POST-METAMORPHIC HYDROTHERMALISM IN THE VOLTRI GROUP: STRUCTURAL-PETROLOGICAL-GEOCHEMICAL APPROACH

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INTRODUCTION

The Voltri Group, one of the ophiolitic massifs of the Western Alps, is located at the eastern edge of the Ligurian Alps. The Oligocene to Present Alpine history mainly developed under brittle-ductile to brittle conditions and can be linked to polyphasic upper crustal deformation (Spagnolo *et al.*, 2007). Hydrothermal, carbon-rich fluids sustained the late-metamorphic deformation stages within the Ligurian Alps metaphiolites of the Voltri Group (Piana *et al.*, 2006), leading locally to gold enrichment.

Compositions of hydrothermal fluids are critical parameters controlling the nature of hydrothermal ore, and they reflect the process that lead to the generation of the fluids and to their evolution along the fluid path between source and deposits during active tectonism (Ridley & Diamond, 2000). Hydrothermal/metasomatic alteration products, *i.e.* metasomatites, are naturally related to the mineralogy of the host rocks and to the fluid nature, in particular in ultrama c terrains results in signi cant amounts and a wide spectrum of metasomatites like listvenites, which are documented by several authors (*e.g.* Buisson & Leblanc, 1985; Auclair *et al.*, 1993; Halls & Zaho, 1995; Uçurum, 2000; Akbulut *et al.*, 2006; Tsikouras *et al.*, 2006).

Listvenites form by intermediate- to low-temperature hydrothermal alteration of ma c, ultrama c rocks and are commonly located within or near major fault and shear zones (Halls & Zhao, 1995). With the in ux of K-bearing hydrothermal fluids in the tectonic fractures, primary ferromagnesian silicates of host rocks are replaced by the Mg-Fe (Ca) carbonates, silica is released to form quartz; and fuchsite forms (Akbulut *et al.*, 2006). Listvenite are often associated to ore minerals enrichments, disseminated pyrite/NiFeAs-sulphides and gold.

Talcitization and listvenitization are recognized as playing a major role in the hydrothermal alteration of ultrabasic rocks. Some authors (Ploshko, 1965; Halls & Zaho, 1995) asses the association of the two alteration paragenesis and their independency. Even if they are spatially associated, talcitization occurs at higher temperature than listvenitization, and is characterized by no influx of potassium, with the sequence serpentine-talc-carbonate rocks, chlorite-quartz-carbonate rocks and chlorite-carbonate rocks. Otherwise Buisson & Leblanc (1985) and, later, Auclair *et al.* (1993), support the consequentiality of the two processes, due to small variations in both temperature and oxidation conditions; they also support the gradual transition from talc-carbonate to listvenites and to a final stage of silicification.

This study deals with the metasomatic alteration products within the serpentinite-matrix of metaultramafites from the Voltri Group by hydrothermal carbonic fluids giving origin, during shearing events, to the listvenite series and to talc-carbonate rocks. The area was selected because of its particular location, at the junction between Alps and Apennines, considered a key area to investigate late orogenic, post-metamorphic Alpine events. Aims of this study were to investigate the structural, mineralogical and geochemical characteristics of alteration assemblages in the metasomatic rocks and the related mineralization. The combination of fluid inclusions, petrological and geochemical analysis may contribute to the genetic problem of listvenitic series rocks. The characterization of the fluid, the petrological constraint on the observed paragenesis were used as input data in the geochemical modeling in order to reproduce, in the most realistic way, the natural case and to point out the relationships between talcitization, listvenitization and simple carbonatization.

DISCUSSION

Mode of occurrence

The field data indicate the occurrence of the hydrothermal veins and metasomatites as a late to post-metamorphic alpine event. The coexistence of both ductile-brittle and brittle structures associated with metasomatic alteration, let suppose a complex post-metamorphic history for this sector of the Ligurian Alps. Tectonic activity creates fractures, which will provide pathways for hydrothermal fluid input, channelling fluids in structures. Therefore, the tectonic activity must be the most effective factor on the alteration process. It is common believe that the hydrothermal events were, small, short-lived episode in the tectonic history of the area.

In accordance to Spagnolo *et al.* (2007), the Lavagnina Lakes area (Fig. 1) suffered three main tectonic events. Two of them were accompanied by active hydrothermalism. In a transpressive regime, two main stages of shear occurred. The first stage is represented by the low-angle shear planes (SZ1), associated with the D_3 kink folds (*senso* Capponi & Crispini, 2002), with WNW-ESE trending. SZ1 is folded by open, large wavelength folds classified as the D_4 folding event in the Voltri Group. This is associated with two main metasomatic rocks, type I and II. Type I, are carbonatic veins (magnesite + Fe-dolomite), with talc + chlorite + carbonate alteration (Alt_1) and Zn-Fe-Cu-Pb sulphide mineralization.

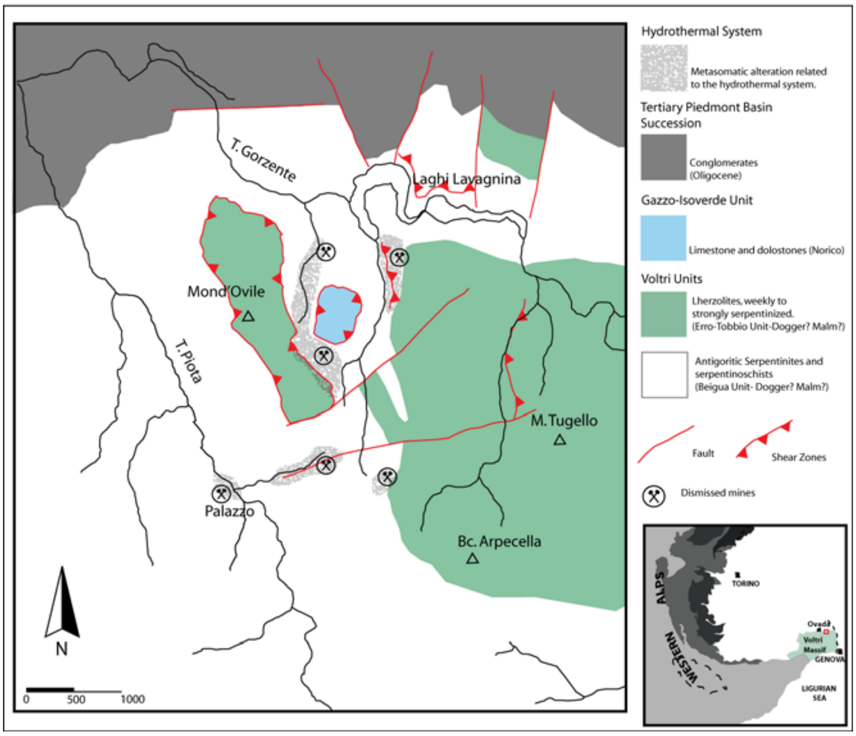

Fig. 1 - Overview of the lithological and structural distribution in the study area.

Type II are carbonate-bearing and quartz-bearing veins, with quartz-carbonate-muscovite-chlorite (listvenitic assemblage) alteration assemblage (Alt_2), and gold, Ni-As-Sb-Co-Fe sulphide mineralization. The area suffered a second event of shear SZ2 with a more brittle behaviour, with mainly NS direction and clearly crosscut the SZ1. This second shearing event it is still related to hydrothermal activity, with carbonate-bearing (magnesite, dolomite and calcite) and chalcedony bearing veins and moderate carbonatization of the host-rock.

The last stage corresponds to a N-S strike-slip to normal, with minor Riedel shear planes. This last event is rarely accompanied by hydrothermal activity, with calcitic veinlets along the secondary planes.

The Adopted approach

The investigated area presented a particular situation in which mostly of the samples lack the fluid inclusion record; almost no tractable inclusions could be found in the gold-bearing veins (Type II and III). Therefore, our strategy has been to sample the gold-free, low-strain veins of magnesite + ferroan dolomite + sulphides (Type I), associated to talc-bearing alteration, where primary and secondary assemblages have been recognized. The alternative approach for going beyond the limit of samples is to obtain all the possible fluid information from one vein type, with its peculiar associated alteration and extrapolate a possible geochemical model for the hydrothermal system. The further constrains- that we have utilized were the two main alteration assemblages treated with petrological grids (P-T, T-X-CO_2, fO_2-T and fO_2-fS_2). This approach of computing equilibria for the closest approximation of our chemical system and compare predicted and observed mineral assemblages, is called forward modeling.

Fluid origin

Some characteristics of the post-metamorphic quartz-gold deposits are remarkably uniform, not relied to age or location, as it has been argued in earlier works, that the chemistry of lode gold deposits is distinct form the other deposits type, and that the hydrothermal fluid at all deposits of this class has a composition within narrow limits (Ridley and Diamond, 2000). The uniformity of fluid composition through time and setting implies that there are one or more critical steps in the generation of the hydrothermal fluid.

In the present study the observed fluid inclusions properties are very similar to those observed in orogenic lode-type gold deposits elsewhere in the Western Alps (Diamond, 1990; Lattanzi, 1990) and worldwide (Ridley & Diamond, 2000), although the fluid densities are somewhat lower than in most deposits (only L+V are stable in our inclusions at room temperature). At room temperature the inclusions contain a weakly saline (7-9%) aqueous liquid and a CO_2-CH_4-N_2 vapour bubble. Most assemblages contain ~17 vol.% vapour. In all assemblages the constancy of the volume fractions of vapour indicates homogeneous entrapment. Microthermometry shows melting of ice T_m(ice) within a range of –3 to –5.5°C; and clathrate dissociation T_m(cla) of 5.5-6.5°C. Homogenisation temperatures T_h (LV $\rightarrow$ L) are between 270 and 300°C. The gas compositions determined by Raman spectroscopy show only slight variations between early mineral growth stages and later ones; pointing out to the absence of N_2 in the early stage.

The Laser ablation ICP-MS analyses on fluid inclusions, revealed that Na and minor K are the main salt components, and also detected a significant amount of Li, B, Rb and Ba. Li, and above all B have significant concentrations. Boron loss, during prograde metamorphism Scambelluri & Phillipot (2004) led to the hypothesis that temperature reached during hydrothermal fluid-rock interaction can led to B depletion in serpentinite and relative enrichment in the fluid. The boron in particular has very high concentration, which even the fluid-rock interaction with a host-rock, like serpentine, considered a source of boron, cannot provide such a quantity of it. It is reasonable to suppose that the fluid was originally enriched in this element, which can derive from other sources, like metasediments. Between the affine-sulphur elements, Cu, and in particular Zn have a slightly higher concentration. Zn is also present in meaningful quantity in the host-mineral, prevalently in magnesite. This difference in concentration is probably caused by the more pervasive presence of sphalerite in the hydrothermal veins. Ba and Rb have noteworthy concentration, even if very low, with a probable connection to the potassium concentration, as it is highlight by several works, phengite is the principal host of large-ion lithophile elements like Ba, K and Rb, which during dehydration at HP and T during subduction process releases K-rich H_2O-bearing fluids with LILE elements enrichment (Catlos & Soresen, 2003). The rapport between Rb/K and Ba/K shows a quite uniform distribution between Fe-dolomite and magnesite, hypothesizing a homogeneous source from the fluid composition.

Listvenites forms when fluids containing CO_2 and K, together with elements such Ba, Au, As, Sb bans S permeate and react with the ultramafic rock. The presence of not negligible concentration of KCl excludes the source of the fluid from the ultramafic rocks. Otherwise the presence of CO_2 also is a signal of the provenance of the fluid from deeper source. The fluid compositions are compatible with the metamorphic fluids that were generated during Alpine metamorphism of Mesozoic calcschists (Pettke *et al.*, 2000).

Genesis of the alteration and ore minerals occurrence

The reactions that the best represent the alteration assemblages associated to the veins types were modelled in petrological grids. The reactions were modelled on an enlarged system, which comprehends the principal alterations, the talc-bearing and the listvenitic ones. The used constrains were the XCO$_2$ and the isochoric path, both data coming from the fluid inclusions study. The petrological approach stabilized three main reactions, considering the appropriate solid solutions for antigorite and carbonates: antigorite = talc + magnesite + dolomite; talc = quartz + magnesite + dolomite; phlogopite + clinochlore = muscovite + quartz + magnesite + dolomite. The modeling predicts the talc stability until 320°C and the Ms + Qtz + Cb (Alt_2) below ~ 320°C (Fig. 2). The combination of fO$_2$-T grids, and the locus of oxygen fugacity calculated for fluid inclusions, narrows the stability field of pyrite + magnesite–siderite, to a value of oxygen fugacity between -31 / -35 bar (Fig. 3). This information

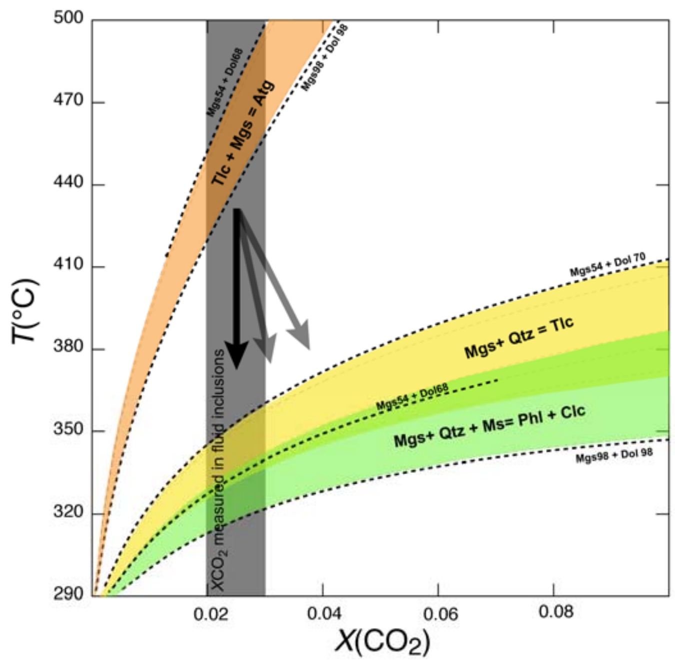

Fig. 2 - *T-P-X*(CO$_2$) projection. Coloured areas outline the location of reactions as a function of magnesite compositional range. The grey bar corresponds to calculated X(CO$_2$). The arrows point out the possible trajectories for the fluid path.

on fO_2 and the composition of the carbonate stable with the pyrite, was used for assign an approximate value to the sulphur fugacity to -8 / -12 bar.

On the basis of the collected data was set a geochemical model with a well-constrained hypothetical incoming fluid for the alteration associated to type I veins. The simulation results in a realistic reproduction of the observed alteration, compatible with a short hydrothermal pulsation, not reaching a steady state. The Alt_1 assemblage is stable until 300°C, in well accordance with the petrologic data (Fig. 4a). The Alt_2 was attained at 250°C. So it is possible to have two different assemblages from the same input fluid, simply lowering the temperature (Fig. 4b).

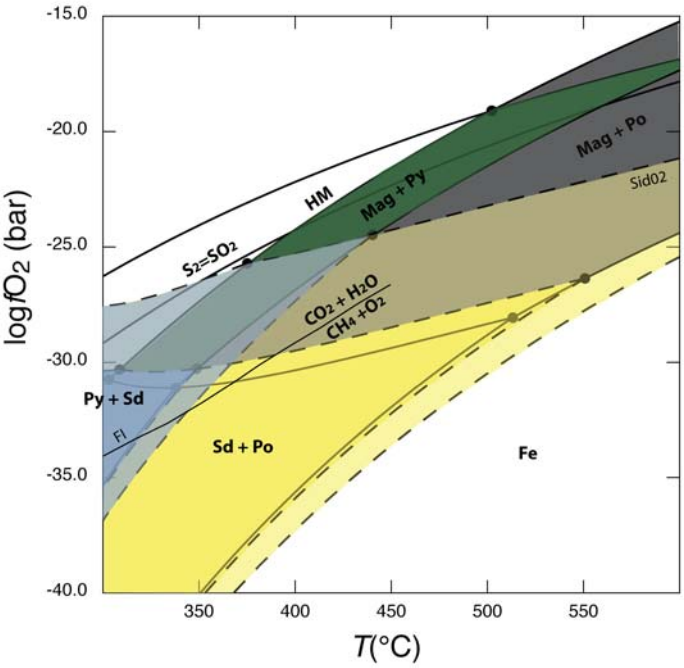

Fig. 3 - fO_2-T diagrams calculated along a geothermal gradient.

The model emphasizes a slight variation also in *p*H, which is slightly more acid in the second case. So, T and *p*H changes in these conditions create temporal and/or spatial phase differentiations. Si solubility increases in high *p*H and high temperature environments, so the fluid input that caused the formation of silica (Alt_2) must have had a lower *p*H and temperature during interaction with the wall

a b

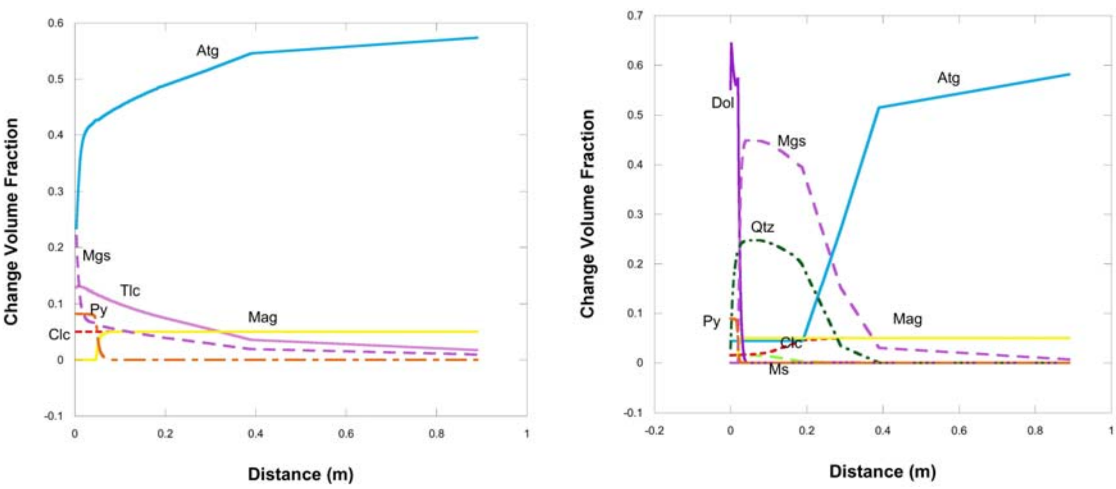

Fig. 4 - Profile of mineral volumes changes over a time interval of 60 years for alteration 1 (a) and 2 (b).

rock. On the contrary, absence of silica indicates a higher *p*H and moderate to high temperature fluid (Uçurum, 2000), which holds the silica in solution and generates carbonate precipitation. The final stage of alteration (Alt_3) is probably due to a further decreasing in temperature results in an increase in the Ca solubility. The depletion in Mg content in the environment due to previous dolomite crystallization and the limited Ca-solubility create small amounts of $CaCO_3$ in veins together with colloform silica.

The sulphide compositions are variable; with Fe-Cu-Pb-Zn in type I and Fe-Co-Ni-As-Sb-(Pb-Cu) in type II. The oxygen and sulphur fugacity (fO_2 and fS_2) are considered as dominant factors in formation of sulphide phases during serpentinization and following metasomatism (*e.g.* Frost, 1985; Auclair *et al.*, 1993). The sulphides that are dissolved during the carbonatization stage would reprecipitate in areas of higher fO_2 and fS_2 (Frost, 1985). Leblanc and Fisher (1990) inferred that the ultramafic rocks maybe source of Co and Au, and also Ni (Auclair *et al.*, 1993). Gold is associated with arsenide-cobalt mineralization and could be interpreted as derived from the ultramafic lithologies as a sulphide complex in the manner explained by Buisson & LeBlanc (1985), tight to the magnetite-pyrite alteration.

CONCLUSIONS

The present study, together with very recent structural study (Spagnolo *et al.*, 2007), defines the late to post-metamorphic structural overview of the area of the Lavagnina Lakes in relationship to the hydrothermal manifestation and the related mineralizations. The coexistence of brittle-ductile and brittle structures associated with the hydrothermal activity suggests the presence of a long-lived system or the action of multiple fluid pulsations in time. The differences in rheological behaviour and in the alteration paragenesis of the veins, suggest the presence of episodic fluid-rock interaction, at different crustal levels and at different *PT* conditions.

The forward modeling predict two main alteration assemblages, which correspond to the described Alt_1 and Alt_2, from a constant composition fluid reacting with an idealized serpentinite, varying in a temperature interval of 300-250°C. The talc bearing alteration is considered as the deeper part of the system, while the listvenitization has taken place in a higher or cooler crustal level. The composite current structural setting probably camouflages the original position of the structural elements composing the hydrothermal system, making difficult an interpretation purely based on geometrical evidences (Fig. 5).

The fluid compositions are compatible with the

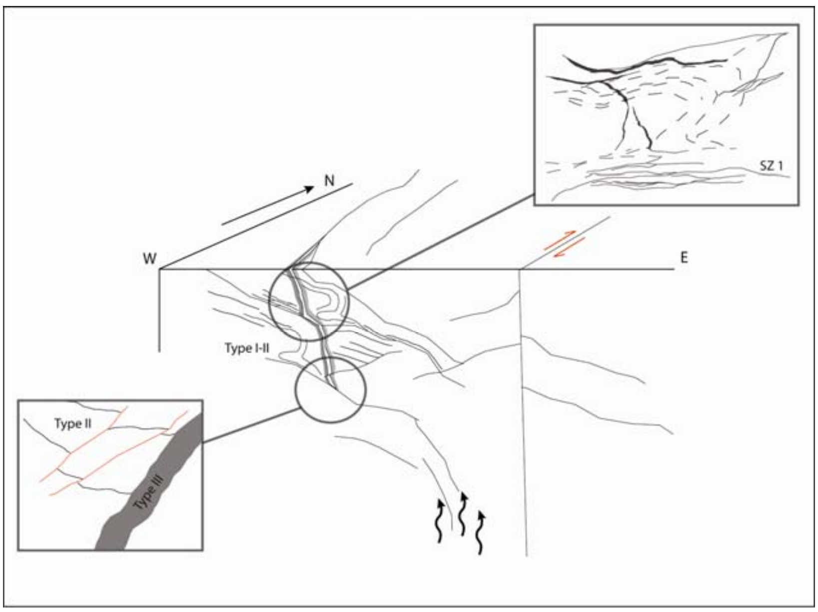

Fig. 5 - Schematic interpretative overview of the study area.

metamorphic fluids that were generated during Alpine metamorphism of Mesozoic calcschists napped deeper in the ophiolitic sequence. Another possibility is the presence of the Liguridi Nappe, which on the basis of the seismic profiles along the southern part of the Piemontese Terziary Basin (PTB) have their extremities that fall under the Voltri ophiolic Massif and the Sestri Voltaggio Zone.

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