

Comparing PT paths of metamorphic rocks determined by quantitative and semi-quantitative approaches: a case study from the Monviso Ophiolite, Italy

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Introduction

Concentrations of major and trace elements are routinely measured on the micrometer scale with instruments like the Electron Probe Microanalyzer (EPMA) and others. Quantitative chemical maps of minerals produced by EPMA (using raw data corrections and standards) are normally favored over semi-quantitative chemical maps produced by Scanning Electron Microscopes (SEM; using raw data corrections *without* standards). Although significantly more cost effective, the latter technique is generally regarded as unsuitable for calculating pressures and temperatures (PTs) of metamorphic rocks with calibrated thermobarometers. However, we hypothesize that a monte-carlo resampling technique applied to semi-quantitative chemical maps can reproduce PT paths determined by alternative methods.

Geologic Setting

The Monviso ophiolite is part of a 350 km belt of metamorphosed (ultra)mafic and sedimentary rocks that extend across the western Alps from Italy to Switzerland (dark green and light blue units shown in Figure 1; Locatelli et al., 2019). These rocks are interpreted as the exhumed remnants of oceanic lithosphere and seafloor sediments that were subducted beneath the African continental margin beginning in the Cretaceous (Angiboust et al., 2012). Previous studies suggested that the Monviso ophiolite formed as a deep subduction mélange, where large blocks and slivers of oceanic lithosphere were exhumed in a serpentine-rich channel along the plate interface (Lombardo 1978). However, more recent studies interpret the Monviso ophiolite as a structurally-coherent section of oceanic lithosphere that was sliced off the subducting plate at eclogite-facies conditions (~80 km depth) and exhumed with only minor modification—evident by consistent PT estimates across all subunits within the Monviso ophiolite (Angiboust et al., 2011, 2012; Locatelli et al, 2019). Thus, the Monviso ophiolite presents a unique opportunity to understand important aspects of plate-interface mechanics in subduction zones, including the extent of strain localization (discrete vs. broad) and deep seismic cycles.

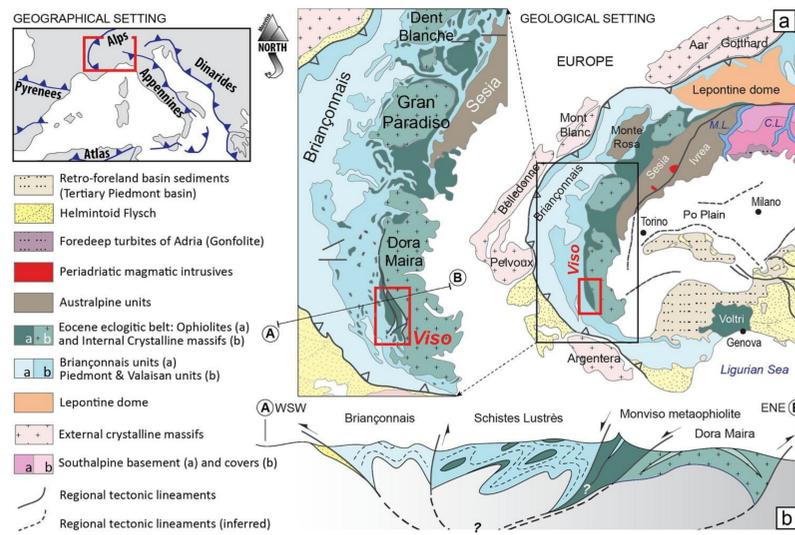


Figure 1. (a) Generalized map showing the distribution of sedimentary (light blues) and mafic/ultramafic (dark greens) units in the western Alps. (b) Simplified cross-section showing the major structures and tectono-metamorphic units across the Liguro-Piemontese domain. From Locatelli et al. (2019).

Field Observations and Sampling

A decameter-size block of eclogite facies Fe-Ti metagabbro (Figure 2) was sampled from within a weak matrix of chlorite- and serpentine-rich ultramylonitic schists that forms the Lower Shear Zone (LSZ) within the Monviso ophiolite, Italy. The sample, M17-K808D01, was collected from the pristine interior of the Fe-Ti metagabbro block, away from the deformed metasomatic rind.

Figure 2. Fe-Ti metagabbro block (pictured) exposed within the LSU, Monviso ophiolite, Italy. Blocks range in size from meters to many decameters and typically have metasomatic rinds.



Methods

M17-K808D01 was prepared into a doubly-polished thick section (100 μm; Figure 3). Metamorphic mineral assemblages and textures were analyzed using optical microscopy. Micro-textures and chemical compositions were analyzed by collecting high-resolution backscatter electron maps (3072x2304) and semi-quantitative chemical maps (1024x786) with a Zeiss Supra 35 VP FEG SEM equipped with a Bruker Quantax 100 Energy Dispersive x-ray microanalysis system (EDS) at the Center for Advanced Microscopy and Imaging (CAMI), Miami University (Figure 4 & 5). Chemical maps were processed using XMapTools 4.1 (Lanari et al. 2014; 2019; 2023).

Figure 3. Full section scan (plane polarized light) of sample M17-K808D01. The sample exhibits little to no foliation fabric (low-strain) with euhedral to subhedral garnet porphyroblasts (red; < 0.5 mm) within a mica-free, omphacite-rich matrix (green). Opaque areas are rutile. Field of view is 27x46 mm.

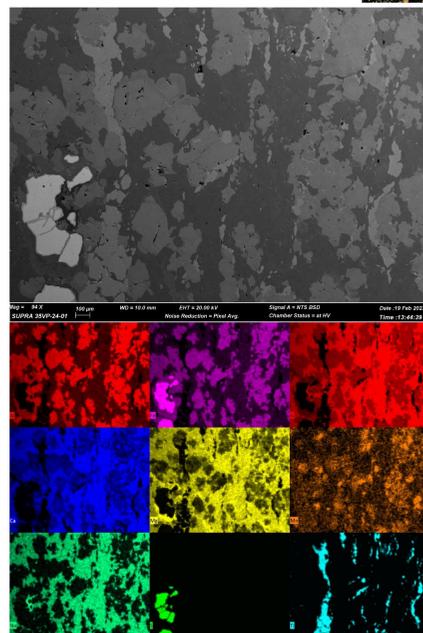
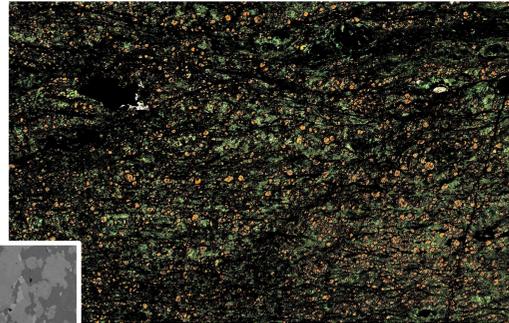


Figure 5. SEM analysis of sample M17-K808D01 showing microtextures and chemical zoning of garnet with backscatter electron (BSE, top) and energy dispersive x-ray spectroscopy (EDS, bottom).

Figure 6. PT diagrams showing optimal PT conditions for sample M17-K808D01 according to Bingo-Antidote. (top row) Score based evaluation showing optimal PT conditions comparing modeled vs. observed mineral assemblage (top left), mineral modes (top center), and total quality (combined score; top right). (bottom row) PT diagrams showing the modal fraction of garnet (bottom left), omphacite (bottom center), and rutile (bottom right) calculated by Theriak-Domino.

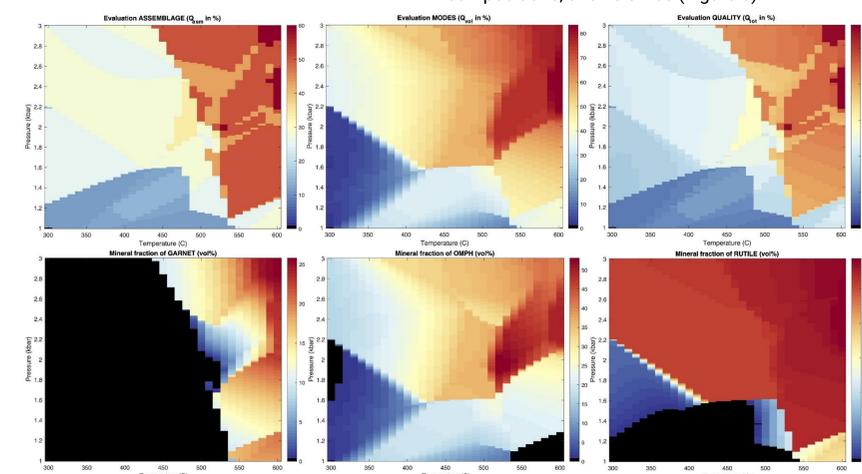


Figure 4. Loading sample M17-K808D01 into the Zeiss Supra SEM at CAMI for micro-textural and chemical analyses.

Estimating Peak PT

Peak metamorphic conditions (PTs) were estimated by modeling metamorphic phase assemblages (assuming thermodynamic equilibrium) with a Gibbs free-energy minimization algorithm (Theriak-Domino; de Capitani & Petrakakis, 2010) within the FeO MgO Al₂O₃ CaO₂ NaO SiO₂ TiO₂ chemical system. We used mineral solution (mixing) models from a modified version of the Berman (1988) thermodynamic database included in XMapTools 4.1 (JUN92). To increase accuracy of the modeled results, an iterative score-based algorithm included in XMapTools 4.1 (Bingo-Antidote; Duesterhoeft & Lanari, 2020) was used to find the optimal PT condition where the modeled vs. observed mineral assemblage match most closely in terms of mineral modes, compositions, and volumes (Figure 6).

Results

Calculations using an iterative score-based approach (Theriak-Domino and Bingo-Antidote) with semi-quantitative SEM data do not compare favorably with PT estimates from the literature that use various phase equilibria modeling techniques with fully-quantitative electron probe microanalyzer (EPMA) data (Figure 7). Only 4% (2/45) of the PT estimates calculated in this work overlap with the range of PT estimates in the literature for the Monviso ophiolite, regardless of the score-based method. The other 96% (43/45) of PT estimates we calculated either fall at higher temperatures (~700 °C vs. 400–600 °C), lower temperatures (~300 °C), or lower pressures (≤ 15 kbar vs. 15–27 kbar; Figure 7).

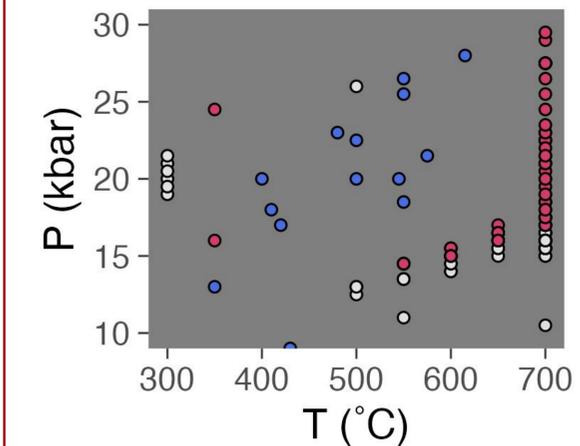


Figure 7. PT diagram comparing peak metamorphic conditions for the Monviso ophiolite. Estimates from the literature (blue points; Agard et al., 2018) were derived from fully-quantitative chemical analyses on EMPA instruments with various phase equilibria modeling techniques. In contrast, estimates from this work (white and red points) were derived from semi-quantitative chemical analysis on SEM instruments with a score based iterative modeling technique (using Theriak-Domino and Bingo-Antidote included in XMapTools 4.1). Qcmp: mineral composition score, Qtot: combined score.

Discussion

Semi-quantitative vs. fully-quantitative approaches

Estimating peak metamorphic PT conditions for rocks is a difficult task that requires careful sample preparation, chemical analyses, assumptions about paragenesis and equilibrium reactions among various mineral phases, and computation with the “right” set of parameters and thermodynamic data. In this work, we attempted to find a quick and cost-effective alternative to calculating PT estimates by collecting semi-quantitative chemical analyses on a well-calibrated SEM instrument. However, our PT estimates do not overlap with other PT estimates derived from more time-consuming and costly methods (e.g. EPMA) applied to similar rocks. We identify a few reasons for this discrepancy:

- Semi-quantitative approach:** Without standardizing EDS detectors on SEM instruments, bulk compositions and compositions of individual phases required to estimate PTs have large uncertainties. These uncertainties propagate through our calculations.
- Non-equilibrium conditions:** Sample M17-K808D01 remained dry and undeformed throughout its PT path (static recrystallization) and its composition may be in a meta-stable (non-equilibrium) state, thus violating fundamental assumptions implicit in our calculations. These uncertainties are difficult to quantify and propagate through our calculations.
- Selection of phase compositions for modeling:** Phase equilibria modeling requires selecting compositions for each phase of the peak metamorphic assemblage (garnet + omphacite + rutile). If we selected compositions from phases that were not in equilibrium, or from earlier generations of zoned minerals, we might inadvertently introduce large errors into our calculations.

Our work demonstrates that these sources of error and uncertainty, if not properly addressed when using quick and cost-effective methods, can lead to spurious results. Thus, the status quo of estimating PTs for metamorphic rocks remains a time-consuming and costly endeavor.

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