ELASTIC THERMOBAROMETRY: METHODS AND APPLICATIONS TO ULTRAHIGH-PRESSURE METAMORPHIC ROCKS

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INTRODUCTION

Ultrahigh-Pressure (UHP) metamorphic rocks retain the evidence of deep-seated petrologic and tectonic processes, which are the source of natural hazards like deep-focus earthquakes and volcanic eruptions.

Mineral inclusions are often the only proof of UHP metamorphism and their study provides insights into the mechanisms of subduction and exhumation of metamorphic rocks. So far, the most frequently used approach to constrain the conditions of rock recrystallization is the application of equilibrium thermodynamics to mineral assemblages assuming a linear relationship between the inferred pressure (P) and the depth of their formation. In this regard, coesite or diamond-bearing systems suggest that rocks could be exhumed from depths in excess of 100 km (*e.g.*, Chopin, 1984). However, a major current controversy is whether high-pressure minerals actually form at such great depths, or they are the result of tectonic overpressure during subduction (Moulas *et al.*, 2013; Tajčmanová *et al.*, 2014). If tectonic overpressure were effective, coesite- and diamond-bearing rocks could come from shallower domains of the lithosphere and a revaluation of the current ideas of rock metamorphism and plate tectonic processes would be necessary.

So far, there are no available techniques to constrain the amount of deviatoric paleo-stress present during metamorphic processes. A first attempt has been recently proposed combining mineral physics and petrology: the elastic thermobarometry (*e.g.*, Angel *et al.*, 2015; Alvaro *et al.*, 2020). The main advantage of this technique is that it is not based on the equilibrium thermodynamic assumption but on the contrast in the elastic properties of two crystals that are constrained within a confined space, such as a mineral inclusion and its surrounding host.

Indeed, the analysis of solid inclusions that are fully buried within their hosts by non-destructive techniques, such as Raman spectroscopy, reveals pressures that can considerably deviate from the external (ambient) one. This is the so-called inclusion residual pressure (P_{inc}) and it arises as a response to the contrast in the thermo-elastic properties between the host and the inclusion if, for example, the entrapment of the inclusion occurred at high P-T conditions (Fig. 1).

Importantly, the amount of residual pressure is linked to the entrapment pressure and knowing the physical properties of the two crystals (*i.e.* their equations of state), using theoretical models, it is possible to back-calculate the P-T conditions of inclusion entrapment (Rosenfeld & Chase, 1961; Angel *et al.*, 2015). Nevertheless, the current theoretical models interpreting the residual pressure in host-inclusions systems are based on simplified assumptions and ideal geometries (*e.g.*, isotropic elasticity for both the host and the inclusion crystals, shape of the inclusions are spherical and the host has infinite size).

To shed light on this issues, in this work, two main topics have been considered: *i*) to understand, how much the deviations from the ideal host-inclusion system can actually influence the residual pressure measurements and the resulting thermobarometric estimates; *ii*) to apply the recent theoretical and experimental developments of elastic thermobarometry to a natural case study. The first topic deals with the use of Raman spectroscopy to measure and determine the strain state of mineral inclusions and of the mineral hosts; the second topic regards the application of the elastic thermobarometry to the UHP rocks of the famous Dora-Maira Massif (Western Alps). Backbone of this work are zircon inclusions in pyrope, since they represent one of the most common accessory minerals in metamorphic rocks and, furthermore, can allow to determine the ages of metamorphic events adding a fundamental tile in the evaluation of geological processes.

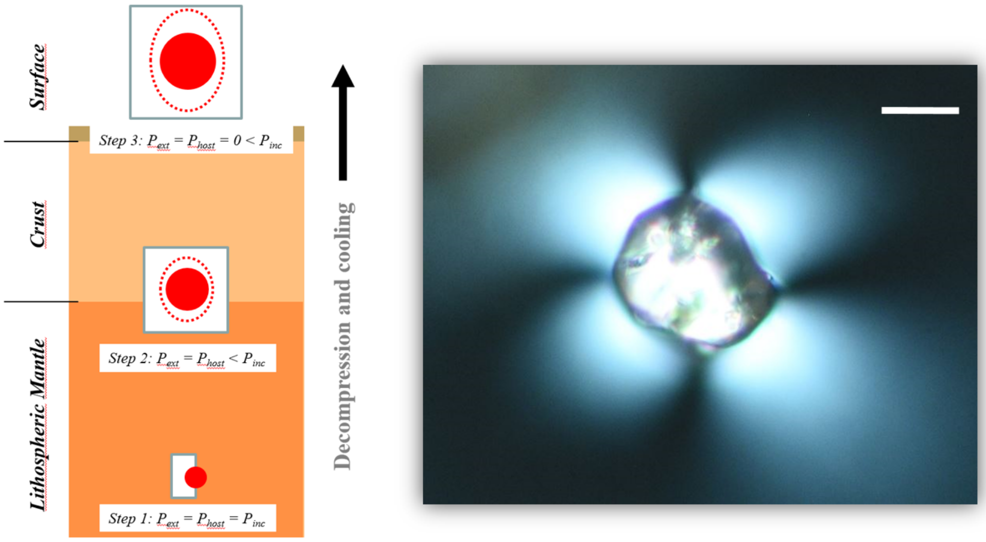

Fig. 1 - On the left, schematic step-representation of inclusion (red) entrapment in a mineral host (white) and development of a residual pressure at room conditions. At step 1, during the entrapment, the two crystals record the same P and T conditions and therefore there is no stress gradient between them. At step 2, the inclusion is completely isolated from the surrounding environment and if the system start to exhume toward the hearth surface, because of the different physical properties, the inclusion can develop a stress field in the surrounding host because it wants to expand more but it cannot since it is constrained by the host in a confined space (step 3). The red dashed line represents the volume of the inclusion as it would be if it was free to expand. Note that, in this case the inclusion is anisotropic, *i.e.* it would expand more along one direction (vertical) with respect the other (horizontal). On the right, one of the most spectacular evidences of stress field between the host (a garnet) and the inclusion (a zircon) as seen at the optical microscope. The garnet host is cubic and then it should be always in extinction under cross polarizers. However, close to the host inclusion boundary, the host can break its symmetry becoming birefringent because of the stress field imposed by the inclusion which want to expand to its "equilibrium" volume. Scale bar is 20 µm.

EXPERIMENTAL RESULTS ON THE EFFECTS OF DEVIATION FROM THE IDEAL HOST-INCLUSION GEOMETRY

In-situ Raman measurements of completely buried zircon and coesite inclusions within garnet show that rounded grains exhibit constant Raman shifts throughout their entire volume. On the other hand, according to numerical simulations (Mazzucchelli *et al.*, 2018), Raman shifts can vary from the centre to the edges and corners of faceted inclusions (Fig. 2).

Moreover, step-by-step polishing of the garnet host shows that the strain in both rounded and prismatic inclusions is gradually released as the inclusion approaches the free surface of the host; even when an inclusion is exposed at the surface of the host grain, it can still exhibit significant amount of residual stresses (Fig. 3).

More importantly, the experimental results coupled with selected numerical simulations confirm that the magnitude and rate of the strain release depends also on the contrast in elastic properties between the host and the inclusion and on the inclusion crystallographic orientation with respect to the external surface (*i.e.*, crystal anisotropy). These results allow a new methodological approach to be outlined in determining the residual strain in host inclusion systems (Campomenosi *et al.*, 2018):

- multiple Raman spectra collected on faceted inclusions should not be averaged if their differences are larger than the instrumental peak precision. In this regard, to avoid the effects of grain shape, only Raman spectra measured at the centre of the inclusions should be used;

- only inclusions whose centres are distant more than 4 radii from the thin section surface and internal surfaces of the host should be used;

- partially entrapped grains as a strain-free standard should be avoided or chosen very carefully against which to measure the Raman shifts of unexposed inclusions.

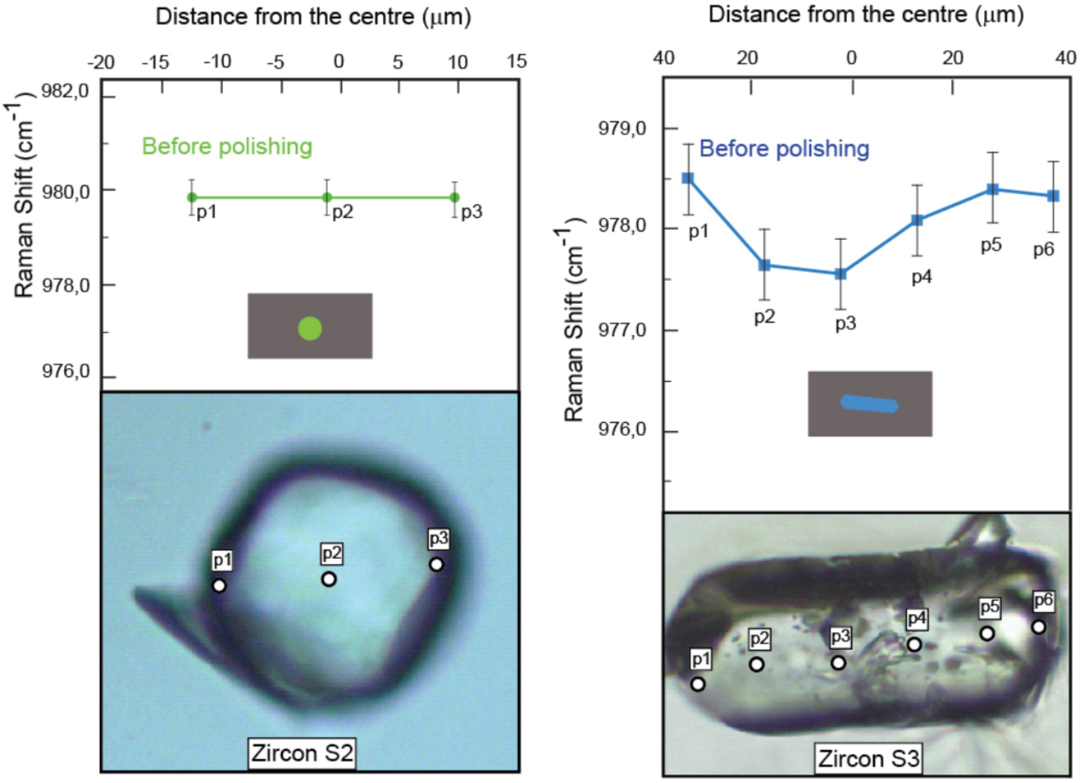

Fig. 2 - Position of the Raman peak A_{1g} ~ 975 cm^{-1} in a rounded (left) and an idiomorphic (right) zircon crystals before polishing. The solid lines in the plots are guides for the eye. Error bars refer to the instrumental uncertainty of 0.35 cm^{-1} in determining the peak position.

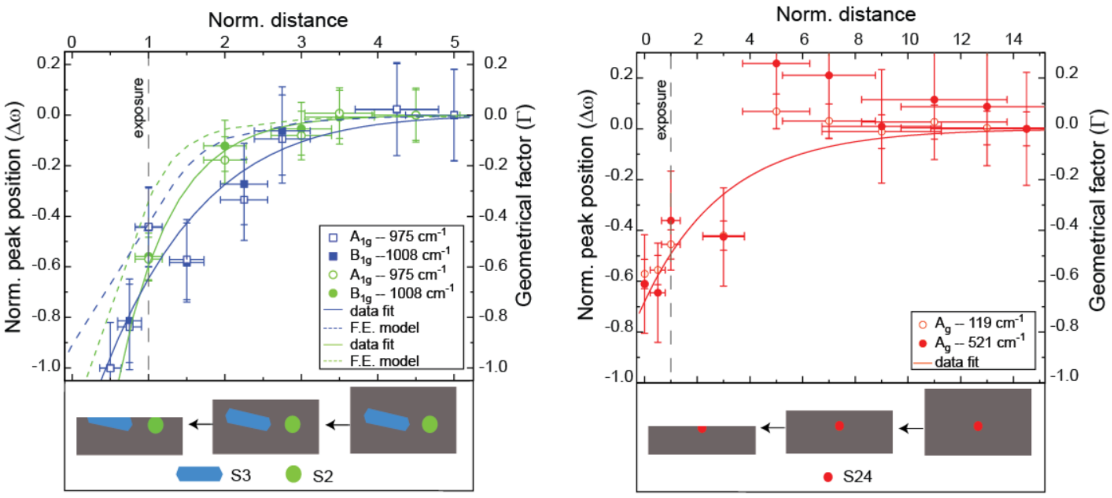

Fig. 3 - The step-by-step polishing effect on stressed mineral inclusions. On the left, measured normalized wavenumber shifts (Δω norm) for zircon S2 (green circles) and zircon S3 (blue squares) *versus* the normalized distance *d* to the host surface along with gaussian fits to the corresponding data A_{1g} ~975 and B_{1g} ~1008 cm^{-1} data sets (solid lines) compared with the calculated geometrical factor Γ (dashed lines) from selected Finite Element (FE) models; Δω norm(d) and Γ(d) show the same trend within uncertainties. On the right, measured Δω norm(d) (red circles) and a Gaussian fit to A_g ~119 and ~521 cm^{-1} (solid line) for S24 coesite inclusion.

DEFORMATION IN THE HOST CRYSTAL: AN ALTERNATIVE APPROACH OF VISUALIZING STRESS AND STRAIN FIELDS USING RAMAN SPECTROSCOPY

In order to define the spatial distribution of the anisotropic strain fields near the host-inclusion boundaries, polarized Raman spectroscopy was applied to host garnet domains exhibiting anomalous birefringence around stressed inclusions of zircon and quartz.

For the first time, the theory of the morphic effect *(external-field-induced change of the symmetry)* in lattice dynamics (*e.g.*, Anastassakis, 1980) was applied to host-inclusion systems, and an alternative Raman spectroscopy approach in the analysis of the stress fields in optically anomalous crystals was developed (Campomenosi *et al.*, 2020a).

The results presented here show a direct relationship between the stress-induced birefringence and the Raman scattering generated by the fully symmetrical phonon modes (the A_{1g} modes in cubic crystals) (Fig. 4).

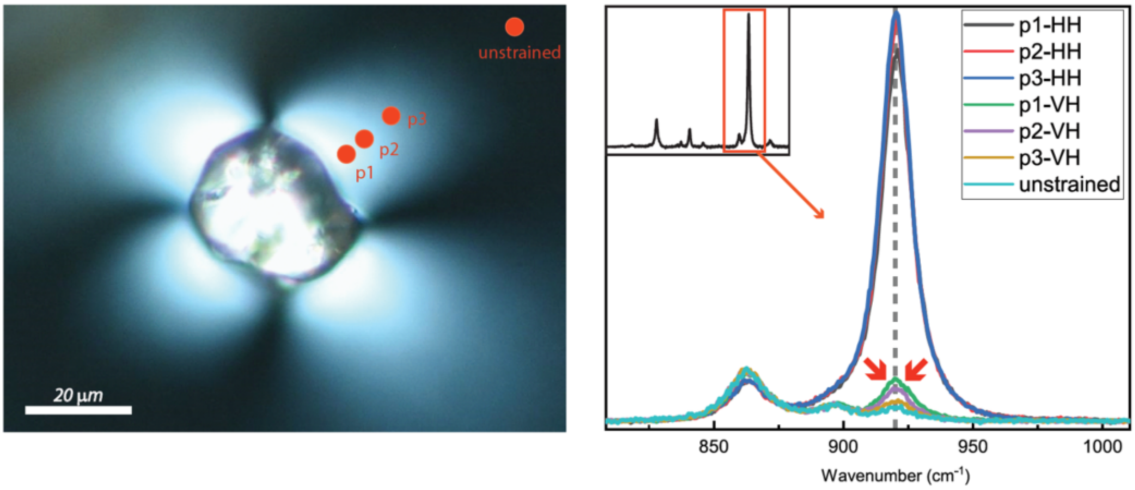

Fig. 4 - Anomalous Raman scattering of totally symmetric vibration A_{1g} near 928 cm^{-1}. VH and HH spectra correspond to cross and parallel-polarized scattering geometry respectively. A_{1g} modes in garnet (the most intense peaks) are not allowed for symmetry constraints under cross-polarized geometry of spectra acquisition as well as is not allowed birefringence under crossed nicols at the optical microscope. However, close to the host-inclusion boundary the stress field propagating from the inclusion breaks the symmetry of the host that becomes birefringent. In the Raman spectra this is visible looking at the anomalous scattering activity of totally symmetric vibrations close to the host inclusion boundary which disappears moving toward unperturbed domains.

The experimental results coupled with selected finite element models show that the ratio between the measured Raman peak intensity collected in cross and parallel polarized scattering geometries of totally symmetrical modes (*i.e.*, depolarization ratio), represents a useful tool to visualize and semi-quantify the radial stress profile in the host around the inclusions. Further, group-theoretical considerations and tensor analysis of the morphic effect on the phonon and the optical properties of the host can help to derive useful information on the symmetry of the stress field.

Finally, these results show that, experimentally, under the same amount of applied stress, this approach is more sensitive than the commonly used approach of measuring differences in the wavenumber of Raman peaks and provides better opportunities to map the spatial variations of strain in crystals (Campomenosi *et al.*, 2020a).

Therefore, this technique represents an alternative way to study structural phenomena associated with anomalous birefringence in host crystals surrounding stressed inclusions, and could be applied to other systems in which similar optical effects are observed.

ZIRCON INCLUSIONS IN ELASTIC THERMOBAROMETRY: DEVELOPING A PROTOCOL FOR THEIR SELECTION USING RAMAN SPECTROSCOPY

As mentioned in the introduction, backbone of this work was the application of the elastic thermobarometry to natural zircon inclusions in garnet. However, zircon is a complex mineral subjected to chemical substitution and self-radiation damage processes that, in general, can affect considerably its physical properties (Geisler *et al.*, 2001; Palenik *et al.*, 2003) and, consequently, the residual pressure estimates. Therefore, a structural and chemical analysis of the properties of partially exposed zircon inclusions within garnet were carried out in detail using Charge Contrast (CC) imaging, Raman spectroscopy and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) (Campomenosi *et al.*, 2020b). Aim of this work was to determine to what extent metamictization, metamorphic recrystallization, inherent structural heterogeneity, chemical composition and zoning, along with the elastic stress imposed by the host mineral, influence the Raman peak position of the zircon inclusion and hence, the residual pressure providing an experimental protocol able to overcome these issues. The experimental results showed and confirmed that metamictization and inherent structural heterogeneity have a major influence in the Raman spectra of zircon in terms of peak position and peak width whereas the effect of chemical composition, being quite homogeneous and very close to the ideal end-member, can be safely neglected. In this regard, it was suggested that for an instrumental spectral resolution of 2 cm^{-1} the peak width of the B_{1g} mode near 1008 cm^{-1} of reliable and completely buried grains must be smaller than 5 cm^{-1} (in terms of *full width at half maximum, Γ*) and the method can be applied to both inherited igneous and newly formed Alpine metamorphic crystals (Fig. 5).

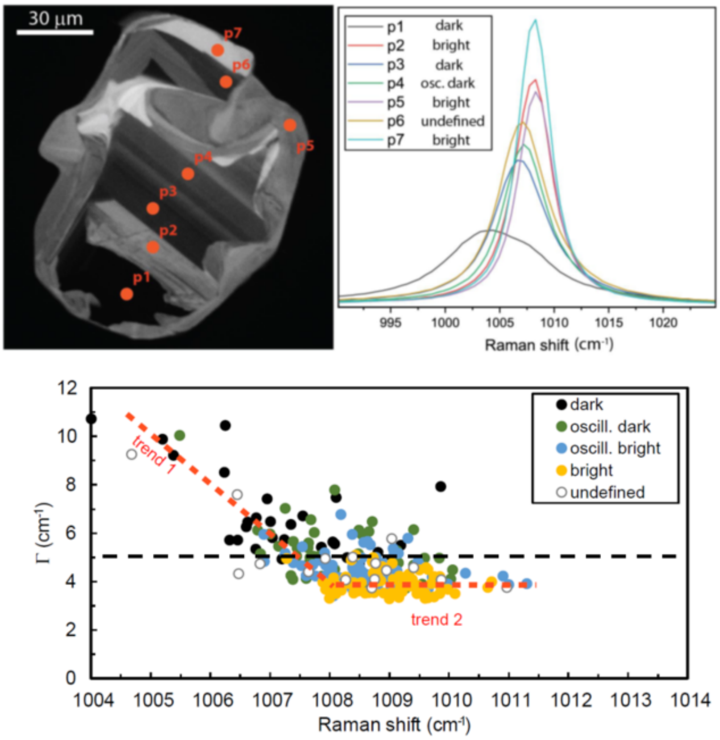

Fig. 5 - On top, relationship between CC imaging and Raman spectra of a partially exposed zircon inclusion. Dark CC domains usually corresponds to partially metamict domains (U rich), with broad Raman peaks (*e.g.* p1). On the other hand, bright zircon domains are usually relative to newly crystallized portions during metamorphic processes and they are mainly characterized by sharp Raman peaks and higher wavenumbers with respect to dark domains. On the bottom, the Raman peak width (Γ) of the B_{1g} mode near 1008 cm^{-1} is plotted against its wavenumbers allowing the distinction between radiation-damaged crystals (trend 1) and well crystalline grains (trend 2). Different colours in the plot refer to different CC domains in zircon crystals. The dashed horizontal lines represent the empirical threshold limit over which it can be distinguished the effect of partial radiation damage processes.

Indeed, by coupling structural and chemical information, it is evident that there are no significant differences between the Raman spectra of zircon with oscillatory-zoned texture, formed during magmatic crystallization, and those formed by fluid-induced Alpine (re)crystallization.

APPLYING ELASTIC THERMOBAROMETRY TO THE DORA-MAIRA UHP WHITESCHISTS

Chemical and elastic thermobarometry were applied to the garnet-bearing whiteschists from the Brossasco-Isasca unit of the Dora-Maira massif (western Alps). Pseudosection modelling together with Zr-in-rutile inclusion geothermometry was applied to constrain the conditions of formation of three garnet megablasts and consequently the conditions under which solid inclusion were trapped within them. Then, such estimates were compared with the zircon-in-garnet elastic thermobarometry model. The two approaches provided significantly different results in terms of garnet formation (*i.e.*, inclusion entrapment) (Fig. 6).

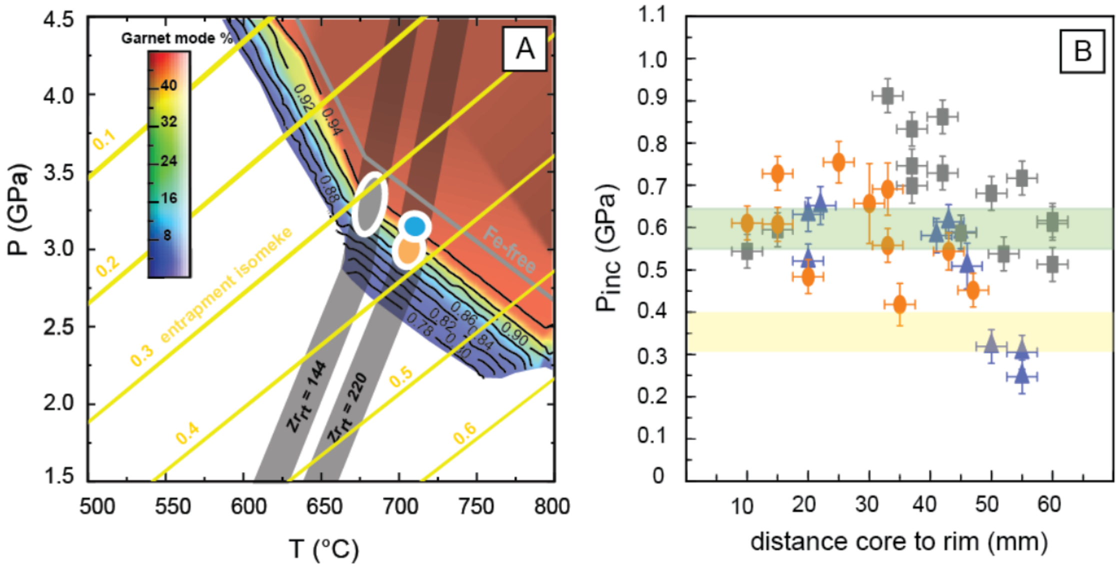

Fig. 6 - (A) P-T pseudosection of garnet stability field in whiteschists. Black labelled lines are the garnet isopleths in terms of pyrope mole fraction. The rainbow coloured area represents the garnet stability field and the different colours refer to different garnet mode abundances as indicated by the vertical legend. Grey shaded areas represent the T values obtained from Zr-in-rutile inclusions within garnet. The yellow lines are the zircon-in-garnet entrapment isomekes (*i.e.* the P-T equilibrium conditions under which the entrapment occurs) as function of different inclusion residual pressure (given in GPa). The three coloured ellipses represent the inferred P-T of garnet formation for three different samples combining garnet chemistry with the Zr-in-rutile thermometry. (B) Residual pressures of several zircon inclusions entrapped from core to rim of the different garnet hosts (colour coding follows Fig. 6A). The greenish line represents the average inclusion residual pressure while the yellow lines indicates the range of residual pressure expected according to pseudosection modelling (Fig. 6A). From this direct comparison it is evident there is a general disagreement between the two techniques.

A detailed analysis of different possibilities giving rise these incongruences was carried out and among them, it turns out that two main processes may have affected the thermobarometric estimates: the presence of local deviatoric stress during inclusion entrapment and the plastic relaxation of the host crystal. In this regard, it is shown how the analysis of the strain state of the measured zircon inclusions in comparison with those resulting from selected numerical simulations can help to clarify this issue. Indeed, thanks to the last methodological and theoretical advances of the elastic thermobarometric method in anisotropic systems (Murri *et al.*, 2018; Angel *et al.*, 2019; Mazzucchelli *et al.*, 2019), it can be shown that local deviatoric stresses occurring during the entrapment can be qualitatively considered when dealing with the metamorphic evolution of a rock. In this case study, for instance, it is suggested that, at the local scale, a small or negligible degree of deviatoric stress was present during garnet growth and inclusion entrapment while a viscous relaxation of the host seems to better explain the disagreement between the two different techniques. Finally, although this last point is under debate, it is important to emphasize how the combination of the elastic and chemical thermobarometry presented here allows to define metamorphic processes in rocks at higher level than envisaged before.

REFERENCES

Alvaro, M., Mazzucchelli, M.L., Angel, R.J., Murri, M., Campomenosi, N., Scambelluri, M., Nestola, F., Korsakov, A., Tomilenko, A.A., Marone, F., Morana, M. (2020): Fossil subduction recorded by quartz from the coesite stability field. *Geology*, **48(1)**, 24-28.

Anastassakis, E.M. (1980): Morphic effects in lattice dynamics. *In*: "Dynamical properties of solids, Vol. 4. Disordered solids, optical properties", G.K. Horton & A.A. Maradudin, eds. North-Holland, Publishing Company, Amsterdam, New York, Oxford, 159-355.

Angel, R.J., Nimis, P., Mazzucchelli, M.L., Alvaro, M., Nestola, F. (2015): How large are departures from lithostatic pressure? Constraints from host-inclusion elasticity. *J. Metamorph. Geol*., **33(8)**, 801-813.

Angel, R.J., Murri, M., Mihailova, B.D., Alvaro, M. (2019): Stress, strain and Raman shifts. *Z. Kristallogr*., **234(2)**, 129-140.

Campomenosi, N., Mazzucchelli, M.L., Mihailova, B., Scambelluri, M., Angel, R.J., Nestola, F., Reali, A., Alvaro, M. (2018): How geometry and anisotropy affect residual strain in host-inclusion system: coupling experimental and numerical approaches. *Am. Mineral*., **103**, 2032-2035.

Campomenosi, N., Mazzucchelli, M.L., Mihailova, B., Angel, R.J., Alvaro, M. (2020a): Using polarized Raman spectroscopy to study the stress gradient in mineral systems with anomalous birefringence. *Contrib. Mineral. Petr.*, **175(2)**, 16.

Campomenosi, N., Rubatto, D., Hermann, J., Mihailova, B., Scambelluri, M., Alvaro, M. (2020b): Establishing a protocol for the selection of zircon inclusions in garnet for Raman thermobarometry. *Am. Mineral*., DOI: 10.2138/am-2020-7246.

Chopin, C. (1984): Coesite and pure pyrope in high-grade blueschists of the Western Alps: a first record and some consequences. *Contrib. Mineral. Petr*., **86(2)**, 107-118.

Geisler, T., Ulonska, M., Schleicher, H., Pidgeon, R.T., van Bronswijk, W. (2001): Leaching and differential recrystallization of metamict zircon under experimental hydrothermal conditions. *Contrib. Mineral. Petr.*, **141(1)**, 53-65.

Mazzucchelli, M.L., Burnley, P., Angel, R.J., Morganti, S., Domeneghetti, M.C., Nestola, F., Alvaro, M. (2018): Elastic geothermobarometry: Corrections for the geometry of the host-inclusion system. *Geology*, **46(3)**, 231-234.

Mazzucchelli, M.L., Reali, A., Morganti, S., Angel, R.J., Alvaro, M. (2019): Elastic geobarometry for anisotropic inclusions in cubic hosts. *Lithos*, **350-351**, 105218.

Moulas, E., Podladchikov, Y.Y., Aranovich, L.Y., Kostopoulos, D. (2013): The problem of depth in geology: When pressure does not translate into depth. *J. Petrol*., **21(6)**, 527-538.

Murri, M., Mazzucchelli, M.L., Campomenosi, N., Korsakov, A.V., Prencipe, M., Mihailova, B.D., Scambelluri, M., Angel, R.J., Alvaro, M. (2018): Raman elastic geobarometry for anisotropic mineral inclusions. *Am. Mineral.*, **103(11)**, 1869-1872,

Palenik, C.S., Nasdala, L., Ewing, R.C. (2003): Radiation damage in zircon. *Am. Mineral.*, **88(5-6)**, 770-781.

Rosenfeld, J.L. & Chase, A.B (1961): Pressure and temperature of crystallization from elastic effects around solid inclusions in minerals? *Am. J. Sci*., **259(7)**, 519-541.

Tajčmanová, L., Podladchikov, Y., Powell, R., Moulas, E., Vrijmoed, J.C., Connolly, J.A.D. (2014): Grain-scale pressure variations and chemical equilibrium in high-grade metamorphic rocks*. J. Metamorph. Geol*., **32(2)**, 195-207.