WORKING WITH SHEAR ZONES: APPLICATION OF PHASE EQUILIBRIUM MODELLING TO CASE STUDIES FROM THE POLYMETAMORPHIC TERRANE OF CALABRIA (SOUTHERN ITALY)

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INTRODUCTION

Shear zones, one of the most renowned and fascinating geologic structures, represent the exhumed expression of stress accumulation and material transport within the Earth's crust. Among them, ductile shear zones – the topic of this doctorate thesis – are active at metamorphic conditions and despite the low permeability characterising metamorphic rocks, they are usually considered as preferential channels for fluid transport in the continental and sub-continental crust (Etheridge *et al*., 1983). It was since the last three decades, when phase equilibrium modelling with internally consistent thermodynamic software became an invaluable technique for investigation, that petrologists began intensively to study ductile shear zones, for deciphering the pressure and temperature conditions at which they were formed (Keller *et al*., 2004) as well as, only more recently, the chemical processes (*e.g*., fluid-rock interaction) to which they were subjected (Goncalves *et al*., 2012).

The aim of this work was to investigate the mineral assemblage variations within ductile sheared rocks and the feedback relations between devolatilization reactions and ductile shearing. To this purpose the phase equilibrium thermodynamic modelling approach has been applied to three specific case studies dealing with Variscan and Alpine shear zones from the polymetamorphic terrane of Calabria (southern Italy) (*e.g*., Cirrincione *et al*., 2015). The examined shear zones were developed in either dominant extensive or compressive tectonic contexts, and comprise the sub-solidus conditions from blueschist to amphibolite facies. A careful microstructural and petrologic analysis of variations in the mineral assemblage of the investigated sheared rocks has allowed to relate these variations either to fluid-consuming/-releasing reactions in a closed system or to fluid-rock interactions in an open system. At the same time, the fluid-present or -deficient conditions during shearing have been defined, whereas the formation of new syn-kinematic minerals and the preservation of relict porphyroblasts was unravelled through the investigation of the chemical potential gradients in the mylonitic rocks.

CASE STUDIES AND STEP-GOALS

Subject of the first case study were the blueschists of the Diamante-Terranova Unit (Liberi *et al*., 2006; Fedele *et al*., 2018), which are exposed in Catena Costiera (northern Calabria) and are affected by ductile shearing and retrogression. The metamorphic and rheologic evolution of these rocks was reconstructed at first, setting the basis for the subsequent investigation of the chemical potential gradients in the sheared rocks. In the second case study, the linking between the deformation history of mylonitised continental rocks and the progress of devolatilization reactions that trigger reaction softening, was investigated in the mylonitic paragneisses of the Mammola Paragneiss Unit, which are part of the southern Hercynian belt exposed in Calabria (Angì *et al*., 2010) and that crop out in the southern Serre Massif. In the third case study, the length scale of rock re-equilibration and the presence of fluids during under-thrusting of already metamorphosed continental crustal rocks involved in a further orogenic cycle, was focussed on by considering the orthogneisses of the Castagna Unit (*e.g*., Langone *et al*., 2006), that were sampled along a strain gradient of the Curinga-Girifalco Line.

The formation of syn-kinematic minerals within the investigated mylonites, along with the preservation of relic porphyroblasts, were eventually examined and discussed in relation to the set up or flatting of the chemical potential gradients characterising the ductilely sheared rocks.

MATERIALS AND METHODS

A detailed geological mapping was first carried out in key areas where the selected shear zones are exposed, aiming to the best choice of samples for petrologic investigation. Oriented samples were collected from the host rock towards the shear zone, where possible, and cut parallel to the stretching lineation. Backscattered electron (BSE) images were acquired using a LEO EVO-50XVP scanning electron microscope (SEM) housed at the Department of Earth and Geo-environmental Sciences, University of Bari Aldo Moro. Depending on the availability, microanalysis was performed on polished thin sections either using the SEM from the Department of Earth and Geo-environmental Sciences, University of Bari Aldo Moro, or electron microprobes (EMP) from the Department of Earth Sciences, University of Florence (a JEOL JXA-8600 EMP model), and from the Department of Geosciences, University of Padova (a Cameca SX50 EMP model). The bulk rock composition of selected samples was obtained through XRF-analysis on pressed powders, using an AXIOS-Advanced automated Panalytical model housed at the Department of Earth and Geo-environmental Sciences, University of Bari Aldo Moro. Thermodynamic modelling was performed through the software THERMOCALC v.3.45 (Powell & Holland, 1988), using the ds62 dataset and its implementations (Holland & Powell, 2011). The activity composition models used are from Green *et al.* (2016) for metabasite-forming minerals, and from White *et al.* (2014) for metapelite-forming minerals.

RESULTS

The La Guardiola Shear Zone

At La Guardiola Cliff (Catena Costiera, northern Calabria), lenses of medium-coarse grained lawsonite-clinopyroxene blueschists contain zoned clinopyroxene crystals, that show core-rim compositional variation from diopside to omphacite and host primary inclusions of lawsonite and titanite. The medium-coarse grained blueschist lenses are enveloped by fine grained sheared blueschists characterised by a mylonitic to ultramylonitic foliation, with alternating glaucophane- and pumpellyite-rich layers. Thermodynamic modelling of lawsonite-clinopyroxene blueschists in the NCKFMASHTO system revealed peak metamorphic conditions of 2.0-2.1 GPa and 475-490 °C for the Alpine subduction in Calabria (Fig. 1a). The subsequent post-peak metamorphic evolution proceeded along a decompression and cooling path up to ~1.1 GPa and ~380 °C (Fig. 1a). The final exhumation stages are recorded in the sheared blueschists where the mylonitic foliation developed at ~0.7 GPa and 290-315 °C (Fig. 1a).

The Levadio Shear Zone

The geometry of the tectonic contact between the upper crustal rocks of the Stilo-Pazzano Phyllite Unit and the deeper crustal rocks of the Mammola Paragneiss Unit was firstly defined after a 1:10,000 scale structural-geological mapping.

The mylonitic paragneisses of the Mammola Paragneiss Unit are characterised by a well-defined main mylonitic foliation, consisting of alternating quartzo-feldspathic and mica-rich layers that anastomose pre-kinematic garnet porphyroblasts. On the basis of the zoning profiles of garnet porphyroblasts and their mineral inclusions, primarily barroisite and epidote, the prograde *P-T-d* trajectory was obtained by calculating phase equilibrium diagrams in the MnNCKFMASHTO model system (Fig. 1b).

The *P-T* modelling shows that peak metamorphic conditions of ~0.9 GPa and 585 °C were reached during a D_{n-1} under-thrusting event, which was followed by exhumation during the D_n mylonitic event, and contact metamorphism during D_{n+1} and D_{n+2} folding events (Fig. 1b). The exhumation trajectory was modelled down to 0.3 GPa with temperatures of 440-460 °C (Fig. 1b), under fluid-deficient conditions, as well as the final late Carboniferous contact metamorphism up to T_{max} of 680-720 °C (Fig. 1b).

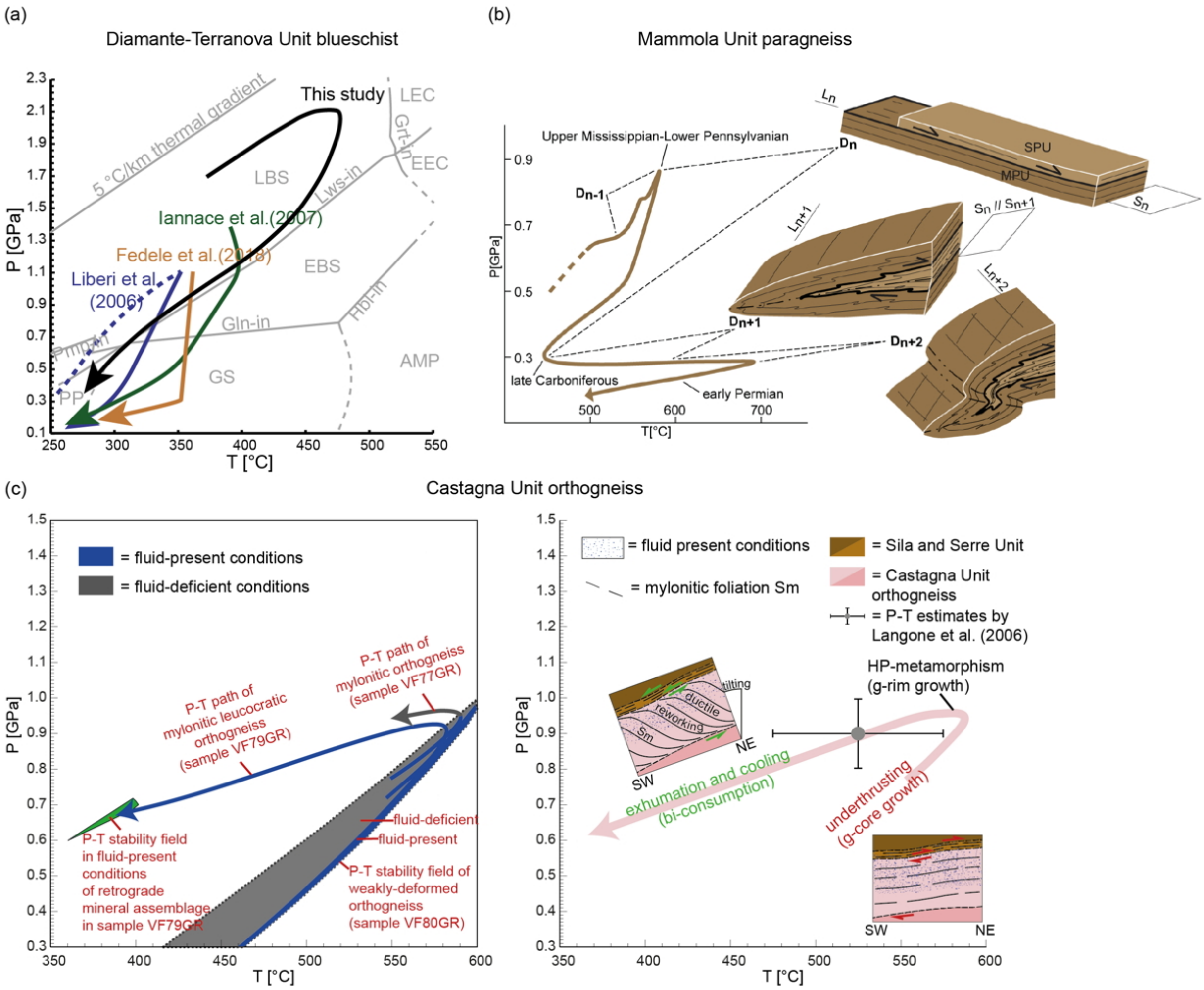

Fig. 1 - (a) *P-T* path for the lawsonite-clinopyroxene blueschist obtained in this study compared with the P-T paths previously published for the Diamante-Terranova Unit blueschists (Liberi *et al*., 2006; Fedele *et al*., 2018) and that for the lowermost part of the Lungro-Verbicaro Unit (Iannace *et al*., 2007). (b) Reconstructed *P-T-d* path for the Mammola Paragneiss Unit (dashed and solid brown line), with sketches of the deformational evolution during the D_n, D_{n+1} and D_{n+2} events (MPU and SPU refer to Mammola Paragneiss and Stilo-Pazzano Phyllite units, respectively). (c) Left side: *P-T* diagram highlighting the overlap of the *P-T-fluid* paths of the mylonitic orthogneisses onto the stability field of the mineral assemblage of the weakly-deformed orthogneiss; fluid-present conditions are promoted in mylonitic samples (VF77GR and VF79GR) closer to the tectonic contact with the Sila and Serre Unit. Right side: *P-T* from this study for the Castagna Unit's orthogneisses during Alpine reworking; the *P-T* estimates (with uncertainties) by Langone *et al.* (2006) for the orthogneisses of the Castagna Unit are also plotted; the Alpine evolution of the orthogneisses is also schematically represented by two sketches for the Eocene underthrusting and the late Oligocene extensional re-activation accompanied by ductile reworking of the CGL; sites of fluid-present conditions are highlighted.

The Curinga-Girifalco Line

Ductile kinematic data were collected from outcrops in the north-western and south-eastern branches of the Curinga-Girifalco Line and suggest coherent top-to-the-NNE kinematics, largely overprinted by top-to-the-SSW kinematics. A detailed microstructural study of the orthogneisses, sampled along a progressively increasing ductile deformation gradient, revealed variation in the mineral assemblage between the weakly deformed orthogneisses and those in the shear zone, the former being garnet-free and biotite-rich while the latter being garnet-bearing, characterised by progressive decrease of the biotite modes. Phase diagram calculations in the MnNCKFMASHTO system indicate that both weakly deformed and mylonitic orthogneiss share the same peak metamorphic conditions of ~0.9-1.0 GPa and ~560-590 °C, but with different degrees of fluid saturation (Fig. 1c). Phase diagrams show that the new equilibrium mineral assemblage was stabilized in the mylonitic orthogneisses along a fluid-conservative prograde path, where devolatilization and fluid-consuming reactions occurred simultaneously. After metamorphic peak, fluid-present conditions were restricted to the mylonitic orthogneisses close to the tectonic contact, which record cooling and exhumation to 0.6-0.7 GPa and 360-400 °C, and show an overall anticlockwise *P-T* path (Fig. 1c).

DISCUSSION AND CONCLUSIONS

Regional implications

Phase equilibrium modelling results for the lawsonite-clinopyroxene blueschists of the Diamante-Terranova Unit evidenced that their *P-T* evolution mostly occurred in the stability field of lawsonite (Fig. 1a), sustained by H_2O-saturated conditions during the exhumation path. Moreover, the retrieved *P-T* evolution, evidences that the blueschists underwent peak metamorphic conditions higher than previously thought (Liberi *et al.*, 2006; Fedele *et al.*, 2018; Fig. 1a), reaching a maximum depth of ~70 km under a very cold geothermal gradient (~6.6 °C/km) during the Eocene subduction of the Ligurian Tethys oceanic crust in Calabria.

As regards the reconstructed *P-T* evolution of the mylonitic paragneisses of the Mammola Paragneiss Unit, the prograde path shows clear evidence for thermal buffering during garnet growth at the expense of chlorite, with a heating-dominated stage after chlorite breakdown (Fig. 1b). A subsequent net steepening of the P/T trajectory towards the pressure peak (Fig. 1b) suggests a rheological change associated with epidote breakdown (*i.e.*, reaction softening). On the basis of the barroisite inclusions within garnet porphyroblasts as well as the "hairpin" shape of the reconstructed *P-T-d* path (before contact metamorphism) (Fig. 1b), it can be inferred that the unusual low *T*/*P* gradient of this unit (Angì *et al.*, 2010), records its involvement in the Palaeotethys-Gondwana subduction beneath Laurussia during D_{n-1} under-thrusting (Fig. 1b).

Results from phase equilibrium diagrams calculated for the progressively sampled, ductilely sheared orthogneisses along the Curing-Girifalco Line indicate that the progressive replacement of relict minerals by new Alpine minerals in the shear zone was related to the presence of fluids during deformation (Fig. 1c).

Fluids were almost consumed during re-equilibration in the sheared orthogneisses up to the metamorphic peak conditions of ~0.9-1.0 GPa and ~560-590 °C while, only the mylonitic orthogneisses close to the tectonic contact record cooling and exhumation to 0.6-0.7 GPa and 360-400 °C (Fig. 1c).

Integrating the thermodynamic results with the collected ductile kinematic data, it is highlighted that the Castagna Unit was brought to lower crustal depths during the Alpine orogeny before re-activation of the Curinga-Girifalco thrust structure under an extensional tectonic regime (Fig. 1c). Moreover, the overall anticlockwise shape of the *P-T* path, characterised by isobaric cooling at HP-conditions (Fig. 1c), suggests the involvement of the Castagna Unit into the Eocene subduction process in Calabria, with the CGL located close to the subducting Ligurian Tethys' oceanic crust.

Chemical potentials as key to understand syn-kinematic mineral assemblages and rocks' fabric

Once fluid-present/-deficient conditions have been defined for the main shearing event in each ductile shear zone, the chemical potential gradients of the fluid phase and that of some major elements within the sheared rocks has eventually permitted to constrain the development of the rock's fabric and mineral assemblages.

Results show that the investigated rocks were not affected by fluid infiltration during ductile shearing, but consumed their OH-bearing minerals, with the fluid released that favoured the formation of new, syn-kinematic minerals within sites where the fluid saturation surface was approached.

In the sheared blueschists of the Diamante-Terranova Unit, syn-kinematic chlorite, pumpellyite, albite and quartz occurred in narrow zones, due to the onset of chemical potential gradients, especially in μH_2O, during mylonitic event (Fig. 2a). In particular, the pumpellyite-rich layers developed in response to locally higher μH_2O

than in the glaucophane-rich layers (Fig. 2a), with the formation of the reaction products that allowed sustaining ductile shearing (Holyoke & Tullis, 2006).

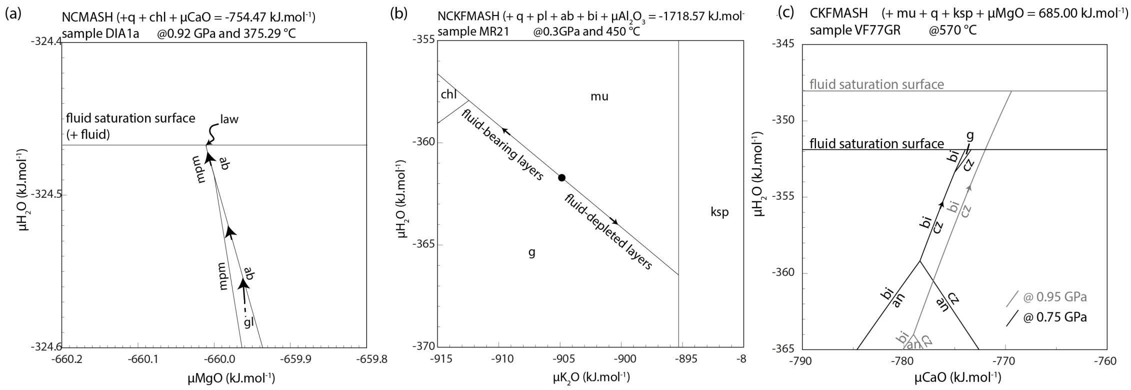

Fig. 2 - (a) Chemical potential relationships in the NCMASH model system, calculated at 0.92 GPa and 375.29 °C; phase relations are shown in the μH_2O-μMgO space. (b) Chemical potential relationships in the NCKFMASH model system calculated at 0.3 GPa and 450 °C; phase relations are shown in the μH_2O-μK_2O space. (c) Chemical potential relationships in the CKFMASH model system calculated at 570 °C and 0.75 GPa (black lines) and 0.95 GPa (grey lines); phase relations are shown in the μH_2O-μCaO space. The diffusion paths in (a), (b) and (c) are highlighted with black and grey arrows.

Another aspect of the set-up of μH_2O gradients in the rock during deformation regards the metastable survival of relict reactant minerals in sites where μH_2O is lower, while product minerals form where μH_2O is higher. This can be appreciated in the Mammola Unit mylonitic paragneiss, where formation of syn-kinematic chlorite required fluid, in apparent contrast with the presence of pre-kinematic garnet porphyroblasts that, instead, survived metastablely. Even in this case, the fluid was internally provided during exhumation and shearing by the breakdown of OH-bearing minerals, after the paragneiss experienced peak metamorphic conditions. Therefore, the fluid released was channelled during shearing, favouring the onset of gradients in μH_2O and chlorite stabilisation within opportune sites where nutrients for its growth were available (Fig. 2b).

Fluid storage during ductile shearing was also revealed in the mylonitic orthogneiss of the Castagna Unit, with the fluid provided internally by the breakdown of biotite and clinozoisite. As shown in the μH_2O-μCaO grid of Fig. 2c, garnet (the reaction product) grew in sites where μH_2O was high. The μH_2O-μCaO diagram of Fig. 2c shows that garnet nucleation in this rock was enhanced when the fluid-saturation surface was approached. On the other hand, garnet was then preserved in this rock during exhumation, favoured by overall fluid-deficient conditions during the re-activation of the Curinga-Girifalco Line (Fig. 1c).

The results obtained by the analysis of chemical potentials for the mylonitic rocks examined, highlight how syn-kinematic minerals form as product of mineral reactions even under overall fluid-deficient conditions, within sites where the μH_2O is higher than in the surrounding (Fig. 2). Therefore, this suggests that strain plays only a second-order effect on mineral equilibria, while the system primarily adjusts with respect to variations of *P*, *T* and μ. In addition, nucleation of new, syn-kinematic minerals allows removal of stress in the deforming rock according to the experimental results by Holyoke & Tullis (2006), with the rock that can further accommodate deformation, also facilitated by the presence of fluid released by devolatilization reactions.

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