

Genesis of carbonate-rich veins in the serpentinites at the Calabria-Lucania boundary (southern Apennines)

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ABSTRACT

In the northern sector of the Pollino massif (southern Apennines, Italy) well-exposed lens-shaped bodies of serpentinites and sediments of the Frido Unit belonging to the Liguride Complex crop-out. Most serpentinite rocks are cross-cut by carbonate and quartz-carbonate veins with different thickness. This study focuses on petrographic, mineralogical, geochemical, and isotopic analysis of the carbonate veins embedded in serpentinite rocks, collected at the Fosso Arcangelo site and at the Pietrapica quarry (Calabria-Lucanian boundary). The paragenesis of the carbonate veins from the Fosso Arcangelo site is dominantly made by calcite and aragonite with minor amount of rhodochrosite. In quartz-carbonate veins from Pietrapica quarry, dolomite, Mg-calcite, quartz, with minor ankerite were observed. The $\delta^{13}\text{C}_{\text{V-PDB}}$ isotope ratios of carbonates in the carbonate veins are in the range from +2.16‰ to -3.66‰ and corresponding $\delta^{18}\text{O}_{\text{V-SMOW}}$ values are between +15.02‰ and +21.53‰. The $\delta^{13}\text{C}_{\text{V-PDB}}$ values of carbonates in quartz-carbonate veins are in the range from -3.60‰ to -1.78‰ and the corresponding $\delta^{18}\text{O}_{\text{V-SMOW}}$ average value is around +21.3‰. The results suggest that the carbonate at both site occurred under the same environmental conditions from crustal-derived and low-moderate temperatures hydrothermal fluids having different chemical composition.

KEY WORDS: Carbonate and quartz-carbonate veins, serpentinite rocks, southern Apennines.

INTRODUCTION

Serpentinized peridotites are recognized as an important component of oceanic basement. Mantle peridotites are commonly exposed on the seafloor at slow and ultraslow spreading mid-ocean ridges in areas of tectonic extension, where oceanic core complexes are exposed by gabbroic intrusives and upper mantle along detachment faults (Cannat et al., 2010). In crust formed at intermediate and fast spreading rates peridotite is exposed locally at propagating rifts and in fracture zones (Hekinian et al., 1996). Peridotites are readily serpentinized over a wide range of conditions, and serpentinization is important as a sink for water, carbon, sulfur, chlorine, boron, arsenic, and nitrogen (Halama et al., 2012). Detachment faults, associated faults and shear zones can focus fluid flow,

leading to serpentinization at high temperatures at various depths, down to the base of the crust (McCaig & Harris, 2012). Gabbro intrusions provide heat that can drive high-temperature ultramafic-hosted hydrothermal systems that result in black-smoker type vents and sulfide deposits atop serpentinite on the seafloor, such as the Rainbow sites on the mid-Atlantic Ridge (McCaig & Harris, 2012).

Lower-temperature serpentinization can occur as seawater fluids circulate through fractures and faults near the seafloor, driven by the general cooling of the lithosphere and exothermic serpentinization reactions (Schwarzenbach et al., 2012). Serpentinization associated with subduction zones is also important for cycling of volatiles and fluid mobile elements. Serpentinization of suboceanic mantle can occur outboard of subduction zones, where flexure of the lithosphere allows faulting and penetration of fluids to hydrate the mantle (Ranero & Sallares, 2004). In addition, the mantle wedge in subduction zones is serpentinized by fluids released from the slab, and can be dragged downward to release fluids and various elements at greater depths (Deschamps et al., 2010). Serpentinization and other hydration reactions in the subduction channel itself also form phases that can carry water and volatiles deep into subduction zones (Padrón-Navarta et al., 2010).

Serpentine is stable to high pressure and temperature, and can carry significant amounts of water to depths of up to 200 km in subduction zones, where dehydration releases volatiles that can trigger melting in the mantle wedge. Seafloor serpentinites are enriched in carbon and sulfur compared to mantle values, and depending on subduction pathways, serpentinite and its dehydration products can release these volatiles to the mantle wedge or recycle them into the mantle (Alt et al., 2012).

Alteration of peridotite by circulation of fluids has profound consequences for rheology of the oceanic lithosphere, geochemical budgets of the ocean and the atmosphere and microbial processes.

Carbonate veins are a common low- to moderate temperature feature in all lithology of altered ocean

lithosphere. This mechanism of carbonate formation is affected by the composition and physico-chemical properties of the carbonate-originating fluid and may thus constrain the “geological” conditions promoting the carbonate genesis under a complex tectonic scenario (e.g. Eickmann et al., 2009) and, additionally, may represent an analogue study for a cost-efficient carbon disposal strategy (e.g. Boschi et al., 2017).

In this paper, we present a comprehensive petrographic, mineralogical, geochemical, isotopic and fluid inclusions study of carbonate and quartz-carbonate veins of the serpentinites from Pollino Massif. Stable isotope compositions of carbon were analysed for the first time to investigate the speciation and sources of carbon in these systems. Additionally, oxygen isotope measurements have been used to estimate temperatures of carbon precipitation whereas carbon isotope date are instead used to estimate the source of carbonate fluid.

GEOLOGICAL SETTING

The Pollino area, located in the southern Apennines at the Calabria-Lucania border zone (Fig. 1), consists of tectonically juxtaposed thrust belts derived from the deformation of the African passive margin (Knott, 1994). The deformation occurred between the Oligocene and the Pleistocene, and involved the Ligurian ocean ophiolitic crust and its sedimentary cover (Knott, 1994; Monaco & Tortorici, 1995). In this area, the Liguride Complex (Knott, 1994), also defined as Liguride Units (Bonardi et al., 1988) is well exposed and is located in the highest position in the tectonics edifice of the southern Apennines. Liguride Complex derived from the NW subduction of Tethyan ocean-continent transition zone and was divided into different tectonic units, where fragments of Jurassic oceanic crust (Knott 1994), associated with slices of continental crust rocks, are preserved (Spadea, 1982; Knott, 1994; Monaco & Tortorici 1995; Laurita et al., 2014). These terrains consist of a Mesozoic to Cenozoic flysch and a series of ophiolitic nappes, widely exposed along the whole Apennine Chain and in Calabria (Knott, 1994). The Liguride Complex has been subdivided into two units, the metamorphosed Frido Unit and the non-metamorphic Calabro-Lucano Unit (Monaco & Tortorici, 1995) or north Calabria Unit (Bonardi et al., 1988). The Frido Unit formed the uppermost thrust sheet, and tectonically overlies the North Calabrian Units, which in turn is split in a number of thrust sheets (Monaco & Tortorici, 1995). Frido Unit consists of a sedimentary sequence (phyllites, meta-arenites, quartzites and isolated bodies of meta-limestones or calcschists) (Rizzo et al., 2016) with blocks of oceanic and continental types of rocks (Knott, 1994). Oceanic crust rocks (ophiolites) (Rizzo et al., 2017) mainly are represented by tectonized serpentinites (Dichicco et al., 2015, 2017; Bloise et al., 2017), containing dismembered metadolerite dykes and metabasalts (Sansone et al. 2011, 2012a, b; Sansone & Rizzo, 2012). These terrains are not structurally coherent, and their distribution indicates that the Frido Unit may be described as a tectonic *mélange* (Spadea, 1982), in which all kinds of rocks have been deeply accreted.

The exhumation age of the underplated rocks investigated by fission track method allows to obtain

information on the thermobaric evolution of the Liguride Complex. The exhumation ages carried out on the continental crust rocks is about 65-56 Ma corresponding to the Paleocene age (Laurita, 2009).

Continental crust rocks mainly consist of weathered granofels, garnet gneisses, garnet-biotite gneisses, leucocratic biotite gneisses and lenticular bodies of amphibolites (Spadea, 1982; Laurita et al., 2014). The systematic association between continental crust rocks and serpentinites indicate that the contact between these two lithologies probably originated during Pre-Alpine evolution. Subsequently, the contact has been reworked during the Alpine events, as shown by the intense brittle-ductile overprint (Spadea, 1982).

The deformation history of the Frido Unit includes different stages (Monaco & Tortorici, 1995). The oldest structures formed during a first HP/LT event, with a penetrative adaptation defined by a cleavage of the phyllites and a foliation in the calcschists and presence of carpholite fibres (Vitale et al., 2013) (Fig. 1). During this event, a planar anisotropy (defined as S1) was developed linked to transposition processes (Knott, 1994) whereas boudinated lens and isoclinal folds with the sides parallel to (S1) further formed. This deformation phase is characterized by a prevalent immersion of the surfaces (S1) towards top to NNE (Monaco & Tortorici, 1995). The detailed structural analysis in the study area allowed recognizing structure related to a polyphase deformation history. In particular two generation of folds are overprinted by a later phase developing E-W folds. D1 folds and related foliation are associated with metamorphism under blueschist facies conditions. Later D2 folds overprint the previous fabric forming a crenulation cleavage. Shear sense indicators obtained from mylonitic bands are mainly coherent with top-to-the-W and top-to-the-NW shear sense (Laurita, 2009).

SAMPLING AND ANALYTICAL METHODS

A total of 60 samples of serpentinite-hosted carbonate veins (CVs) and serpentinite-hosted talc-rich bodies associated with quartz and carbonate veins (QCVs) were collected (Fig. 1). The samples come from two main localities: the Fosso Arcangelo site, near San Severino Lucano village and in the Pietrapica quarry, at the Calabria-Lucanian boundary (Basilicata region, southern Italy). In the investigate area, based on field observations, the serpentinites outcropping in the Fosso Arcangelo site, are brownish-grey and green in colour and appears intensely reworked by strong brittle and ductile deformation, evidenced by several slip surface and by the presence of isoclinal and tight fold and some intrafolial fold often associated with crenulation cleavage. The fractures are commonly filled by carbonate minerals and display changes in both thickness and length (CVs). The serpentinites outcrops in the Pietrapica quarry shows a complex exposure of dark-green cataclastic serpentinites with several slip surface and badland-like morphology. The serpentinites-hosted talc-rich bodies are associated with quartz and carbonate veins (QCVs).

The mylonitic-cataclastic structures observed in the two sites are characterized by the development of composite foliations (shear bands) S-C1, the kinematic

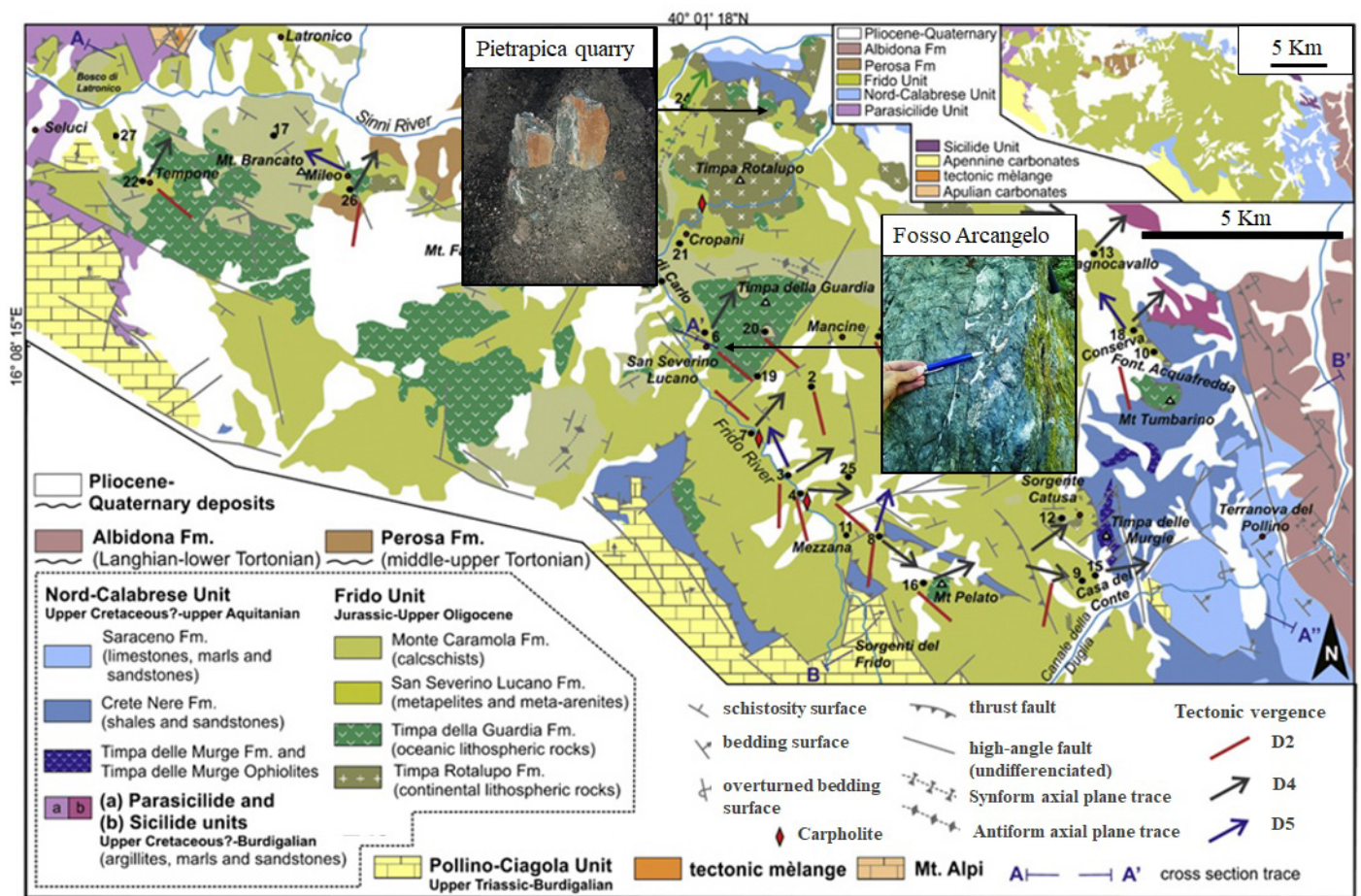


Fig. 1 - Geological sketch map of the southern Apennines and location of the study area (modified after Vitale et al., 2013).

indicators observed are all consistent with a sense of shear top to W-NNW (Laurita et al, 2014) with a slight difference in the direction of transport of the different tectonic structures.

The development of late shear bands indicates a reactivation of the structures in a semi-ductile domain, probably occurring in an extensional context. This is consistent with literature data suggesting the activation of low-angle extensional faults in a semi-ductile context, with a sense of shear top towards East (Knott, 1994), finally, the presence of shear band is compatible with a top movement to the south (Laurita et al., 2014).

Preliminary petrographic characterization of all the samples was carried out by optical microscopy on thin section of rock samples oriented following their foliations and lineations.

X-ray powder diffraction (XRPD) analyses were performed at the Department of Sciences, University of Basilicata (Italy), on randomly oriented powdered samples of both bulk rocks and vein infill, using a Siemens D5000 equipment with $\text{CuK}\alpha$ radiation, 40 kV and 32 mA, 2 s per step, and step scan of $0.02^\circ 2\theta$. The Raman analyses were carried out at the Department of Sciences, University of Basilicata, using a Horiba Jobin-Yvon LabRam HR800 spectrometer equipped with a HeNe laser source with a wavelength of 633 nm, a CCD detector operating at -70°C and an edge filter that exclude from detection shift below 150 cm^{-1} . Minerals chemistry was determined at

the Centro Nacional de Microscopía Electrónica (CNME) of the Universidad Complutense (Madrid, Spain) by electron microprobe (EMP) analyses using an EMP JEOL Superprobe JXA-8900 M, equipped with four wavelength dispersive spectrometers. Silicate and oxide analyses were conducted at an accelerating voltage of 15 kV, an electron beam current of 20 nA, and a beam diameter of $5\ \mu\text{m}$. An accelerating voltage of 20 kV, an electron beam current of 10 nA, and a beam diameter of $5\ \mu\text{m}$ were used for carbonate minerals. Fourier transform infrared spectroscopy measurements were carried out at the Department of Sciences, University of Basilicata with a Jasco FT-IR 460 Plus interferometer. The spectra have been acquired by collecting 30 scans at 4 cm^{-1} resolution. Major, trace, and rare earth element concentrations were determined by ICP and ICP-MS analysis at Activation Laboratories (Ancaster, Canada), after vein sample powders were digested using a four acid attack (HF , HClO_4 , HNO_3 , and HCl). For stable oxygen and carbon isotope analysis, about 0.1 mg of powder samples was put in a 12 ml screw cap Exetainer^(R) vial and then flushed with pure helium to remove the air in the headspace. Therefore, about $50\ \mu\text{l}$ of 100% H_3PO_4 was added to each sample for the conversion to carbon dioxide. The analyses were performed using a Thermo GB-II peripheral coupled with a Thermo Delta V Plus CF-IRMS at INGV-Sezione di Palermo (Italy). For $^{87}\text{Sr}/^{86}\text{Sr}$ analyses, one sample of calcite-aragonite of the carbonate veins (CVs) and one sample of dolomite-calcite of the quartz carbonate

veins (QCVs) were fully dissolved in 0.5 M acetic acid, dried end redissolved in 3M HNO₃. To eliminate the solid residue resulting from re-precipitation after chemical dissolution, sample were centrifuged at 4000 rpm during 10 min before being charged in chromatographic columns. Samples were analysed on Re single filament with 1 µl of H₃PO₄ 1 M and 2 µl of Ta₂O₅ on a TIMS-Phoenix mass spectrometer at CAI de Geocronología y Geoquímica Isotópica of the Universidad Complutense (Madrid, Spain).

Some quartz-bearing samples from quartz carbonate veins (QCVs) were selected for the study of fluid inclusions, based on preliminary microscope study. This study was carried out at the Departamento de Estratigrafía, Universidad Complutense (Madrid, Spain). The microthermometric study was performed on the selected portions of samples in a linkam THMSG-600 heating and freezing stage. The stage was calibrated with synthetic fluid inclusions, including triple point of CO₂, melting point of H₂O, and critical point of H₂O. Melting point of H₂O standards shows that the accuracy for low-temperature measurements is better than ± 0.1°C. Critical point standards shows that accuracy for high-temperature measurements is better ± 0.1°C.

RESULTS

PETROLOGY, MINERALOGY AND CHEMISTRY

The serpentinites with carbonate-rich veins in the Fosso Arcangelo site are characterized by a complex brecciated texture with angular fragments (serpentine, chlorite and titanite) of variable size, a protomylonitic fabric and a schistosity with crenulation cleavage defined by recrystallized serpentine, clinopyroxene and opaque minerals. Different type of carbonate veins have been recognized, and distinguished in sheeted veins (Fig. 2a), micrite-filled veins, carbonate veins with serpentine, carbonate veins with amphibole, fibrous calcite veins, carbonate veins with clinopyroxene, and carbonate veins of different thickness cross-cutting the others carbonate veins (Fig. 2b). Serpentinites from the Pietrapica quarry are characterized by an irregular patchy texture or replacement texture which a gradual replacement of the serpentine by carbonate minerals (Fig. 2c). The carbonate minerals are also present in the veins as elongated rhombohedral crystals (Fig. 2d) and microcrystals, together with talc and rare fibrous tremolite. The serpentinites-hosted talc-rich

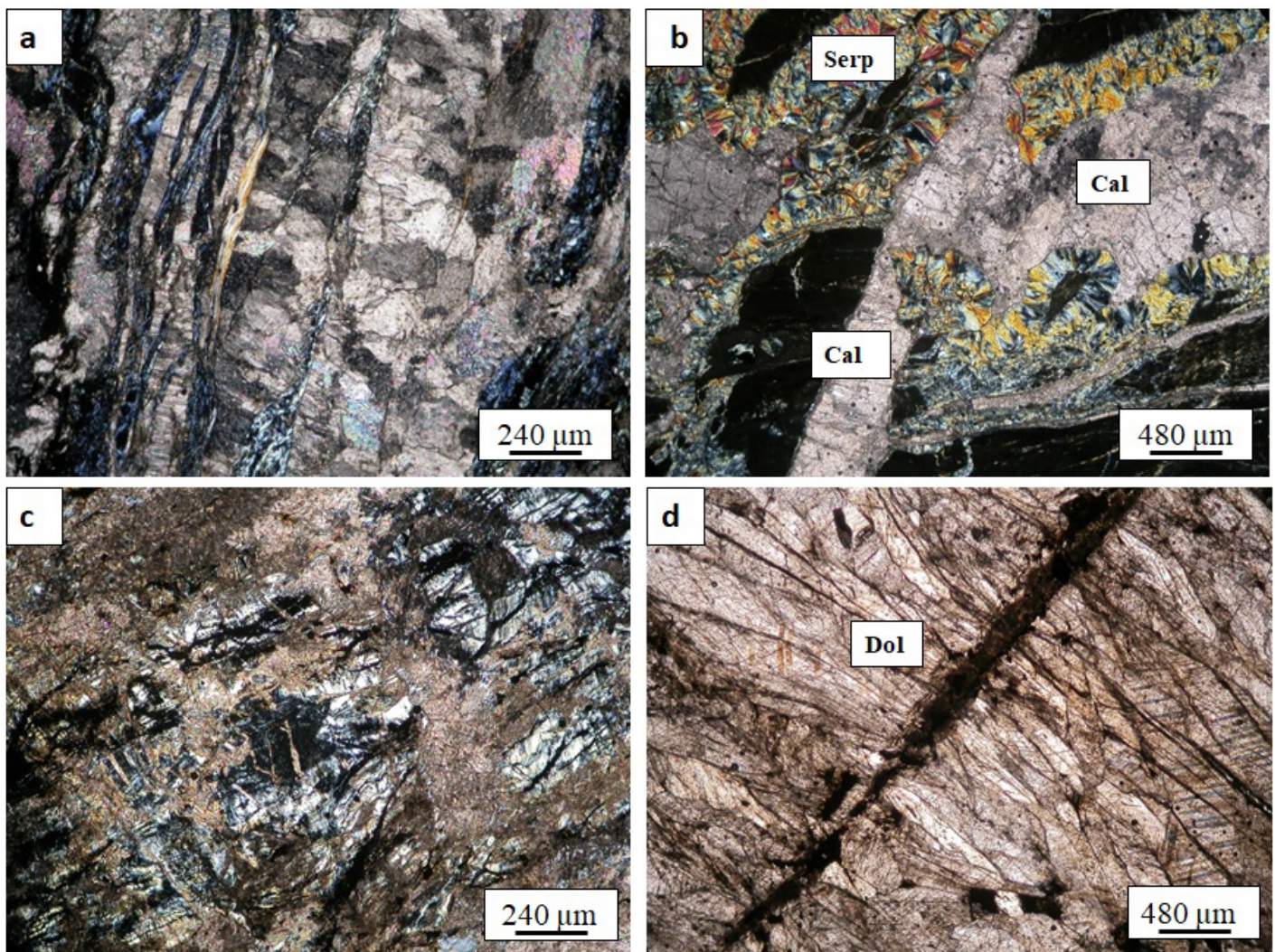


Fig. 2 - (a) Sub-parallel carbonate veins 4X, NX and (b) two generation of carbonate veins, 2X, NX from Fosso Arcangelo site. (c) Irregular patchy texture, 4X, NX and (d) carbonate veins with elongated rhombohedral crystals 2X, 1X from Pietrapica quarry.

bodies are cross-cut by quartz and carbonate veins and characterized by brecciated textures with multiple stages of mineral growth.

Quartz shows a well-developed polygonal texture with fluid and mineral inclusions (not distinguishable under optical microscope) and smaller and larger cracks. Typical fabric of dynamic recrystallization in quartz grains undulose extinction and elongate subgrains passing laterally into domains of small, dynamically recrystallised grains. Talc mostly occurs as massive coarse- to medium-aggregated and as fine fibres. Talc is often associated with serpentine and chlorite. The tabular crystals have a perfect cleavage [001]. In some cases, talc is cross-cut by quartz veins and in other cases; the crystals of quartz are cross-cut by big-massive grain talc, indicating the occurrence of at least two talc-quartz generations.

The paragenesis of the veins, assessed by μ -Raman spectroscopy and X-ray diffraction analysis, indicate that the carbonates in CVs are composed dominantly by calcite and aragonite with minor amount of rhodochrosite (Fig. 3), while, the carbonates in QCVs are composed dominantly by dolomite, Mg-calcite, with minor ankerite (Fig. 3). The paragenesis of the whole rocks has been assessed by petrographic study, μ -Raman spectroscopy, X-ray diffraction analysis and electron microprobe analyses. The paragenesis of the whole rocks in the Fosso Arcangelo site mainly consist of serpentine (lizardite, chrysotile, antigorite, polygonal serpentine), amphibole minerals (actinolite, tremolite, edenite, magnesio-ferro-hornblende, cannilloite and cummingtonite), phyllosilicates (clinochlore), iron oxides (magnetite), inosilicates (diopside), nesosilicates (hydrogarnet, titanite), with different carbonate phases. The paragenesis of the bulk rocks in the Pietrapica quarry is made of serpentine (lizardite, chrysotile, antigorite), amphibole minerals (actinolite, tremolite), phyllosilicates (clinochlore, talc), oxides (Cr-spinel) with different carbonate phases.

The rare earth elements (REEs) abundances in the carbonate veins (CVs) are below detection limits, therefore are not taken into consideration. The REEs distribution patterns for QCVs, normalised to both chondrite and Post-Archean Shale (PAAS), show positive Eu/Eu* whereas when normalized to seawater carbonates positive Ce/Ce* also occurs.

ISOTOPIC AND MICROTHERMOMETRY DATA

The C and O isotope ratios in carbonates from CVs record two distinct ranges: the $\delta^{13}\text{C}$ values range from -0.81‰ to $+2.16\text{‰}$, and from -3.66‰ to -2.79‰ vs. V-PDB except for only one sample having an intermediate $\delta^{13}\text{C}$ value ($\delta^{13}\text{C} = -1.57\text{‰}$) (Fig. 4). Corresponding $\delta^{18}\text{O}$ values are between $+15.02\text{‰}$ and $+16.38\text{‰}$ vs. V-SMOW except for four samples having $\delta^{18}\text{O}$ values slightly more positive, ranging between $+18.36\text{‰}$ and $+21.53\text{‰}$ vs. V-SMOW. The $\delta^{13}\text{C}$ values of carbonates of mineralized QCVs are in the range from -3.60‰ to -1.78‰ vs V-PDB and the corresponding $\delta^{18}\text{O}$ average value is around $+21.3\text{‰}$ vs. V-SMOW (Fig. 4). Overall, the isotopic ratios in CVs and QCVs fall in the typical range for marine carbonates ($\delta^{13}\text{C}$: $0 \pm 2\text{‰}$; $\delta^{18}\text{O}$: $10\text{--}26\text{‰}$; Shields & Veizer, 2002) and for hydrothermal carbonates ($\delta^{13}\text{C}$: -3‰ to -9‰ ; $\delta^{18}\text{O}$: $16\text{--}23\text{‰}$, Zheng & Hoefs, 1993). Equilibrium temperatures for CVs and QCVs samples were computed from 18-Oxygen data and considering the calcite and dolomite-water fractionation curves respectively. Temperatures of calcite/dolomite precipitation are in the 61 to 120 °C range for CVs and between 83 and 110 °C for QCVs. The pristine $\delta^{13}\text{C}_{\text{CO}_2}$ values of the fluid were computed from 13-Carbon data and considering the isotope composition of the carbonate mineralogical phase (calcite for CVs and dolomite for QCVs) and the equilibrium fractionation factor for carbon between calcite or dolomite and CO_2 . Average fluid $\delta^{13}\text{C}_{\text{CO}_2}$ of mineralized CVs is in the range of -3.79‰ to -5.24‰ . The fluid $\delta^{13}\text{C}_{\text{CO}_2}$ of mineralized QCVs is in the range of -5.83‰ to -9.15‰ . These values are well within the $\delta^{13}\text{C}$ range of CO_2 of carbonates precipitated from hydrothermal fluids.

Fluid inclusions were examined in quartz crystals from quartz-carbonate veins (QCVs). Most of the fluid inclusions in the quartz are arranged along lines of crystal growth and thus they are considered as primary and/or pseudo-secondary fluids according to the criteria defined by Roedder (1967). Some fluid inclusions occur along secondary trails and necking down is occasionally seen. Two major types of fluid inclusions were recognised: predominantly all-liquid fluid inclusions (single-phase inclusions: $L_{\text{H}_2\text{O}}$) and liquid-vapour inclusions (biphasic inclusions: $L_{\text{H}_2\text{O}} + V_{\text{H}_2\text{O}}$). In the fluid inclusions study, we did not find any evidence for the presence of CO_2 - and CH_4 -

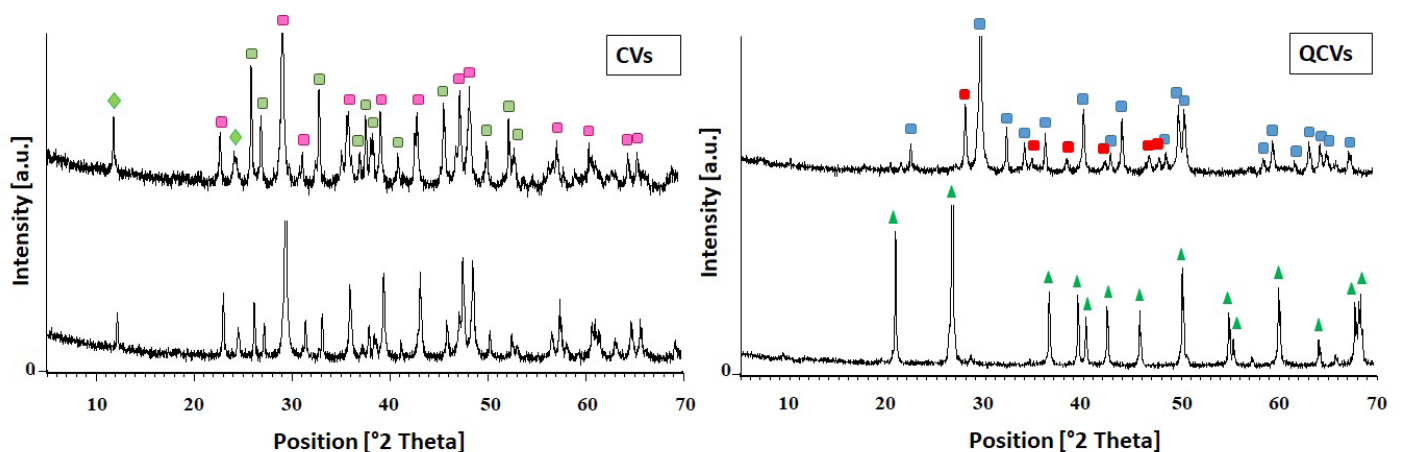


Fig. 3 - XRPD patterns of selected carbonate and quartz-carbonate veins. Legend: pink square = calcite; green square = aragonite; blue square = dolomite; red square = Mg-calcite; green triangle = quartz; green diamond = serpentine.

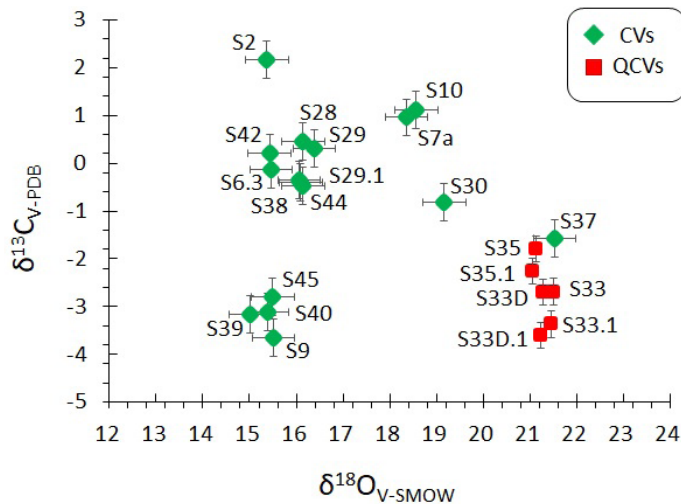


Fig. 4 - $\delta^{13}\text{C}_{\text{V-PDB}}$ vs. $\delta^{18}\text{O}_{\text{V-SMOW}}$ plot of calcite/dolomite in the carbonate (CVs) and quartz-carbonate veins (QCVs) from the Fosso Arcangelo site and the Pietrapica quarry.

phase (- 56.6 and - 147.0 °C respectively). In fact, during the cooling phase, we went down until liquid nitrogen temperatures and no melting process different than melting of ice was observed. This means that the gas is likely water vapour. However, the presence of another gas different from water vapour cannot be discarded although, even if present, this gas would have very low density, resulting undetectable by microthermometry. The temperatures of final ice-melting $T_m(\text{Ice})$ values range from -0.3 to -1.9 °C. Many inclusions present positive ice-melting temperatures which means that they are under high pressure out of their stability field. Temperatures of the first melting (eutectic temperature, T_e) were observed around -30 °C, which is the metastable temperature of the $\text{H}_2\text{O}+\text{NaCl}$ system. Based on the $T_m(\text{Ice})$ and taking in account the $\text{H}_2\text{O}+\text{NaCl}$ system, the biphasic inclusions are found to be of low salinity, between 0.53 and 3.23 NaCl mass % equivalent. The all biphasic inclusions homogenize to liquid, with final homogenization temperature (T_h) in two different range of temperature: the first one from 93 to 140 °C and the second one from 185 to 335 °C.

DISCUSSIONS

Petrographic observation have revealed different parageneses and structures that reflect a complex metamorphic and deformational histories and a varied array of calcite habits and multiple cross-cutting, truncation, and replacement textures.

In this study, the parageneses of the serpentinite-hosted carbonate-rich veins (CVs) from the Fosso Arcangelo site has been attributed to the blueschist facies, in particular for the presence of the clinopyroxene and garnet, that may appear together only at high pressure conditions.

The analysed SiO_2 and estimated H_2O for hydrogarnets from this study indicate about 4 OH pfu, suggesting temperatures of 300 - 250 °C similar to the temperature range associated to serpentine formation. The formation of metamorphic diopside is encouraged by an increase of SiO_2 in the fluids. Therefore, diopside may crystallize

from Si^{4+} , Mg^{2+} , and Ca^{2+} released during serpentinization and from calcium-bearing fluids. Calcite/aragonite hosted in serpentinites from the Fosso Arcangelo site has been interpreted as direct precipitation by fluid.

The paragenesis of the serpentinites-hosted talc-rich bodies associated with quartz and carbonate veins (QCVs) from Pietrapica quarry has been attributed to the blueschist facies, in particular for the presence of variable mineral assemblages including talc-tremolite; talc-quartz-dolomite (or Mg-calcite); talc-serpentine assemblages with minor chromite and clinocllore.

Dolomite/Mg-calcite hosted in serpentinites from Pietrapica quarry has been interpreted as replacement of serpentine minerals during multistage water/rock interaction or as direct precipitation by fluids. The quartz has been interpreted as direct precipitation by hydrothermal fluids. The talc, most likely form from interaction of the serpentinites with silica-saturated fluids: $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{SiO}_{2(\text{aq})} \rightarrow \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + \text{H}_2\text{O}$ and/or from interaction of the dolomite and quartz: $3\text{CaMg}(\text{CO}_3)_2 + 4\text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 3\text{CaCO}_3 + 3\text{CO}_2$, or by carbonation reactions: $2\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{CO}_2 + 3\text{CaCO}_3 \rightarrow \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 3\text{CaMg}(\text{CO}_3)_2 + 3\text{H}_2\text{O}$.

The carbonate (CVs) and quartz-carbonate (QCVs) veins were examined for the first time to unveil the origin of the fluids from which veins formed. REEs distribution patterns for QCVs showing positive Eu-anomalies may suggest that the fluid have hydrothermal origin.

The carbon isotope compositions of carbonate in CVs and QCVs indicate that crustal-derived hydrothermal fluids generated them. Oxygen isotope analyses of the calcite for CVs and QCVs revealed a relatively large temperature range (61-120 °C for CVs and 83 and 110°C for QCVs).

The fluid inclusions in quartz crystals have abundant aqueous ($\text{LH}_2\text{O}-\text{VH}_2\text{O}$) and low salinity features (between 0.53 and 3.23 NaCl mass % equivalent) thus confirming the hydrothermal origin of the fluid. Further, the decrease of both homogenization temperature and salinity may be related to large infiltration of shallow, diluted and fresh waters that led to a progressive cooling of the hydrothermal system. The decrease of fluid temperature and/or mixing processes between hot mineralizing fluids and shallow fresh waters likely promoted silica deposition.

CONCLUSIONS

The results suggest that the carbonate (CVs) and quartz-carbonate veins (QCVs) occurred under the same environmental conditions from crustal-derived hydrothermal fluids at low-moderate temperatures (around 100°C) with a different chemical composition. The mineral assemblages represents evolving conditions of alteration, and an increase in variable activity of the carbonic-rich fluids (HCO_3^- , CO_3^{2-} , Ca^{2+}) for CVs and the carbonic-silica-rich fluids (HCO_3^- , CO_3^{2-} , Ca^{2+} , Mg^{2+} , Si) for QCVs. It is proposed that the carbonic-rich fluids and the carbonic-silica-rich fluids, responsible for the intense metasomatism, are the result of interaction between hydrothermal fluid, serpentinites and major lithological interfaces (calcschists/metalimestone and gneiss/amphibolites/metagranitoids). In Pietrapica quarry, the fluid inclusions study suggest that the hydrothermal fluids are probably diluted with meteoric water.

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