

## Raman spectroscopic study of omphacites at variable pressures: implications for elastic geobarometry

Baratelli L.\*<sup>1</sup>, Murri M.<sup>2</sup>, Mihailova B.<sup>3</sup>, Prencipe M.<sup>4</sup>, Cámara F.<sup>1</sup> & Alvaro M.<sup>2</sup>

<sup>1</sup> Dipartimento di Scienze della Terra “A. Desio”, Università degli Studi di Milano. <sup>2</sup> Dipartimento di Scienze della Terra e dell’Ambiente, Università di Pavia. <sup>3</sup> Department of Earth Sciences, University of Hamburg. <sup>4</sup> Dipartimento di Scienze della Terra, Università di Torino.

Corresponding author e-mail: [lisa.baratelli@unimi.it](mailto:lisa.baratelli@unimi.it)

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The widespread occurrence of omphacitic clinopyroxenes (a solid solution of jadeite, augite and aegirine, with the general chemical formula  $(\text{Ca},\text{Na})(\text{Mg},\text{Fe}^{2+},\text{Al},\text{Fe}^{3+})\text{Si}_2\text{O}_6$ ) in several geological settings and rock-types (e.g. high pressure eclogites, mantle xenoliths etc.), make them ideal candidates to be exploited for Raman elastic geothermobarometry applications. Raman elastic geobarometry uses the deformation recorded by a mineral inclusion trapped in its host to retrieve the pressure and temperature conditions at which the inclusion has been entrapped (Angel et al., 2019), because Raman scattering is very sensitive to structural deformations in crystal structures developed upon heating or compression. Several host-inclusion systems have been studied so far, but clinopyroxene inclusions have not been thoroughly investigated yet. Therefore, the application of Raman elastic geobarometry to omphacites in various mineral hosts requires an accurate calibration of the Raman-peak positions against hydrostatic pressure.

However, the Raman-peak positions and their pressure evolution depend also on the chemical composition. Besides, natural omphacite crystals can show a significant degree of cationic ordering related to the crystallization temperature, which can also affect the elastic behaviour of omphacite. Therefore, we have started with the study of natural ordered ( $P2/n$ ) and experimentally disordered ( $C2/c$ ) crystals of omphacite coming from Münchberg Massif, Bavaria, Germany (peak conditions  $P > 2$  GPa,  $T = 600\text{-}650^\circ\text{C}$ ; O’Brien, 1997). On these samples, we carried out in situ high-pressure Raman spectroscopy measurements using a diamond anvil cell. As expected, the modes frequencies increase as pressure increases.

Since the study included omphacite crystals with different degrees of order, obtained with isothermal annealing experiments at different times, we were able to observe that progressive cationic disorder causes essentially a broadening of the peaks, whereas the changes in the Raman peak positions and FWHM are mostly due to pressure variations.

To better understand the elastic behaviour of the modes best suitable for elastic geobarometry, the Raman spectrum of a completely ordered omphacite of composition  $\text{Jd}_{50}\text{Di}_{50}$ , has been simulated at variable pressures with *ab initio* Hartree-Fock / Density Functional Theory simulations and compared with experimental spectra. The calculated data resulted to be in a good agreement with experiments and allowed us to understand changes in the pressure dependence of some modes.

Our results readily enabled us to calculate the entrapment pressure of omphacite inclusions still trapped in their host rocks by determining the Raman shifts of the main peaks along with changes in the cation order.

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