatives of the full potential of the crystal with respect to the mass-weighted atomic displacements (Pascale et al. 2004). Furthermore, in order to directly compare the computational data with the experimental ones, we followed the procedure reported in Ghignone et al. (2023) for the estimate of EoS parameters at a temperature of 298 K.

### Results

#### Crystal chemistry

The EMPA results for sample natural-8, annealed-3, and annealed-7 are reported in Table 1. Within uncertainties the compositions of all three specimens are the same as those reported by
Boffa Ballaran et al. (1998a). Sample natural-11 was unfortunately lost during the polishing procedure, so in the subsequent analyses we assumed that it has the same chemical composition of sample natural-8.

The structure of samples natural-8 and natural-11 is refined in $P2/n$, indicating chemical ordering, whereas samples annealed-3 and annealed-7 exhibit $C2/c$ space symmetry typical of chemically disordered omphacites. The unit-cell parameters for all samples are given in Table 2, along with those calculated by HF/DFT simulations for fully ordered Jd$_{50}$Di$_{50}$ omphacite. The M1 site is commonly occupied by small cations such as Mg$^{2+}$, Al$^{3+}$, Fe$^{3+}$ and Fe$^{2+}$, while larger cations such as Ca$^{2+}$ and Na$^+$ are at the M2 site. In the case of chemical order-disorder phenomena, the site occupancy factors are used to calculate the order parameters $Q_{M1}$ and $Q_{M2}$ (Carpenter et al. 1990a) as follows:

\[
Q_{M1} = \frac{(Al + Fe^{3+})_{M1} - (Al + Fe^{3+})_{M11}}{(Al + Fe^{3+})_{M1} + (Al + Fe^{3+})_{M11}} + \frac{(Mg + Fe^{2+})_{M1} - (Mg + Fe^{2+})_{M11}}{(Mg + Fe^{2+})_{M1} + (Mg + Fe^{2+})_{M11}}
\]

\[
Q_{M2} = \frac{Na_{M2} - Na_{M21}}{Na_{M2} + Na_{M21}} + \frac{Ca_{M2} - Ca_{M21}}{Ca_{M2} + Ca_{M21}}
\]

In natural samples the long-range order parameter at M1 is commonly twice larger than that at M2, i.e. $Q_{M1} \sim 2Q_{M2}$. (Boffa Ballaran et al. 1998a; Skelton and Walker 2015). The refined values of the site occupancy factors and subsequently calculated order parameters (see Table 3) are in a good agreement with those reported by Boffa Ballaran et al. (1998a). Sample natural-8 is slightly less ordered than natural-11 (Table 3). In Table S1 in the Online Materials the bond distances and the polyhedral volumes are reported.

Raman scattering at ambient conditions

According to group theory (e.g., Kroumova et al. 2003), at the Brillouin-zone centre there are $\Gamma_{opt} = 14A_g + 13A_u + 16B_g + 14B_u$ optical phonon modes in chemically disordered omphacite.
(C2/c) and $\Gamma_{\text{opt}} = 28A_u + 27A_g + 32B_g + 30B_u$ in chemically ordered omphacite ($P2/n$). The $A_u$ and $B_u$
are infrared-active, while $A_g$ and $B_g$ modes are Raman-active. Only $A_g$ modes should appear in
parallel polarized Raman spectra measured when the pyroxene prism axis is parallel or
perpendicular to the polarization of the incident light, as it was in our scattering geometry.
Therefore, 28 peaks are expected in the Raman spectra of samples natural-8 and natural-11 and
14 peaks in the spectra of samples annealed-3 and annealed-7. Indeed 14 peaks were observed for
chemically disordered omphacite (see Figure 2 and Table 4), but only 22 peaks were resolved for
chemically ordered omphacite. This can be due to peak overlapping (e.g. the peaks near 1021 and
1029 cm$^{-1}$) or weak diagonal components (e.g. the peaks near 158, 281 and 452 cm$^{-1}$) of the
Raman polarizability tensor, as indicated by the results of HF/DFT calculations. The calculated
phonon wavenumbers of $A_g$ modes in $P2/n$ at zero pressure match very well the observed Raman-
peaks positions at atmospheric pressure (Table 4). The calculated and observed relative peak
intensities in the parallel-polarized Raman spectra are also in a very good agreement (see Fig. 3a).
A complete list of the Raman active phonon modes in fully ordered Jd$_{50}$Di$_{50}$ omphacite as well as
the Raman polarizability tensors derived from HF/DFT calculations at $P = 0$ GPa and $T = 0$ K are
given in the Online Materials (Table S2).

The assignment of each Raman peak to a definitive atomic vibration can be achieved by
direct inspection of the calculated atomic vector displacements. The strongest experimentally
observed Raman signals are then assigned as follows:

- The $A_g$ modes in the range 950 and 1050 cm$^{-1}$ are related to the Si-O$_{nb}$ bond stretching
($O_{nb} =$ non-bridging oxygen, which is not shared between two TO$_4$). Chemically disordered
omphacite exhibits one peak observed near 1017 cm$^{-1}$, whereas ordered omphacite is
characterized by the splitting of this peak into two components at about 1007 and 1029 cm$^{-1}$, due
to the reduction of the translational symmetry.
- The strong peak at 688 cm$^{-1}$, typical of both chemically ordered and disordered omphacite, arises from A$_g$ mode comprising Si–O–Si bond bending vibrations.

- The A$_g$ modes at 375, 382, 402 and 411 cm$^{-1}$ are related to M1O$_6$ and M11O$_6$ bending and TO$_4$ rotation around c.

- The A$_g$ mode at 337 cm$^{-1}$ in ordered omphacite is related to M1-cation vibrations parallel to the b axis and TO$_4$ rotation around the c axis. Note that the tilt angle is defined as the out-of-plane tilting of the basal face of the tetrahedra with respect to the plane (100) (Cameron et al. 1973).

- The A$_g$ mode at 300 cm$^{-1}$ in chemically ordered omphacite is due to M1-cation and $^{M2}$Na vibrations parallel to b.

- The A$_g$ mode at 271 cm$^{-1}$ is associated with vibrations of M-site cations along b and TO$_4$ translation along a.

- The A$_g$ mode at 215 cm$^{-1}$ is mainly related to SiO$_4$ rotation around a.

Sketches of selected vibrational modes are presented in Figure S1 in the Online Materials.

It should be emphasized that the peak FWHM is affected by the ordering of the cations at the six- and eight-coordinated sites and it increases with cation disorder, as reported by Katerinopoulou et al. (2008).

**Pressure dependence of Raman spectra**

Figure 4 shows the pressure evolution of Raman spectra of chemically ordered omphacite.

No change in the number of observed peaks occurs in the investigated pressure range. In accordance with theory, the strongest peak at 688 cm$^{-1}$ gradually increases in wavenumber upon pressure increase, while its FWHM increases slightly, but within the spectral resolution (see Figure 5). The former is due to the pressure-induced decrease in the atomic distances and the
subsequent increase in the effective interatomic force constants, whereas the latter is related to
the fact that the phonon decay and hence the peak FWHM should not change with pressure in the
absence of structural transformations. Figure 5 also demonstrates that the phonon compressibility
\[ \beta_\omega = \frac{1}{\omega_0} \frac{d\omega}{dP} \]
of the A_g mode near 688 cm\(^{-1}\) does not depend on the chemical order, which makes
this peak a potential candidate for wavenumber-pressure calibration. The linear fit \( \omega(P) = \omega_0 + \frac{d\omega}{dP} \)
\( P \) to the experimental data points gives \( \omega_0 = 680.3(2) \), \( \frac{d\omega}{dP} = 3.32(3) \), and \( \beta_\omega = 0.00488(5) \) GPa\(^{-1}\).

Then using the relation \( P = \frac{\omega - 680.3}{3.32} \), the pressure can be determined with an accuracy of \( \sim 0.1 \) GPa.

Further experiments can improve the statistics of \( \omega(P) \) data points, which in turn will reduce the
errors in the coefficients of polynomial fit and consequently, will reduce the propagating
uncertainties in \( P_{\text{inc}} \), that is the residual pressure.

A few Raman peaks for chemically ordered omphacite show anomalous behavior near 4.5-
5 GPa: (i) the pressure dependence of the average wavenumber of the two components related to
the Si-O_{nb} bond stretching shows a discontinuity near 5 GPa (Figure 6a), although the \( \frac{d\omega}{dP} \) value
remains nearly the same above 5 GPa; (ii) the slope of \( \omega(P) \) of the peaks near 375 cm\(^{-1}\) and 337 cm\(^{-1}\), both arising from M1O_6 vibrations and SiO_4 rotations, changes around 4.5 GPa (Figure 6b and c)
and above this pressure the corresponding phonon compressibility equals to that of disordered
omphacite; (iii) the FWHM of the peak near 271 cm\(^{-1}\), generated by M-cation vibrations and SiO_4
translations, becomes smaller above 5 GPa (Figure 6d).

In order to simulate the pressure dependence of the phonon modes, unit-cell parameters
(reported in Table 2) and fractional coordinates were optimized by analytical gradient methods
and the equation of state (EoS) at room temperature was modelled. As can be seen in Table 5, the
calculated EoS parameters are in good agreement with previously published experimental results
The pressure dependence of the phonon wavenumbers of fully ordered omphacites was simulated in the pressure range 0-11 GPa, while the Raman intensities were calculated at 0, 2, 4, 5 and 6 GPa. The correspondence between experimental and calculated spectra at high pressure is very good (Figure 3b). The calculated $\frac{d\omega}{dP}$ of the main peaks also match very well the corresponding experimentally observed $\omega(P)$ slopes (see Figure 7).

**Discussions**

The hybrid HF/DFT simulations reveal that the anomalous $\omega(P)$ behavior of the peak ~337 cm$^{-1}$ for chemically ordered omphacite can be explained by enhanced phonon-phonon interactions near 4.7 GPa. The ab initio simulations reveal that in this spectral range there are actually two $A_g$ modes, at 337 and 349 cm$^{-1}$. Having the same symmetry and similar energies, these $A_g$ modes can interact and exchange intensity via the so-called *avoided intersection*, also referred to as energy-level anticrossing (Dresselhaus et al. 2008); that is, two modes of the same symmetry approach one another in energy but without energy crossing. Indeed, the wavenumbers of the two $A_g$ modes become very close to each other at a volume of about 413 Å$^3$ (see the insert in Figure 7), corresponding to a pressure of 4.7 GPa, while at higher pressure they diverge. These two Raman peaks could be experimentally distinguished for sample natural-8 when measured in air, but not under high pressure in DAC, so that only one peak at about 337 cm$^{-1}$ was used in the fitting model for high-pressure spectra. However, as can be seen in Figure 7, the experimental and simulated pressure trend for the $A_g$ mode near 337 cm$^{-1}$ are in a very good agreement.

It should be emphasized that above the pressure of $A_g$-phonon anticrossing, the phonon compressibility of the mode near 337 cm$^{-1}$ in chemically ordered omphacite becomes the same as that in chemically disordered omphacite. The same is valid for the $A_g$ mode near 375 cm$^{-1}$. Both phonon modes involve SiO$_4$ tilting and M-cation vibrations and the change in $\beta_\omega$ should be related...
to a change in the M-O-Si interactions. External pressure alone cannot mobilize M-site cations to form a chemically disordered state above 4.5 GPa. However, pressure can trigger a redistribution of the local elastic strains related to the difference in the ionic sizes of the M-site cations, leading to unified MO$_6$ volumes and consequently, averaged effective M-O-Si force constants that appear to be the same as a state of site-occupancy disorder. In addition, both the zenithal and azimuthal components of the out-of-plane basal tilts of tetrahedra, which change as a function of the degree of order (for exact definitions see Boffa Ballaran et al. 1998a and Cámara et al. 1998), may also change as a consequence of compression, related also to the unified volume compressibility of the M1 and M11 octahedra. Chemical disorder is difficult to implement in ab initio simulations. However, based on the combined experimental and HF/DFT results presented here, we speculate that the pressure-enhanced phonon-phonon interactions near 4.5-5 GPa trigger the homogenization of local elastic strains associated with chemical order at the (M1, M11) and (M2, M21) sites, respectively. This phenomenon should be responsible also for the anomaly in the averaged $\omega(P)$ of the Si-O$_{nb}$ bond stretching mode observed near 1017 cm$^{-1}$, because M-O interactions have a secondary effect on the energy of this phonon mode. The experimentally observed reduction of the FWHM of the 271-cm$^{-1}$ peak, resulting primarily from M-cation vibrations, is also consistent with the assumption for a smaller dispersion in the MO$_6$ size above ~4.5 GPa.

For ordered omphacite a slight anomaly in the pressure dependence of the M1,11O$_6$ volumes has been reported at about 4 GPa by Pandolfo et al. (2012b), which was attributed to a pressure-induced change of the tilt angle for both T1O$_4$ and T2O$_4$ tetrahedra. This observation corroborates with the anomalies reported here for the phonon modes at about 1017, 375, 337, and 271 cm$^{-1}$. Moreover, we show that the position of the well resolved Raman peak at 688 cm$^{-1}$, generated by Si-O$_{br}$-Si bond bending $A_g$ mode, exhibits a strong pressure dependence, which is not
affected by the presence or absence of chemical order. That is, the temperature-induced change of the translational symmetry due to site-occupancy order-disorder processes does not influence the wavenumber of the Si-O\textsubscript{br}-Si bond bending and therefore, this phonon mode properly reflects the strained state of an omphacite inclusion associated with the metamorphic conditions. Besides, HF/DFT calculations indicate that this mode exhibits the strongest polycrystalline isotropic Raman intensity (see Table 4), ensuring that the peak near 688 cm\textsuperscript{-1} can be experimentally detected in any random orientation of an omphacite inclusion. Thus, as garnets do not show Raman scattering in this spectral range (Kolesov and Geiger 1998), this peak seems to be a promising candidate to be used for estimating the residual pressure for omphacite-in-garnet inclusion-host systems. On the other hand, the FWHM of this peak does not change with pressure, but it is indicative of the absence or presence of chemical cation order. When an instrumental resolution of 2 cm\textsuperscript{-1} is used, disordered omphacite shows a FWHM for the 688-cm\textsuperscript{-1}-peak around 16 cm\textsuperscript{-1}, whereas for omphacite with \( Q_{M1} \cong 2Q_{M2} \cong 0.8 \) the peak FWHM is around 12 cm\textsuperscript{-1}. A cation order parameter \( Q_{M1} \cong 0.83 \) corresponds to a closure temperature of about 600 K (Carpenter et al. 1990a). Therefore, a FWHM above 12 cm\textsuperscript{-1} implies that the omphacite inclusion has been trapped at \( T > 600 \) K. However, the Raman spectrum of omphacite and in particular the position of the wavenumber of the Si-O-Si bond bending mode depends on the chemical composition (Wang et al. 2001; Prencipe et al. 2012). Hence, further comprehensive studies on the compositional effect on the phonon compressibility for omphacites with diverse chemistry is required before utilizing omphacite-in-garnet systems for Raman elastic geothermobarometry applications.

**Implications**

Conventional thermobarometry techniques are commonly used in geological sciences for determining pressure and temperature conditions of mineral formation. These methods rely on...
mineral assemblages and chemical compositions, providing valuable insights into metamorphic processes, but they are limited by assumptions of chemical thermodynamic equilibrium under hydrostatic pressure (Powell and Holland 2008; Gilio et al. 2022). On the other hand, Raman elastic thermobarometry provides a non-destructive in situ approach for estimating pressure and temperature conditions based on the elastic properties of an inclusion and its host. This technique, which is mostly independent of chemical equilibration, holds great promise for providing accurate thermobarometric data, but it is restricted to a few host-inclusion systems. The lack of calibrations of Raman shifts with pressure, as well as of elastic properties at variable pressure and temperature, requires further experiments to improve and validate this method in geological studies (Kohn et al. 2023).

The present study represents the first step towards enabling the use of omphacite inclusions for elastic geothermobarometry purposes using Raman spectroscopy. We demonstrate that knowing the EoS and the composition of the inclusion, determined by EMPA analysis, it will be possible to a first approximation to estimate its residual pressure using Raman spectroscopy. For this purpose, one should comprehensively study the effect of the relevant thermodynamic variables on the phonon wavenumbers, namely elastic stress (or hydrostatic pressure), chemical composition, degree of chemical order. That is, one should: (i) establish relationships between phonon wavenumber and external elastic stresses/hydrostatic pressure, i.e. $\omega(P)$; (ii) a robust relationship between the chemical composition, denoted here for simplicity with $\{x\}$, and the phonon wavenumber, i.e. $\omega(\{x\})$, (iii) the effect of chemical composition on phonon compressibilities, i.e. $\beta_{\omega}(\{x\})$; and (iv), the effect of chemical order on $\omega$ and $\beta_{\omega}$. At the current stage, this can only be done using empirical calibrations such as $\omega(P) = \omega_0 + (d\omega/dP)P$ for selected phonon modes, which have been proved to be insensitive to the degree of chemical order, so that at least one parameter influencing the phonon frequencies can be eliminated. Further ab initio
calculations will enable, at least for the ordered structure, to calculate the Grüneisen tensor for a correct estimate of the residual strains (see Murri et al. 2018 for further details). The subsequent key point to enable the use of omphacite for elastic geobarometric purposes is the contrast in their elastic properties with respect to those of the host. Garnet is a significantly stiffer material compared to omphacite. Synthetic Prp$_{60}$Alm$_{40}$ garnet has a bulk modulus ($K_{T0}$) of 167.2 (17) GPa (Milani et al. 2015); on the other hand, omphacite has a lower $K_{T0}$, ranging from 122(1) to 119(2) GPa (Pandolfo et al. 2012a, b), thus implying a larger relaxation of omphacite volume than its host garnet and the building up of a significant remanent inclusion pressure from which it is possible to calculate the entrapment conditions (Korsakov et al. 2009). Furthermore, omphacite has a softer bulk modulus compared to zircon, but it is stiffer than quartz. The combination of their thermoelastic properties contributes to the isomekes trends: the isomekes of omphacite resemble those of quartz, making it a potential barometer.

To the aim of recalculating the entrapment conditions, knowing the elastic behavior as a function of composition and ordering state becomes crucial. Previous high-pressure single-crystal XRD analyses on omphacite from the same location as that of omphacite used in our study revealed $K_{T0} = 122(1)$ GPa and $K' = 5.1(3)$ for ordered omphacite, and $K_{T0} = 119(2)$ GPa and $K' = 5.7(6)$ for the disordered omphacite (Pandolfo et al. 2012a, b), i.e. within the uncertainties ordered and disordered omphacite exhibit a very similar volume compressibility up to 7.5 GPa (Table 5). Regarding the composition, Pandolfo et al. (2012a) discussed the bulk modulus dependence on the composition in terms of jadeite and diopside solid solution and proposed the following equation:

$$K_{T0} = 106(1)GPa + 0.28(2) \times Jd_{(mol\%)}$$

Our preliminary results based on the calculated EoS of omphacite indicate that the slope of omphacite-in-garnet isomeke is close to the slope of quartz-in-garnet isomeke (Figure 8) which...
makes omphacite a good candidate for elastic geobarometry. Here we present an example of garnet host with omphacite inclusions because it is a widespread host-inclusion system in several geological settings. For example, omphacite in garnet could be extremely useful in low-silica systems like metabasites (the most widespread lithotype of eclogites) where quartz is not stable and omphacite becomes a suitable common phase for retrieving metamorphic peak conditions. Furthermore, omphacite-in-garnet host-inclusion system will provide fundamental hints for low-pressure and high-temperature geological settings where both quartz and zircon inclusions in garnet have considerable shortcomings. The first comes from the high temperature $\alpha$-quartz $\leftrightarrow$ $\beta$-quartz phase transition and related effects on the atomic dynamics (e.g., Murri et al. 2019a) and the latter because of the high-temperature elastic reset in zircon (Campomenosi et al. 2022).

While the slope of the isomekes and the different character of the phase transition provides significant advantages for omphacite-in-garnet with respect to quartz- and zircon-in-garnet because it extends significantly the PT space of potential applicability, however the large spacing between the isomekes, far greater than that of quartz and zircon, may be a significant shortcoming. Because of the large spacing, omphacite inclusions in garnet will require higher precision in determining $P_{inc}$ from Raman spectroscopy.

In this paper we show that below $\sim$4.5 GPa the phonon compressibility of MO$_6$ octahedra is larger for the chemically ordered omphacite than for its disordered counterpart, whereas above 4.5 GPa the elastic behavior is unified, probably because the external pressure leads to homogeneous distribution of the internal chemically-induced local stresses. The strong Raman peak near 688 cm$^{-1}$, arising from Si-O$_{br}$-Si bond bending, seems to be a promising Raman marker for residual pressure via its position, and indicative of closure temperature via its width. However, further comprehensive analysis of the effect of composition and the cation order degree on all...
omphacite Raman-active modes and their pressure behavior is required to develop a protocol for
the proper utilization of omphacite-in-garnet systems in Raman elastic geothermobarometry.

Acknowledgements

This work was funded by the Italian Ministry of University and Research (MIUR) through a
PhD grant to L. Baratelli and to F. Cámara and L. Baratelli through the project “Dipartimenti di
Eccellenza 2023–2027”, and by European Research Council under the European Union's Horizon
2020 research and innovation program grant agreement 714936 (ERC-STG TRUE DEPTHS) to M.
Alvaro. M. Murri is supported by an A. von Humboldt research fellowship. This work has also been
partly supported by the PRIN-MUR project “THALES” Prot.2020WPMFE9_003. M. Alvaro is also
supported by the Highlight funded by Fondi Regione Lombardia DGR 3776.
References cited


Captions

Table 1. Electron microprobe analyses in oxide wt% and chemical formulae in atoms per formula unit, based on six oxygen atoms

Table 2. Unit-cell parameters of the analyzed crystals, compared to the ab initio calculated ones

Table 3. Site occupancy factors, order parameters and mean bond distances (given in Å) refined from single-crystal XRD data with chemical constraints

Table 4. Calculated and experimental wavenumbers ($\omega$, in cm$^{-1}$) of the $A_g$ modes and relative intensities normalized to 688 cm$^{-1}$ mode ($I$, in arbitrary units) of omphacite

Table 5. Bulk modulus $K_0$, its pressure derivative $K'$, the zero-pressure volume $V_0$ as well as the order parameters $Q_{M1}$ and $Q_{M2}$, pressure ($P$) and temperature ($T$) conditions of each study. The EoSs were determined using single-crystal XRD for all experimental studies except for Pavese et al. (2001), who used powder XRD

Figure 1. A structural fragment of ordered omphacite (space group symmetry $P2/n$). SiO$_4$ tetrahedra are shown in dark blue, M1 sites in orange, M11 sites in yellow, M2 in blue, and M21 in light blue. The structure was prepared using the VESTA software package (Momma and Izumi 2008).

Figure 2. Raman spectra of chemically ordered (red and grey lines) and chemically disordered (blue and green lines) omphacite, collected in (c||$E_i$||$E_s$) (samples natural-8 and annealed-3) or (c$\perp$ $E_i$ || $E_s$) (samples natural-11 and annealed-7) scattering geometry at room temperature and atmospheric pressure. The signals marked by * are not related to omphacite Raman-active phonon modes.

Figure 3. Experimental and calculated Raman spectra of ordered omphacite ($P2/n$), at ~0 GPa (a) and at ~5 GPa (b).
Figure 4. Pressure evolution of $\langle c || E_i || E_j \rangle$ Raman spectra of chemically ordered omphacite (sample natural-11).

Figure 5. Pressure dependence of the wavenumber and FWHM of the strongest Raman peak at 688 cm$^{-1}$. Filled symbols are related to the ordered omphacites, while open symbols to the disordered omphacites.

Figure 6. Pressure dependence of the wavenumber or FWHM of the peaks that show an anomaly at about 5 GPa in ordered omphacite, along with the corresponding trends for disordered omphacites: the average wavenumber of the two peaks near to 1007 and 1029 cm$^{-1}$ (a); the slope of the peaks at about 375 cm$^{-1}$ (b) and 337 cm$^{-1}$ (c) changes around 4.5 GPa; the FWHM of the peak near 271 cm$^{-1}$ becomes smaller above 5 GPa (d).

Figure 7. Experimental and calculated pressure dependence of the wavenumber of the $A_{g}^{337}$ mode. The slopes of the curves and the pressure at which they change are reported. The insert shows the calculated wavenumbers of the two $A_g$ modes that are involved in the anticrossing.

Figure 8. Calculated isomekes for quartz, zircon and omphacite inclusion in an almandine host, obtained from the $P_{inc}$ (equal to 0.0, 0.2, and 0.4 GPa) with the EoSFit–Pinc software (Angel et al. 2017b), using the equation of state of quartz (Angel et al. 2017a), zircon (Ehlers et al. 2022) and almandine (Angel et al. 2022), while the HF/DFT calculated EoS was used for omphacite ($J_{d50}D_{i50}$). The $\alpha$-$\beta$ transition of quartz is represented in a red dashed line, line and the shaded vertical strip represents the $P2/n$-to-$C2/c$ omphacite transition.
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**Unit-cell parameters**

- $a$ (Å): 9.5962(2) – 9.5935(2)
- $b$ (Å): 8.7897(2) – 8.7725(2)
- $c$ (Å): 5.2586(2) – 5.2508(1)
- $\beta$ (°): 106.789(2) – 107.22
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Note: $ep_{s0}$ = electron per site; $ep_{s0}$ = electron per site, calculated without chemical constraints.
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<tr>
<td>(A_g)</td>
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<td>(A_g)</td>
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<td>23.77</td>
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<td>(A_g)</td>
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<td>294.75</td>
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<td>(A_g)</td>
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<td>1000.00</td>
<td>680(1)</td>
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<td>737(2)</td>
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<td>734(2)</td>
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<tr>
<td>(A_g)</td>
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<td>882(2)</td>
<td>90.90</td>
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<td>911(2)</td>
<td>110.11</td>
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<td>(A_g)</td>
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<td>508.12</td>
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<tr>
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<td>840.22</td>
<td>1023(2)</td>
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<td>(A_g)</td>
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<td>25.90</td>
<td>1096(2)</td>
<td>211.75</td>
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</table>

Note: the calculated intensities correspond to polycrystalline material, whereas the listed experimental intensities for natural-8 and annealed-3 correspond to the square of \((zz)\)-component of the Raman polarizability tensor measured in scattering geometry \((\mathbf{c} \parallel \mathbf{E}_i \parallel \mathbf{E}_s)\), whereas the experimental intensities for natural-11 and annealed-7 correspond to a weighted sum of squared \((xx)\)- and \((yy)\)-components of the Raman polarizability tensor measured in scattering geometry \((\mathbf{c} \perp \mathbf{E}_i \parallel \mathbf{E}_s)\), with weight coefficients depending on the \(b\)-axis orientation with respect to the laser-beam propagation (random in our study).
### Table 5

<table>
<thead>
<tr>
<th></th>
<th>Calculated (HF/DFT)</th>
<th>Pandolfo et al., 2012b</th>
<th>Pavese et al., 2001</th>
<th>Zhang et al., 2016</th>
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<tbody>
<tr>
<td>Di (wt%)</td>
<td>50.00</td>
<td>48.0</td>
<td>47.4</td>
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<tr>
<td>Jd (wt%)</td>
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<td>46.5</td>
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<td>Ae (wt%)</td>
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<td>K₀ (GPa)</td>
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<td>117(3)</td>
<td>116(2)</td>
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<tr>
<td>K'</td>
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<td>5.1(3)</td>
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<td>4.3(2)</td>
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<tr>
<td>V₀ (Å³)</td>
<td>426.52(3)</td>
<td>421.43(4)</td>
<td>422.2(1)</td>
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<tr>
<td>Q⁺M₁</td>
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<td>0-13</td>
<td>0-47</td>
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<td>T (°C)</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
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</tbody>
</table>

Note: Q⁺M₁ and Q⁺M₂ of ordered omphacite are derived from ab initio simulations and experimentally determined in previous XRD studies (Di = diopside, Jd = jadeite, Ae = aegirine). For Zhang et al. (2016) Q⁺M₂ is calculated based on the site occupancy factor, while Q⁺M₁ as a function of the bond distances (Carpenter et al. 1990a).
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6

[Graphs showing data points for different conditions]
Fig. 7
Fig. 8