

Supplementary material for
RAMAN ELASTIC GEOBAROMETRY FOR ANISOTROPIC MINERAL
INCLUSIONS

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Voigt notation

The band position under a strain $\boldsymbol{\varepsilon}$ is determined by the second-rank symmetric mode Grüneisen tensor $\boldsymbol{\gamma}^m$ (Ziman 1960, Key 1967, Cantrell 1980) for each Raman mode:

$$\frac{-\partial\omega}{\omega} = \boldsymbol{\gamma}^m : \boldsymbol{\varepsilon} \quad 1)$$

The “:” in equation (1) is a double-scalar product between the two tensors. Because both tensors are second-rank and symmetric this can be written out in full in Voigt (1910) notation as:

$$\frac{-\partial\omega}{\omega} = \gamma_1^m \varepsilon_1 + \gamma_2^m \varepsilon_2 + \gamma_3^m \varepsilon_3 + \gamma_4^m \varepsilon_4 + \gamma_5^m \varepsilon_5 + \gamma_6^m \varepsilon_6 \quad 2)$$

Note that under the Voigt convention here for strains, the values of the shear strains $\varepsilon_4, \varepsilon_5, \varepsilon_6$ are one-half of the values of the corresponding tensor components $\varepsilon_{23}, \varepsilon_{13}, \varepsilon_{12}$. Instead, γ_4^m, γ_5^m and γ_6^m are equal of the values of the corresponding tensor components $\gamma_{23}, \gamma_{13}, \gamma_{12}$.

This equation means that the changes in the Raman peak positions in general depend on all of the strains in three dimensions experienced by the crystal, not just the volume. In principle, the values of the six components, γ_i^m with $i = 1$ to 6, of a mode Grüneisen tensor may change with pressure and temperature, and with the magnitude of the strains. And, as

we will show for quartz, the values of γ_i^m are different for different modes. The mode will be indicated by the superscript m , in various forms.

Because the mode Grüneisen tensor is a symmetric second-rank property tensor, it is subject to the same symmetry constraints on its component values as other second-rank property tensors, such as the thermal expansion and compressibility tensors. This is required to make the frequency shift given by (1) and (2) invariant under coordinate transformations. Thus, in all crystals with orthorhombic symmetry or higher, $\gamma_4^m = \gamma_5^m = \gamma_6^m = 0$. For uniaxial crystals in the standard setting $\gamma_1^m = \gamma_2^m$, and for cubic crystals and isotropic materials $\gamma_1^m = \gamma_2^m = \gamma_3^m$. Therefore, for the trigonal symmetry of quartz $\gamma_1^m = \gamma_2^m$. For the specific case of quartz inclusions in an isotropic host, such as garnet, the strain imposed by the garnet does not break the symmetry of the quartz crystal. Therefore, we are interested specifically in the cases when $\varepsilon_1 = \varepsilon_2$, for which the shift in the wave numbers of modes should be given by:

$$\frac{-\partial\omega}{\omega} = 2\gamma_1^m \varepsilon_1 + \gamma_3^m \varepsilon_3 \quad 3)$$

Computational details

The hybrid Hamiltonian WC1LYP 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 to correct for the self-interaction error (the interaction of an electron with itself), which is typical of both pure DFT local density (LDA) and generalized gradient approximation functionals. The Hamiltonian also includes the LYP correlation functional (Lee et al. 1988). The grid for the evaluation of the DFT exchange–correlation functionals was chosen by the keyword XLGRID of the CRYSTAL14 user

manual (Dovesi et al. 2014) and corresponds to a total of 37547 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 quartz we obtained 90.00003 electrons out of 90 for the reference volume at 0K and 0GPa static pressure. The localised *contracted* atomic basis sets used were Si 86-311G** (Pascale et al. 2005) and 8-411G(2d) (Valenzano et al. 2006) for Si and O, respectively, which were successfully employed to calculate *ab initio* structures and properties of silicates (e.g. Stangarone et al. 2017). Within the CRYSTAL code the accuracy in evaluating the Coulomb and Hartree-Fock exchange series is controlled by the keyword TOLINTEG, for which we set the five parameters to 8 (T1, T2, T3 and T4) and 18 (T5) (Dovesi et al. 2014). The diagonalization of the Hamiltonian matrix was performed at 7 independent k vectors in the reciprocal space (Monkhorst net; Monkhorst and Pack 1976) by setting to 3 the shrinking factor IS (Dovesi et al. 2014). Cell parameters and fractional coordinates were optimized by analytical gradient methods, as implemented in CRYSTAL14 (Civalleri et al. 2001; Dovesi et al. 2014). Geometry optimization was considered converged when each component of the gradient (TOLDEG parameter in CRYSTAL14) was smaller than 0.00003 hartree/bohr and displacements (TOLDEX) were smaller than 0.00012 bohr with respect to the previous step. Lattice parameters and fractional coordinates were optimized at the WC1LYP level (static values: no zero point and thermal effects included), at the static pressures from 0 to 10 GPa (with step of 0.5 GPa from 0 to 5 GPa and then a simulation at 10 GPa). For the non-hydrostatic simulations, the cell parameters were fixed at the chosen strain conditions and only the fractional coordinates were optimized with the keyword ATOMONLY (Civalleri et al. 2001; Dovesi et al. 2014).

Vibrational wavenumbers of all of the normal modes were calculated at the Γ 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).

Residual plots from the fitting procedure

The Grüneisen tensor components for all modes were then determined by fitting Eqn (2) (in the main text) by least-squares to the wavenumber shifts at different strain states simulated by HF/DFT calculations. The maximum misfits (i.e. $\delta\omega_{\text{obs}} - \delta\omega_{\text{calc}}$) are -1.76 cm^{-1} and -3.41 cm^{-1} for the 464 and 696 cm^{-1} bands, respectively, considering only the values in the black box because is where we could assume this surface to be planar (area of small strains). Outside from this box the misfit increases and therefore we did not include the other values in the fitting.

Raman spectroscopy details

Raman spectra were excited by the 514.532 nm line of a Coherent 90C Fred Ar⁺ laser. The laser power on the sample surface was approximately 14 mW, while the laser spot on the sample surface was approximately 2 micrometers. Spectra were collected for 15 s averaging over 3 accumulations. These conditions were proven not to cause overheating of the sample. The spectrometer was calibrated to the silicon Raman peak at 520.5 cm^{-1} . The spectral resolution was 2 cm^{-1} , while the precision in measuring the peak positions was 0.35 cm^{-1} . In the case of the quartz inclusion i6, the angle between the c axis of the quartz inclusion and the polarization of the incident light was 30°. For the inclusion a series of spot measurements were carried out along the two crystallographic axes. The OriginLab-Pro 2018 software package was used for data fitting and evaluation. The collected spectra were baseline corrected for the continuum luminescence background when necessary, temperature-reduced to account for the Bose-Einstein occupation factor (Kuzmany, 2009) and normalized to the acquisition time. Peak positions, full-widths at half maximum (FWHMs), and integrated

intensities were determined from fits with pseudo-Voigt functions [$PV = (1 - q) \cdot \text{Lorentz} + q \cdot \text{Gauss}$, q is the weight coefficient]. The criterion for the maximum number of fitted peaks was $\Delta I < I/2$, where I and ΔI are the calculated magnitude and uncertainty of each peak intensity, respectively.

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