DOI: 10.19276/plinius.2021.01005 PLINIUS n. 47, 2021

GARNETS AND THEIR INCLUSIONS AS KEY TO UNRAVEL P-T PATHS, DEFORMATION HISTORY, AND FLUID-ROCK INTERACTION IN THE ULTRAHIGH-PRESSURE METAMORPHIC LAGO DI CIGNANA UNIT, WESTERN ALPS, ITALY

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INTRODUCTION

The dynamic upper zone of the Earth, particularly at subduction zones, is host to volcanism, earthquakes and other natural hazards, large-scale elemental cycles, and the formation of economically viable mineral deposits. However, our knowledge of processes during subduction is hindered by the challenge of *in-situ* studies and limited exhumation of (ultra)high-pressure metamorphic rocks. Topics like the stress state and fluid-rock interaction at depth are of particular interest, as these factors are crucial in the behaviour of rocks at depth, yet are poorly understood. The aim of this work is to further develop and utilize the analysis of garnets and inclusions therein as tool of unravelling metamorphic conditions, fluid-rock interaction, deformation, stress, and strain, in systems where these are otherwise challenging to unobtainable. Petrological, microstructural, geochemical, and mineralogical aspects of garnet, rutile, quartz, and zircon, are studied to gain a better understanding of the processes at work during (ultra)high-pressure metamorphism. Five studies are presented in this work, each on a different aspect of the intersection between fluid-rock interaction, deformation, metamorphism, and stress.

GEOLOGICAL SETTING

The ultrahigh-pressure metamorphic Lago di Cignana unit (LCU) in the Western Alps of Italy is the focal point of this work. This locality provides an example of subducted and exhumed rocks that underwent metamorphism and deformation in a fluid-rich environment, an ideal setting to improve our combined understanding of the extent and interaction of stress state, deformation, and fluid-rock interaction. Subducting of the LCU during the Alpine orogeny culminated at ~40 Ma (Rubatto *et al*., 1998; Amato *et al*., 1999; Skora *et al*., 2015), at which time the unit underwent peak metamorphic conditions of 2.7- 3.2 GPa, 590- 630 °C (Reinecke, 1998; Groppo *et al*., 2009). This unit consists of oceanic crust, comprising ultramafic and mafic rocks and a variety of metasediments. Most of the lithologies found within the LCU contain garnetite lenses and layers, which together with their respective hosts formed the majority of the targeted samples.

EXTENSIVE FLUID-ROCK INTERACTION AND PRESSURE SOLUTION IN A UHP FLUID PATHWAY RECORDED BY GARNETITE

Evidence recorded within garnet revealed an extreme case of fluid-rock interaction in a long-lived fluid pathway (Van Schrojenstein Lantman *et al*., 2021). The combination of microstructures, mineral inclusions, and garnet compositions (Fig. 1a) provide a record of metamorphism and fluid-rock interaction of a garnetite-bearing quartzite. This fluid-rock interaction record showcases the longevity of this system as a major fluid pathway throughout subduction. The results also elucidate how fluids derived from dehydrating serpentinites led to high amounts of dissolution and mass removal of matrix minerals by intergranular pressure solution (IPS). Due to its relatively low solubility, garnet was concentrated into garnetite stylolites, constituting a new potential mechanism for the formation of garnetite (Fig. 1b).

Quartz inclusions in garnet that grew coeval with garnet pressure solution were analysed for their elastic strains using Raman spectrometry. Using the elastic strains, the inclusion pressure and thus entrapment conditions were revealed of around 1.5 to 2.0 GPa along the prograde path of the LCU. The elastic strains are within uncertainty of strains expected for entrapment under hydrostatic conditions, indicating that the system was at low differential stress.

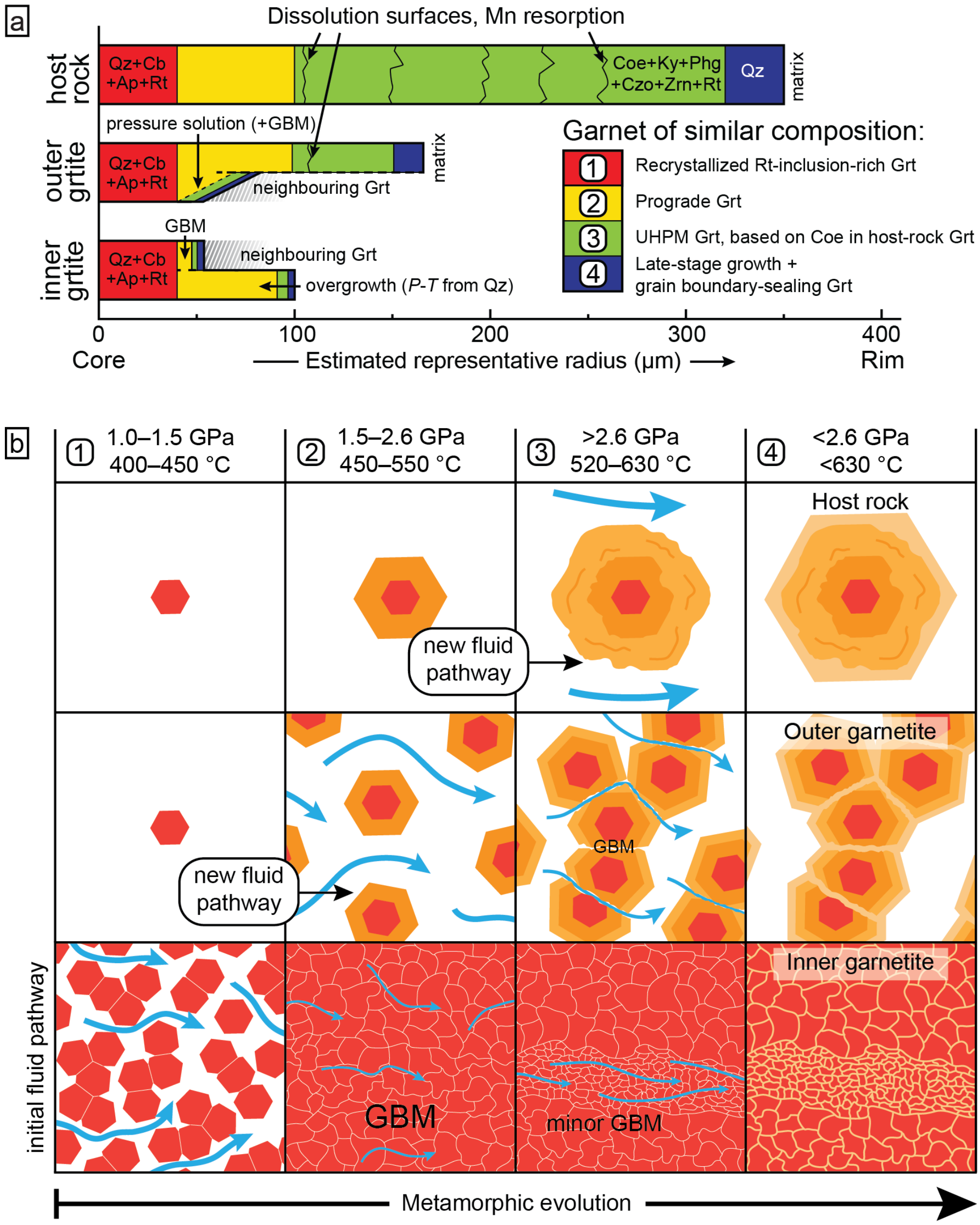

Fig. 1 - a) Schematic overview of garnet zones, inclusions, microstructures and thickness for the three studied zones of the system. b) Evolution of the garnetite and host quartzite by metamorphism and fluid-rock interaction during subduction. From Van Schrojenstein Lantman *et al*. (2021).

Considering IPS as the main mechanism of mass removal, the fluid-rock interaction also operated as a means of exerting control on deformation during metamorphism. The fluids that circulated through these garnetites resulted in unique microstructures that reveal a history of pressure solution, grain-boundary migration, radial fracturing, and partial replacement accommodated by infiltrating fluids.

GARNET DEFORMATION AND RECRYSTALLIZATION AT (U)HP-LT CONDITIONS: PRESSURE SOLUTION AND GRAIN-BOUNDARY MIGRATION

Microstructural aspects of the garnet in the system that was described previously, but also in other garnetites of the LCU, contain abundant evidence on deformation and recrystallization during subduction. Based on a compositional link between coesite-bearing garnet in the host quartzite and inclusion-poor garnet in the garnetite, IPS in garnet is found to have operated under UHP conditions, the first recognition of this mechanism specifically constrained to such pressures.

Grain shape analysis of garnets indicate that IPS resulted in low strain (Fig. 2), indicating that IPS in garnet does not result in weak garnetite layers. Furthermore, strain localized in a small fraction of the grains, generally smaller grains. Additionally, the preferred shape orientation of the deformed garnets has locally recorded a change in relative stress orientation, but also that local microstructures can be correlated to this shape preferred orientation, possibly indicating complex internal stresses within the garnetite. Evidence for garnet recrystallization by grain-boundary migration (GBM) is observed in all studied garnet-rich lithologies in the LCU, both metasedimentary and eclogitic. GBM in garnet has previously only been recognized in two other localities, and the particular driving force suggested here has not been described before. Therefor it appears that the LCU experienced a unique case of interaction between garnets and a fluid.

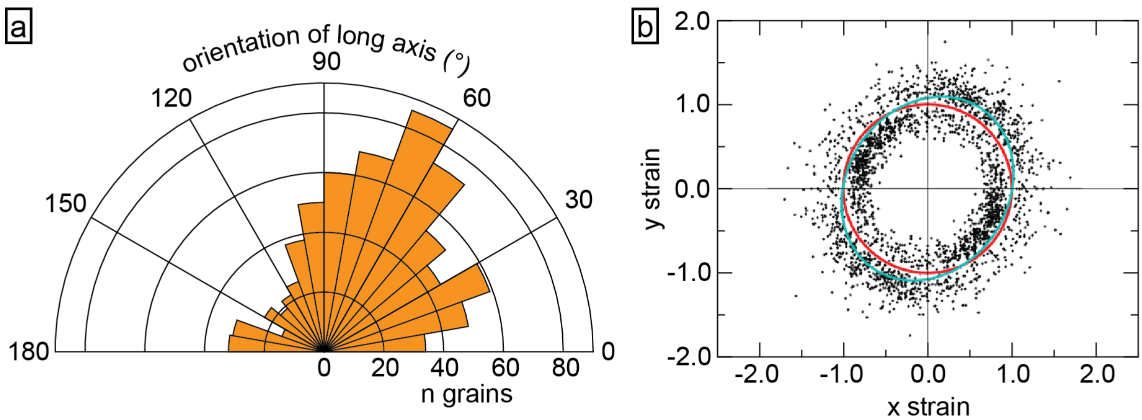

Fig. 2 - a) Polar histogram of long-axis orientations for ellipses fitted to grains from EBSD. b) Long and short axes for grains in the same EBSD map as in a) plotted with their orientation, normalized to the same area as a circle with r = 1, given in red. Long axis apexes plot outside the red circle, short axis apexes plot within the red circle. A strain ellipse, shown in blue, was fitted to the data points.

ELASTIC GEOTHERMOBAROMETRY ON ZIRCON IN GARNET: RESETTING OF A HOST-INCLUSION SYSTEM BY FRACTURING AND SEALING, AND THE PRESERVATION OF METASTABLE INCLUSIONS

The fracturing and sealing of garnets as is described previously is investigated, focusing on the elastic strains of zircon inclusions in the coesite zone of garnets in the quartzite. The aim of this investigation is to understand the resetting of elastic strains in the zircon and the preservation of coesite. Based on the selection procedure by Campomenosi *et al.* (2020), metamictization is not an issue for the majority of analysed zircons. Elastic strains obtained for these zircons cluster within uncertainty around strains that correspond to zircon under hydrystatic stress, and relate to inclusion pressures of 0.47 and 0.65 Gpa. Two inclusions under significantly higher inclusion pressures were found to contain small inclusions of unidentified minerals. Although an unresolved issue regarding the application of geothermobarometry or the host-inclusion system resulted in an overestimation of temperature conditions of resetting, radial fracturing and garnet replacement are suggested at ~1 GPa and

> 500 °C. Coesite inclusions did not break down to quartz despite this fracturing and resetting, with potential implications for the coesite-quartz reaction.

TRACE ELEMENT ANALYSIS OF GARNET AND ITS INCLUSIONS: SEPARATING CONTAMINATION FROM MINERAL COMPOSITION

The same garnetite-quartzite system as in the previous chapters is approached here from a perspective of trace elements. The growth of garnet is studied by their rare earth element composition, and the trace element compositions of sub-micron zircon and rutile inclusions within garnet cores is calculated based on contaminated garnet measurements. By determining the base Zr level in garnet, and by comparing Ti to Zr in LA-ICP-MS analysis, an approximate concentration of Zr in rutile could be determined. Zr-in-rutile thermometry applied to the calculated Zr concentrations in contaminant rutile inclusions yields temperatures that overlap with the majority of the near-isothermal decompression path of the LCU (Fig. 3), which is also in agreement with the conditions suggested for zircon inclusion resetting. The observations and analyses suggest that rutile inclusions originated from re-equilibration of Ti-bearing garnet as result of garnet recrystallization. Neither of the contaminant minerals can be linked to positive anomalies of light to mid rare earth elements (REE), which therefore represent the composition of the fluid that induced the garnet replacement. REE patterns in garnets in the host-rock quartzite, and Y element distribution mapping, suggest that HREEs were redistributed during the metamorphic evolution.

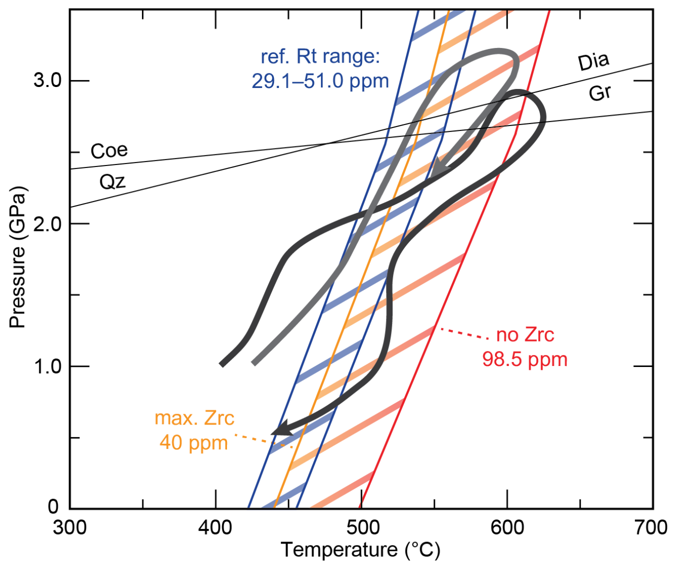

Fig. 3 - *P-T* paths for the LCU after Reinecke (1998) and Groppo *et al.* (2009) compared to Zr-in-rutile thermometry results for matrix rutile (blue; 29.1-51.0 ppm) and contaminant rutile (yellow-red; 40-98.5 ppm).

INCREASED TRACE-ELEMENT MIGRATION IN CRYSTAL-PLASTICALLY DEFORMED UHP RUTILE: DISLOCATIONS IN LOW-ANGLE BOUNDARIES AS HIGH-DIFFUSIVITY PATHWAYS

Rutile, like garnet, is also capable of retaining information on geological events. Here, rutile is studied for the effect that deformation has on its composition, using a variety of analytical techniques including Atom Probe Tomography. Zr-in-rutile thermometry combined with quartz inclusions in rutile, and coesite inclusions in the host omphacite vein, suggest that rutile grew just before the quartz-coesite transition. Deformation of the rutile formed low-angle boundaries that acted as fast diffusion pathways for various elements, some foreign to rutile such as Ca. In the case of Ca, the fluid that formed the omphacite vein is a likely source from which the element could have diffused into the rutile. Diffusion had no significant effect on Zr-in-rutile temperatures in this example, but at higher T, longer timescales and/or smaller spot size analyses, this deformation-accommodated diffusion must be taken into account for this method.

SUMMARY

Overall, this thesis highlights an extreme case of fluid-rock interaction in a long-lived fluid pathway. Fluids derived from dehydrating serpentinites led to high amounts of dissolution of matrix minerals, resulting in the accumulation of garnet. The fluids that circulated through these garnetites resulted in unique microstructures that reveal a history of IPS, GBM, radial fracturing, and partial replacement accommodated by infiltrating fluids. The study of elastic strains in inclusions revealed that garnet growth in this fluid-rich environment occurred at (near-) hydrostatic stresses, and elastic strains in zircon were used to show that host fracturing and resealing results in elastic strain resetting. Overall, the results of this thesis combine new insights into subduction zone deformation and fluid-assisted mass transfer, and the utility of garnet and rutile as hosts to inclusions rich in information. In both cases, deformation needs to be studied in detail to properly utilize the insights into the geological history that is stored in these host minerals, be it chemical, morphological, or from inclusions.

ACKNOWLEDGEMENTS

This project has received funding from the European Research Council under the European Union's Horizon 2020 research and innovation program grant agreement 714936 to M. Alvaro, and from the Italian MIUR to the PRIN program n. 2017ZE49E7. Part of the study on rutile was performed at the Geoscience Atom Probe Facility at Curtin University and part of the Advanced Resource Characterization Facility (ARCF). The ARCF, under the auspices of the National Resource Sciences Precinct, is supported by the Science and Industry Endowment Fund.

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