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PERVASIVE CRYSTALLIZATION OF ANTIGORITE IN NORTHERN APENNINE OPHIOLITES: THE EXAMPLE OF MONTECARELLI PERIDOTITES (TUSCANY, CENTRAL ITALY)

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ABSTRACT

The occurrence of pervasive crystallization of antigorite associated to brittle tectonics is described for the first time in the External Ligurian peridotites of the Northern Apennine (Italy). Antigorite was found in a slide block of subcontinental peridotites included in the tectonized sedimentary mélange of the Leo Unit (western External Ligurian units). This mélange, as those from the External Ligurian units, originated in Santonian-early Campanian time span from a source area corresponding to the Ocean-Continent Transition Zone at the Adria plate margin. The antigorite was found within veins belonging to four systems, from V1 to V4, each characterized by different attitude and morphology. The morphology of the veins ranges from massive to fibrous, with the latter characterized by fibers both parallel and perpendicular to the vein walls. Rare occurrence of chrysotile and calcite were identified within the veins.

The antigorite crystallization in the peridotites cannot be interpreted as related to an orogenic high-pressure metamorphism but most likely can be regarded as developed at shallow structural level in the late stage of the rifting phase when subcontinental mantle was progressively exposed at the surface, intruded by gabbro bodies, and cut by basaltic dykes.

INTRODUCTION

In the Northern Apennine collisional belt, the Ligurian Units preserve the remnants of the oceanic lithosphere of the Mesozoic Ligurian-Piemontese oceanic basin and its transition to the Adria continental margin (Marroni et al., 2001; Marroni and Pandolfi, 2007). Whereas the fragments of oceanic lithosphere are slightly metamorphosed and well-preserved in the Internal Ligurian Units as coherent sequences ranging in age from Middle Jurassic to early Paleocene (e.g., Meneghini et al., 2007), the Ocean-Continent Transition Zone (OCTZ) to the Adria margin can be only found as dismembered slide blocks within the Late Cretaceous sedimentary mélange of the External Ligurian Units (e.g., Marroni et al., 2017).

Most of these slide blocks, sometime huge, consist of subcontinental peridotites and their study allowed to collect useful information about the origin and evolution of the OCTZ. Typically, these peridotites preserve a pre-orogenic tectono-metamorphic history reflecting a long-lived multistage evolution including an old pre-Jurassic magmatic event followed by metamorphic and deformation events related to the tectonic exhumation. Multiple melt-rock interaction and intrusion events occurred at different lithospheric depths during the progressive extension-related uplift (Müntener and Piccardo, 2003; Piccardo et al., 2007; Rampone and Borghini, 2008; Müntener et al., 2010; Borghini et al., 2016; Basch et al., 2020; Rampone et al., 2020). Very few contributions (Bertolani et al., 1964; Veniale and van der Marel, 1968; Mellini and Zanazzi, 1987; Laurora et al., 2011) are however devoted to the history developed at shallow structural levels when the mantle was already exhumed in the OCTZ. The available literature data indicate that this history includes a multiple, brittle tectonic events associated to pervasive serpentinization processes (Müntener and Piccardo, 2003; Rampone and Borghini, 2008; Müntener et al., 2010; Piccardo et al., 2010; Borghini et al., 2016; Basch et al., 2020; Rampone et al., 2020) characterized by the predominant recrystallization of lizardite and chrysotile (e.g., Regione Emilia Romagna, 2004).

In this paper we provide a geological, structural, and mineralogical dataset proving the occurrence, for the first time in the External Ligurian peridotites of the Northern Apennines exposed in the Montecarelli area (Florence), of a pervasive crystallization of antigorite associated to brittle deformation.

GEOLOGICAL SETTING

The Northern Apennines (Fig. 1) is a collisional belt built up during the Late Cretaceous-Middle Eocene by the closure of the Ligure-Piemontese oceanic basin and the subsequent Middle Eocene-Late Oligocene collision between the European and Adria plates (e.g., Elter and Pertusati, 1973; Bortolotti et al., 1990; Molli, 2008; Malusà et al., 2009; Molli and Malavieille, 2011; Marroni et al., 2017; Di Rosa et al., 2020). The highest units of the Apenninic belt belong to the Ligurian Domain, representing the remnants of the oceanic lithosphere of the Ligure-Piemontese basin and its OCTZ to the nearby continental margin. During the continental collision, the Ligurian Units were thrust over the Sub-Ligurian and Tuscan Units, both representative of inner domains of the Adria continental margin. Whereas the Internal Ligurian Units (IL) are representative of the Middle to Late Jurassic oceanic lithosphere of the Ligure-Piemontese oceanic basin (Elter, 1975; Abbate et al., 1980; Marroni, 1991; Marroni and Pandolfi, 1996; 2001; Marroni et al., 2004; 2017; Principi et al., 2004; Frassi et al., 2017), the External Ligurian Units

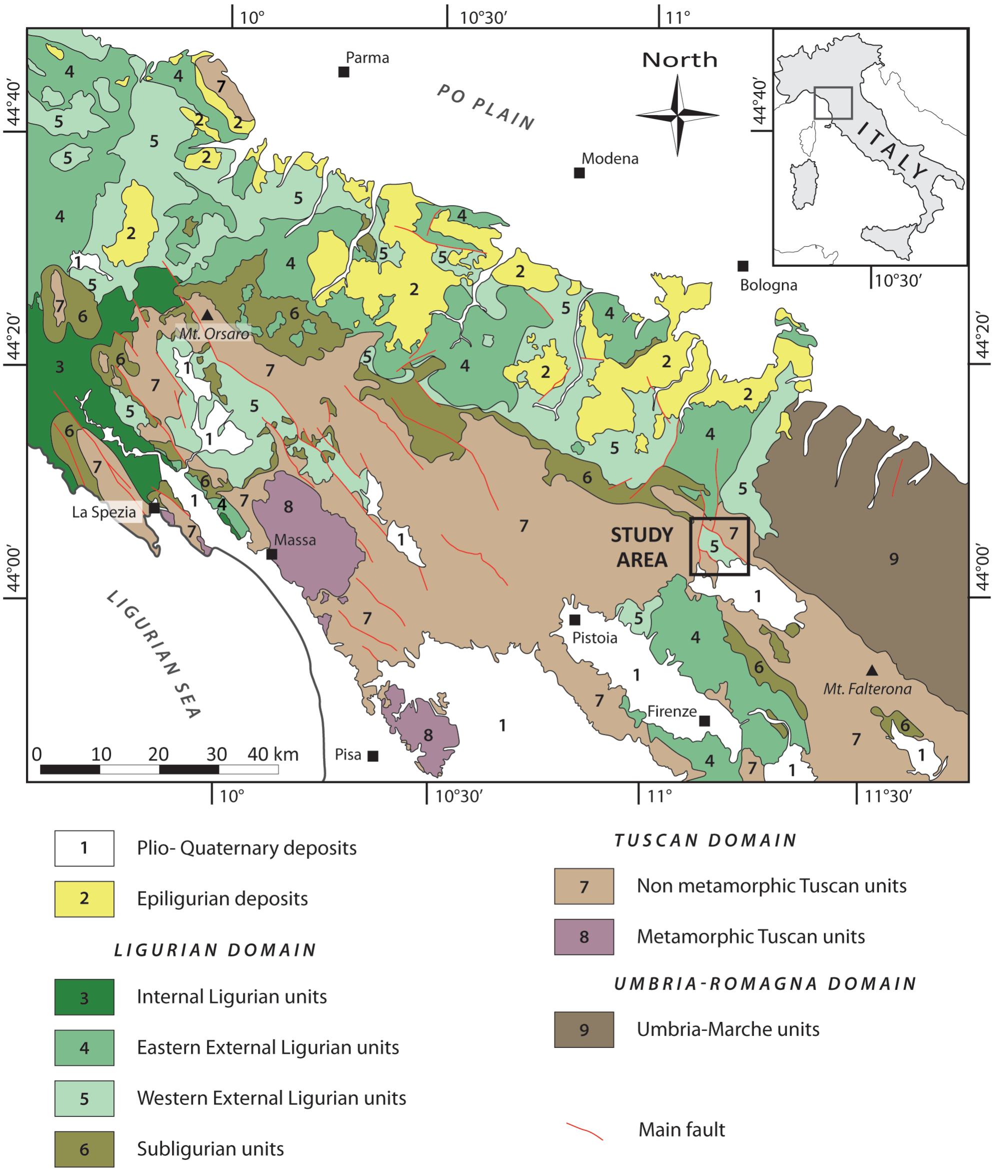

Fig. 1 - Geological sketch map of Northern Apennines. The location of the area of Fig. 2 is shown.

(EL) are regarded as derived from the OCTZ to the Adria plate (Marroni et al., 1998; 2001; Molli et al., 2010).

The EL are characterized by the widespread occurrence of the Late Cretaceous Helminthoid Flysch and can be subdivided into two groups according to the lithostratigraphic features of the successions at its base (Marroni et al., 2001; 2017). The first EL group (“Western successions”) includes all the successions characterized by the occurrence of Santonian-early Campanian sedimentary mélanges, whereas the second group (“Eastern successions”) displays successions showing a Triassic-Jurassic sedimentary base derived from the thinned Adria continental margin.

The sedimentary mélanges of the western EL successions crop out extensively in eastern side of the Ligurian-Emilian Apennine, up to the Po plain (Fig. 1). These mélanges are all detached from their stratigraphic base and consist of huge slide-blocks enclosed in a matrix made of polymict, clast- and matrix-supported breccias interbedded with coarse-grained, turbidite-derived rudites, arenites and shales (e.g., Elter et al., 1991). The huge blocks consist of subcontinental mantle peridotites, gabbros and basalts. Slide-blocks of deep-sea sedimentary rocks, derived from the Cherts (Middle to Late Jurassic), Calpionella Limestone (Early Cretaceous) and Palombini Shale (Early to Late Cretaceous) Formations, also occur. Slide blocks of continental crust-derived rocks are also recognized, mainly consisting of late Paleozoic granitoids showing primary relationships with basalts. Slide blocks of Permian mafic granulites, generally associated to slide blocks of felsic granulites, have been also found. Other continent-derived rocks, found as clasts in polymict breccias, mainly consist of micaschists, ortogneisses and garnet-bearing paragneisses. For a complete description of the slide blocks from EL western successions see Marroni and Tribuzio (1996), Balestrieri et al. (1997), Montanini (1997), Marroni et al. (1998; 2017), Marroni and Pandolfi (2007), Montanini et al. (2008), Rampone and Borghini (2008), Piccardo et al. (2010), Borghini et al. (2016), Basch et al. (2020) and Rampone et al. (2020).

The EL mélanges have been subdivided into the Casanova, Monte Ragola and Pietra Parcellara Complexes by Marroni et al. (2001). Among them, only the Casanova Complex is stratigraphically overlain by the Helminthoid flysch, whereas the Monte Ragola and Pietra Parcellara Complexes are bounded by thrusts and their original stratigraphic relationships with the Helminthoid flysch can be only inferred. However, the main differences among these mélanges concern the lithotypes found as slide blocks. The Monte Ragola Complex includes peridotites, gabbros, basalts, sedimentary rocks and both lower and upper continental crust-derived rocks. The Casanova Complex shows the same composition of the slide blocks from Monte Ragola Complex but the slide blocks representative of lower continental crust are missing. In turn, the Pietra Parcellara Complex is totally devoid of continental-derived rocks (i.e., granulites, granitoids and associated metamorphic rocks) whereas peridotites, gabbros and basalts are well represented.

In summary, all the sedimentary mélanges recognized in the EL western successions seem to be derived from a source area corresponding to an OCTZ at the margin of the Adria plate. This margin was deformed and uplifted in Santonian-early Campanian time span by the convergence-related tectonics thus leading to a sedimentation of huge volume of mélange in the neighbouring basin (Marroni et al., 2001; Marroni et al., 2017). This basin was characterized by a basement of subcontinental mantle and lower continental crust, covered by extensional allochthons of upper continental crust, and intruded by gabbros and basalts (Marroni et al., 2017 and quoted references). Even if characterized by some differences, mainly consisting of the occurrence of the continental-derived rocks, the overall characteristics as, for instance, the widespread occurrence of subcontinental mantle peridotites, suggest that all the mélanges probably belong to the same geodynamic setting (i.e., the OCTZ). These differences probably reflect the heterogeneity in the source area of the sedimentary mélanges that consists in a thrust sheet system located at the rear of an accretionary wedge where different segments of the OCTZ were involved (Marroni et al., 2010; 2017; Molli and Malavieille, 2011).

The studied slide block of peridotites occurs as a 0.06 km^2 body located about 500 m east of the village of Montecarelli, Florence, central Italy (Fig. 2). This slide block is included in the tectonized sedimentary mélange of the Leo Unit, belonging to the EL western successions (Bettelli and Boccaletti, 2002). According to Conti et al. (2020), the sedimentary mélange of the Leo Unit can be correlated with the Pietra Parcellara Complex cropping out in the northward side of the Emilian Apennine. As the Pietra Parcellara Complex, the sedimentary mélange of the Leo Unit includes slide blocks of peridotites, gabbros, basalts and sedimentary rocks (derived from Cherts, Calpionella Limestone and Palombini Shale Formations) whereas the slide blocks of continental crust are lacking (Bocchi et al., 1976; Calanchi et al., 1987; Bortolotti et al., 1995). In the study area, the Leo Unit occurs as several klippens thrust over the Monte Morello Unit (Fig. 2).

THE ANTIGORITE OCCURRENCES IN PERIDOTITES FROM ALPINE-APENNINE BELTS

Antigorite is extensively reported from Western and Ligurian Alps in serpentinized peridotites deformed and metamorphosed during the Late Cretaceous-Early Tertiary Alpine tectonics (Mellini et al., 1987; Scambelluri et al., 2004; Groppo et al., 2006; Groppo and Compagnoni, 2007; Schwartz et al., 2013; Luoni et al., 2019). These peridotites are considered as suboceanic to subcontinental mantle fragments that underwent high pressure-low temperature metamorphism (HP-LT) during their burial and exhumation in subduction channel (e.g., Scambelluri et al., 1995; Guillot et al., 2004; Federico et al., 2007). During these processes, lizardite and chrysotile dominate below 300°C and 0.4 GPa, while antigorite progressively replaces lizardite in the 320-390°C temperature range at higher P and in the presence of SiO_2-enriched fluids (Schwartz et al., 2013). Antigorite has, therefore, been generally regarded as the HP-LT polymorph of serpentine, as opposed to lizardite and chrysotile (e.g., Evans and Trommsdorf, 1978; Mellini et al., 1987; Schwartz et al., 2013).

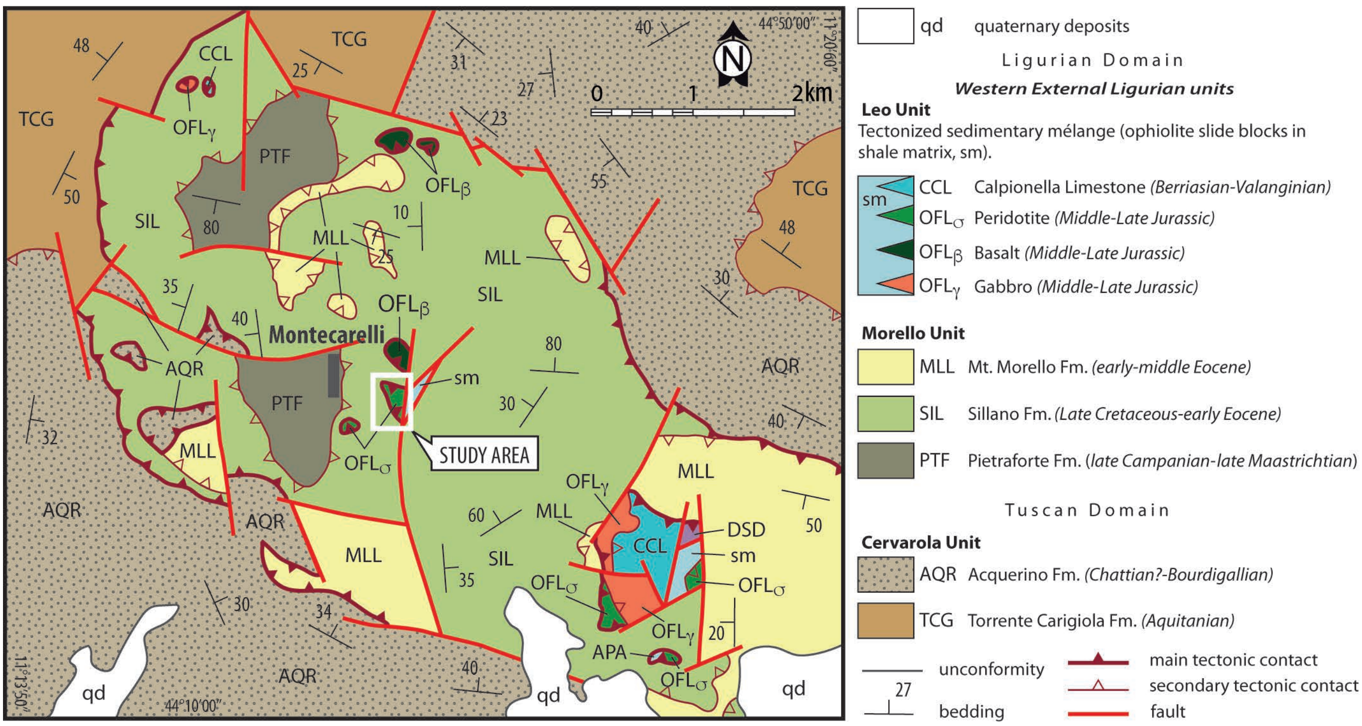

Fig. 2 - Geological sketch map of the Montecarelli area (modified after Bettelli and Boccaletti., 2002).

However, antigorite has been also reported in the peridotites from Internal Ligurian Units of Northern Apennines. These units, even if involved in the subduction process, suffered only very low-grade metamorphism (Leoni et al., 1996; Ellero et al., 2001), according to their deformation at shallow depth (Marroni, 1991; Marroni and Pandolfi, 1996; Marroni et al., 2004; 2017). Despite these characteristics, the crystallization of fibrous antigorite has been reported in the oceanic peridotites in Eastern Liguria by Gaggero et al., (2013) and in western Tuscany by Donatio et al. (2013), even if these authors describe the occurrence of lizardite and chrysotile as largely predominant in these rocks. The crystallization of serpentine minerals in peridotites is regarded as acquired during the Middle to Late Jurassic time span in a slow- and ultra-slow spreading mid-oceanic ridge (e.g., Menna, 2009; Sanfilippo and Tribuzio, 2011). Donatio et al. (2013) have reconstructed in Internal Ligurian peridotites from the Pomaia quarry (Pisa) a sequence of veining starting with veins filled by lizardite with interlocking texture, subsequently cut by veins filled by chrysotile with both interlocking and fibrous texture and lastly veins filled by fibrous antigorite. These events were interpreted as reflecting a history dominated by alternance of tectonic- and magmatic-controlled hydration of the peridotites in a slow-spreading ridge setting (Donatio et al., 2013). The crystallization of antigorite during the last event indicates a re-heating with temperature above 300°C, whereas its morphology indicates stress-controlled crystallization. These conditions suggest a tectonic-controlled fluid circulation in the host peridotites during the transition between amagmatic and magmatic stage. No occurrence of antigorite in the mantle peridotites from External Ligurian Units has been so far reported in the literature.

MATERIALS AND METHODS

Field investigation focused on the lithological characterization of the peridotites exposed in the quarry. Particular attention was paid on the geometrical relationships between the different vein systems and on the characterization of their infilling. To have a complete picture of the entire slide block, 9 samples of infilling veins, and 5 sample of peridotites were collected for petrographical and mineralogical analyses in 8 sites (Fig. 3a, Table 1).

Petrographical and microstructural observations were performed using a Leitz Ortoplan optical microscope with a 2.5×, 4×, 10x and 50× objective lens. X-ray powder diffraction patterns were collected using a Bruker D2 Phaser diffractometer operating at 30 kV and 10 mA in θ-θ scan mode with Ni-filtered Cu*K*α radiation and equipped with a one-dimensional Lynxeye detector. Unpolarized micro-Raman spectra were collected on unpolished samples in nearly back-scattered geometry using a Horiba Jobin-Yvon XploRA Plus apparatus, equipped with a motorized *x-y* stage and an Olympus BX41 confocal microscope, with a 50× objective lens. The 532 nm line of a solid-state laser was used, attenuated to 25% (i.e., 6.25 mW) through a series of density filters to avoid sample damage. The system was calibrated using the 520.6 cm^{-1} line of Si before each experimental session. Spectra were collected through multiple acquisitions (3) with single counting times of 60 s. Backscattered radiation was analysed with a 1200 gr/mm grating monochromator. Quantitative chemical data on antigorite and chrysotile were collected using a Superprobe JEOL JXA 8200 electron microprobe at the Eugen F. Stumpfl laboratory, Leoben University, Austria. The analytical condi-

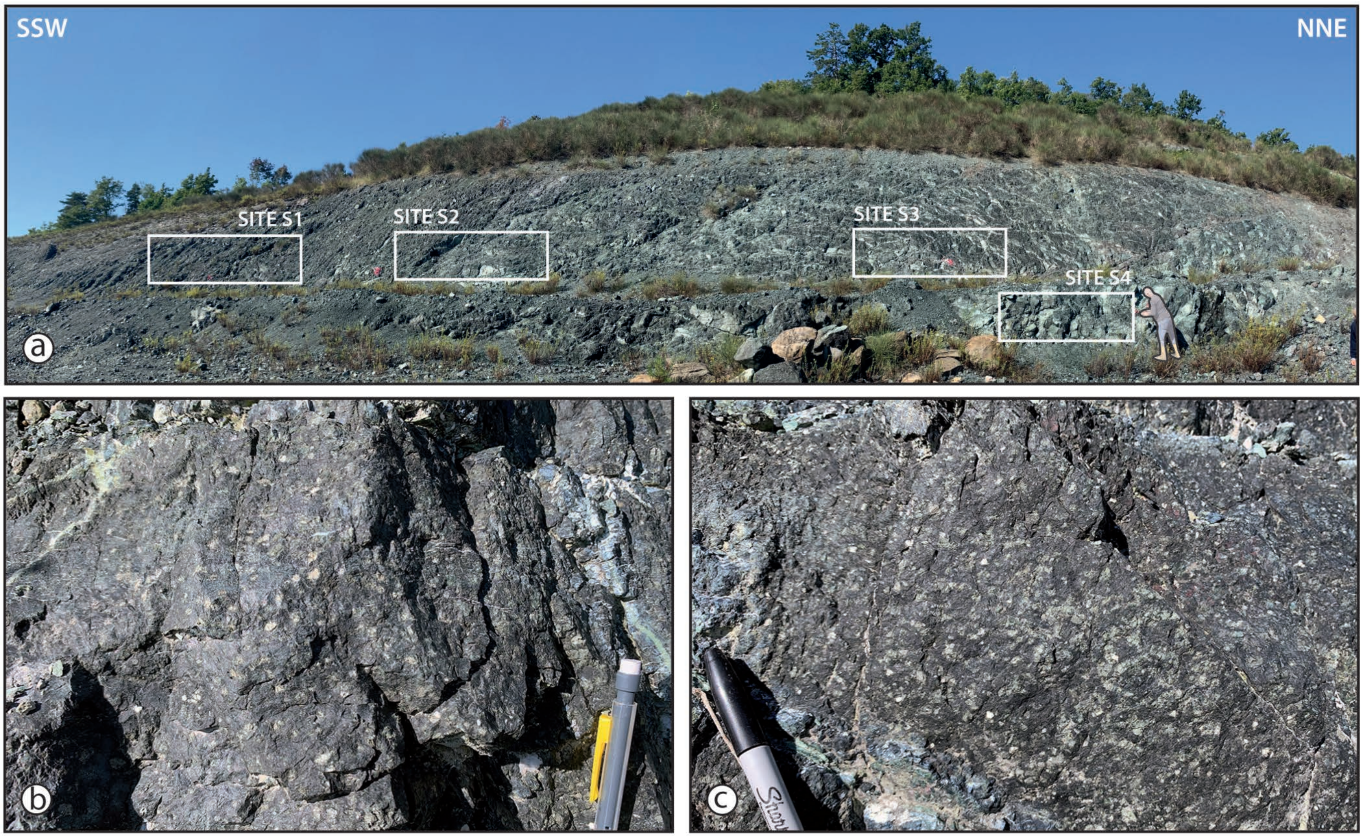

Fig. 3 - (a) Panoramic view of the western sector of the Montecarelli quarry with location of four structural sites S1-S4. (b) and (c) Medium grade serpentinized peridotites with mm-sized pyroxene crystals exposed in the quarry.

Table 1 - List of collected samples and results of micro-Raman spectroscopy and X-ray diffraction.

Site	GPS coordinates	Sample	Lithotype	Methodology	Vein constituent minerals
S1	44.050111N 11.267636E	MC-1M	peridotite	Petrography and structural geology	
		MC-1 V1-V2	V1-V2 vein	X-ray powder diffraction Micro-Raman spectroscopy	antigorite
		MC-1 V3	V3 vein	X-ray powder diffraction Micro-Raman spectroscopy	antigorite, *chrysotile*
S2	44.050224N 11.267669E	MC-2M	peridotite	Petrography and structural geology	
		MC-2 V4	V4 vein	X-ray powder diffraction Micro-Raman spectroscopy	antigorite
S3	44.050498N 11.267765E	MC-3M	peridotite	Petrography and structural geology	
		MC-3 V4	V4 vein	X-ray powder diffraction Micro-Raman spectroscopy	antigorite, calcite, *chrysotile*
S4	44.050456N 11.267941E	MC-4 V1-V2	V1-V2 vein	X-ray powder diffraction Micro-Raman spectroscopy	antigorite, calcite
S5	44.050239N 11.268141E	MC-5 V1-V2	V1-V2 vein	X-ray powder diffraction Micro-Raman spectroscopy	antigorite, calcite
S6	44.049634N 11.268178E	MC-6 V1-V2	V1-V2 vein	X-ray powder diffraction Micro-Raman spectroscopy	antigorite
S7	44.049455N 11.268275E	MC-7M	peridotite	Petrography and structural geology	
		MC-7 V1-V2	V1-V2 vein	X-ray powder diffraction Micro-Raman spectroscopy	*chrysotile*, chlorite, calcite
S8	44.049242N 11.268329E	MC-8M	peridotite	Petrography and structural geology	
		MC-8 V1-V2	V1-V2 vein	X-ray powder diffraction Micro-Raman spectroscopy	antigorite, calcite, *chrysotile*

In italics: mineralogical phases identified exclusively by micro-Raman spectroscopy.

tions were: WDS mode, accelerating voltage 15 kV, beam current 10 nA, beam size ~ 1 μm. The following standards (element, emission line) were used for both studied phases: olivine (Mg*K*α and Fe*K*α), "adularia" (Al*K*α and Si*K*α), skutterudite (Ni*K*α) and rhodonite (Mn*K*α). Cobalt and Zn were sought but were found below the detection limit. ZAF routine was applied for the correction of recorded raw data. Counting times were 20 s for peak and 10 s for left and right background, respectively.

The studied peridotites belong to a slide block well exposed in a quarry near Montecarelli owned by Sades S.p.A. It consists of a homogenous body of serpentinized peridotites characterized by a medium degree of serpentinization (c. 30-50% of serpentine minerals) showing tectonitic texture marked by oriented, mm-sized pyroxene crystals (Fig. 3). Rare mm-thick bands of pyroxenites have been observed whereas dykes of rodingitized gabbros seem to be lacking at all. The main feature of this peridotites body is represented by a complex network of veins filled by serpentine and calcite. These veins show both massive and/or fibrous infilling minerals. The network consists of four systems of veins (namely V1, V2, V3 and V4) on the base of the reciprocal geometrical overprinting relationship (Fig. 4), showing a systematic attitude across the whole outcrop. Brittle shear zones marked by 2-3 m thick cataclasites made of up to cm-sized angular fragments of peridotites in fine-grained matrix cut the peridotites and the network of veins.

THE MONTECARELLI SERPENTINITE

Structural analyses

Veins belonging to the V1 system are the oldest recognized in the field. They are very common in the quarry and show two orientations: the main is N030-060E with 40-70° dip toward E and the secondary is N000-080E dipping 40-70° both toward E and W (Figs. 4 and 5). V1 veins are laterally continuous and spaced from 15 cm to 1 m. Their thickness generally varies from 1 mm to 1 cm (Fig. 6a, b), even if rare veins with 5 cm thickness were also documented (i.e., sample MC-8-V1-V2). They are filled by massive to fibrous white to light green coloured minerals with fibres oriented both orthogonal (i.e., extensional vein) to oblique to the vein walls (Fig. 6b). In the northern sector of the quarry, calcite also fills V1 veins.

V2 system is interpreted as conjugated to V1 system. V2 veins are filled by the same minerals of V1 system and have the same texture (i.e., both fibrous and massive). They are less widespread in the quarry, wider spaced (ca. 1 m) with a main orientation of N120-160E with 35-70° dip both toward NE and SW (Fig. 5).

The third system of veins (V3) is characterized by shallow dip (< 30°) both toward NW and SE. For this reason, their strike varies greatly even if it is possible to recognize two main directions (Fig. 5): NW-SE and NE-SW. V3 veins are laterally continuous and are characterized by a variable spacing

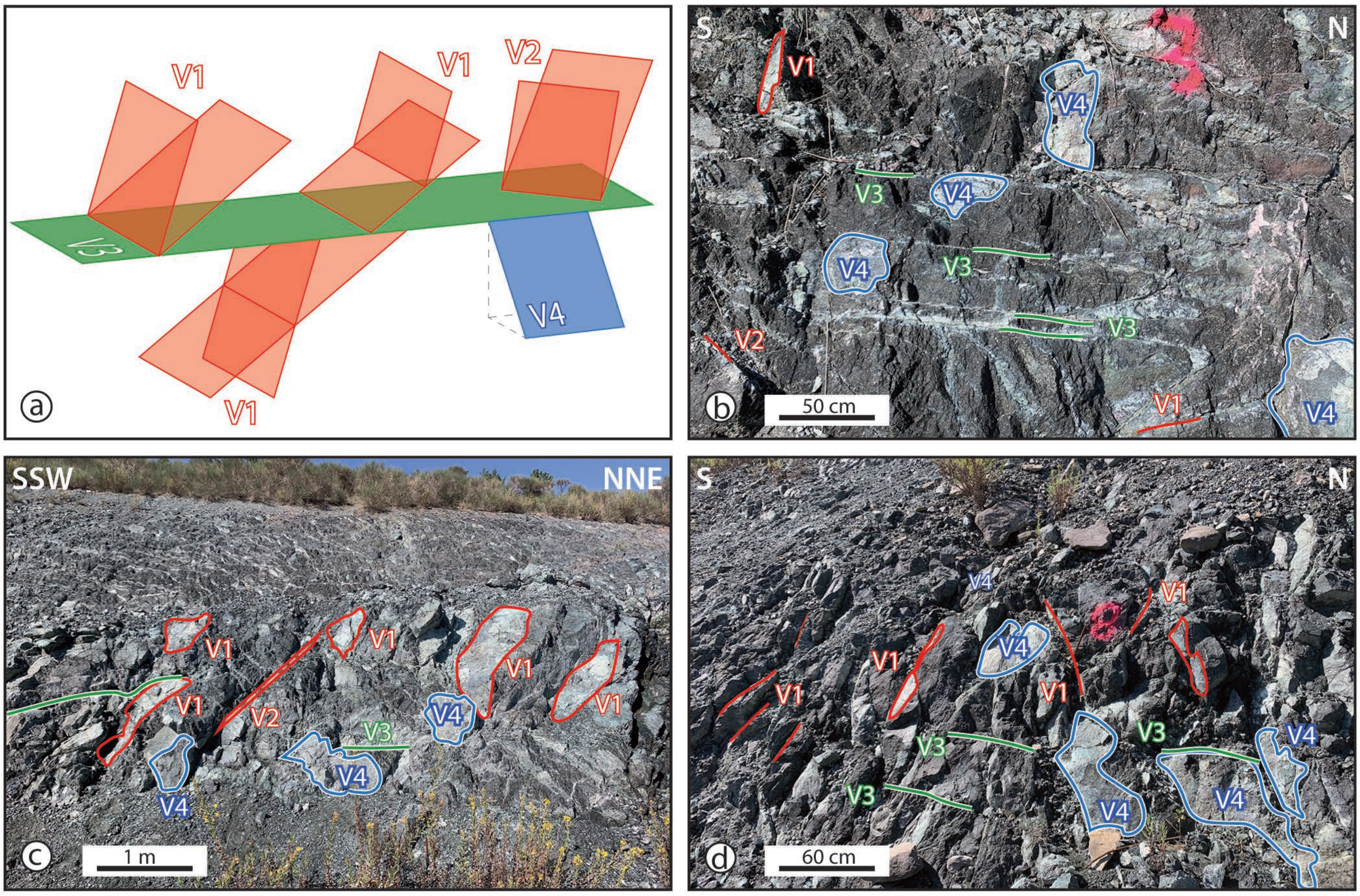

Fig. 4 - Sketch of the geometric relationship between the four vein systems recognized in the quarry (a) and pictures of site S3 (b), S4 (c) and site S8 (d). V1: V1 vein system; V2: V2 vein system; V3: V3 vein system; V4: V4 vein system.

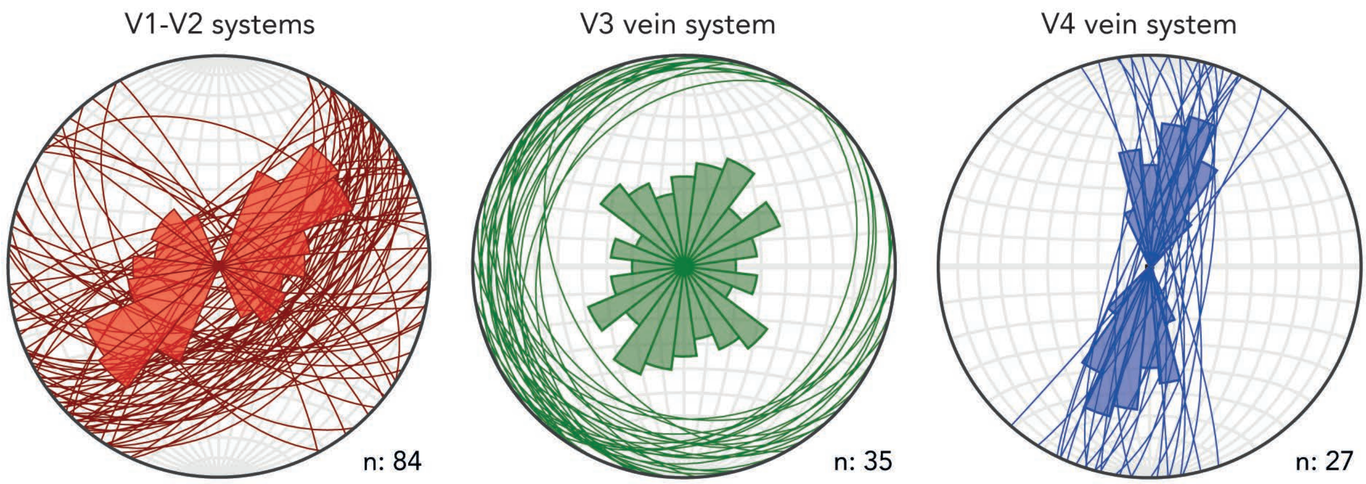

Fig. 5 - Stereographic projection of the four vein systems. The veins are projected both as great circle and as rose diagrams.

from less than 10 cm to about 40 cm, with a thickness of 2-5 cm (Fig. 6c, d). The infilling is represented by light green fibrous minerals with fibres that are oriented parallel to the vein walls (shear veins; Fig. 6c, d).

Veins belonging to the last system (V4) are parallel or sub-parallel to the outcrop surface (Figs. 4 and 6). For this reason, it is very difficult to understand and constrain their spacing. The V4 veins have two main directions: N000-040E and N170-180E with sub-vertical dip (> 75°) both toward W and E (Fig. 5). Their thickness varies along-strike from 1 to 4 cm and the infilling consists of light green coloured fibres (up to 10 cm length) parallel to the vein walls (shear veins; Fig. 6e, f). In the northern sector of the quarry, calcite crystals also fill V4 veins.

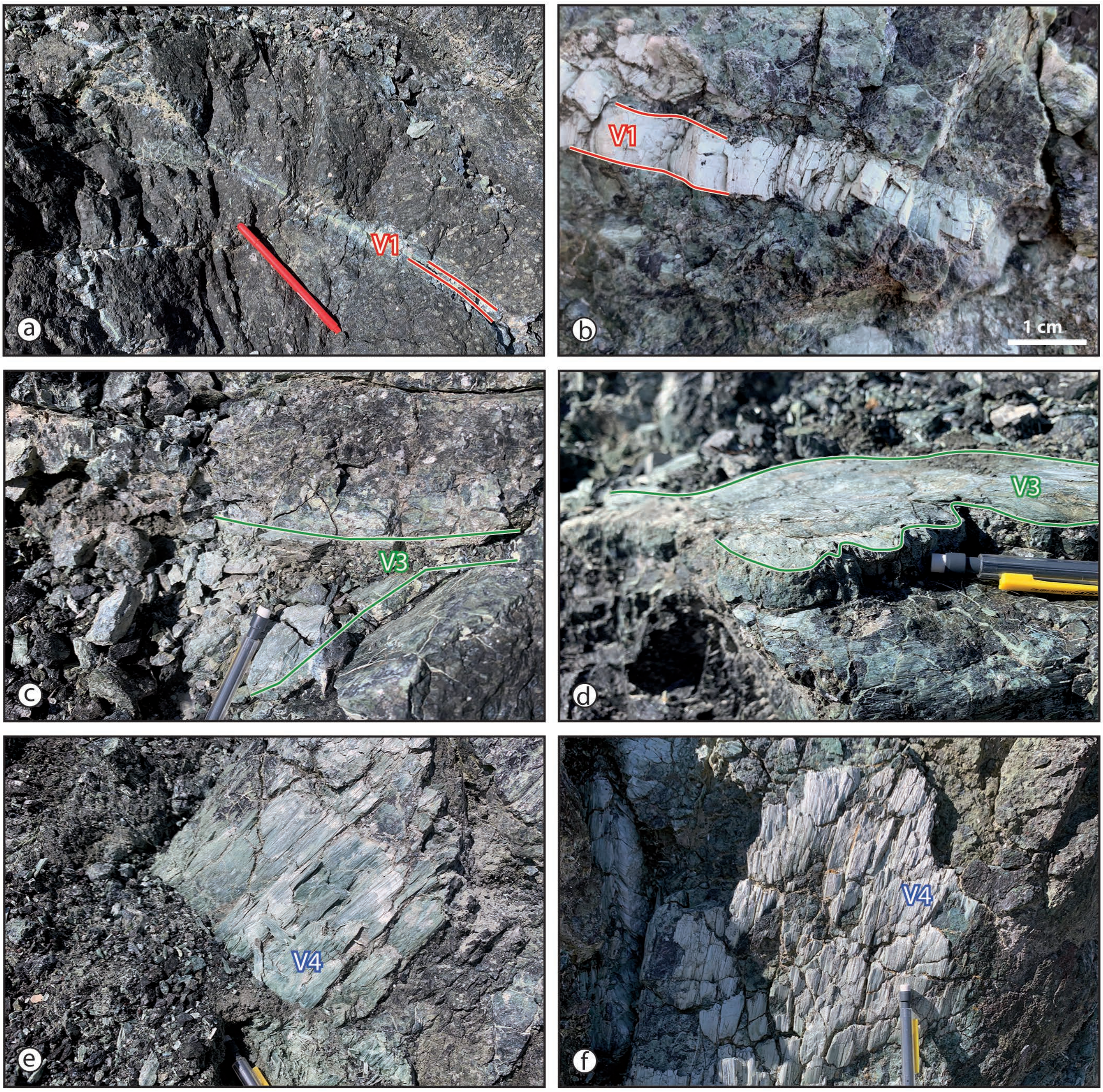

Fig. 6 - Outcrop features of the four vein systems documented in the peridotite exposed in the Montecarelli quarry. (a) V1 vein, less than 1 cm thick, and filled by light green coloured fibres orthogonal to the vein walls (site S1). (b) V1 vein with fibrous texture more than 1 cm thick (c) and (d) V3 veins filled by light green coloured fibrous minerals oriented parallel to the vein walls. (e) and (f) V4 veins oriented parallel or sub-parallel to the outcrop surface. They are filled by a whitish to light green fibrous mineral grow parallel to the vein walls that can reach 10 cm in length (e: site S4; f: site S6).

Petrography

Microscale petrographical and structural analyses have been performed on the thin sections of peridotites (Fig. 7, Table 1). These rocks are characterized by a moderate degree of serpentinization with several relicts of pyroxene, olivine and Cr-bearing spinel wrapped in a fine-grained matrix of serpentine and magnetite, producing mesh texture (Fig. 7a). In the peridotites serpentinized at a lesser extent, the microstructural evidence indicates that their primary texture was probably tectonitic with large, oriented orthopyroxene porphyroclasts in a fine-grained recrystallized protogranular aggregate of pyroxene and olivine. In the studied thin sections, olivine is almost entirely replaced by serpentine minerals, even if it is occasionally still present in the mesh textured domains. The pyroxenes are partially transformed in "bastite" (i.e., fine-grained aggregates of serpentine fibres that replaced and mimicked the pyroxene). Some large crystals (up to 1 cm in size) of pyroxene show undulatory extinction and microkinks (Fig. 7b). Spinel remains unaltered also in the more serpentinized samples.

The massive veins belonging to V1 and V2 systems have a sub-mm thickness quickly changing across a single thin section, whereas the termination of these veins occur as a single tapering (Fig. 7c). These veins are characterized by an infilling consisting of very fine-grained, isotropic homogenous network of minerals without any preferred orientation that can be defined as interlocking texture. They are generally cut by the fibrous veins belonging to the same system.

The most common texture of V1 and V2 vein systems, however, is the fibrous texture (Fig. 7d), their infilling consisting of fibres arranged perpendicularly or sub-perpendicularly to vein walls (Fig. 7d). These veins are characterized by mm thickness and by a significant persistence with single tapering termination. Their thickness has a strong lateral variation with a maximum of 4-5 cm. They do not show crystallographic relationships with the vein walls and can be defined as antitaxial veins according to Ramsay (1980). The crystallographic orientation of the different segments of these fibres produces at cross-polarized light a finely spaced banding parallel to vein margins (Fig. 7d, f). These bands, separated by low birefringence lines, are irregular but reproduce the vein walls along the whole vein length. In addition, all the fibrous veins are commonly characterized by median lines and bands of wall rock fragments parallel to the bands (Fig. 7d). The internal structure of the vein is often asymmetric close to the

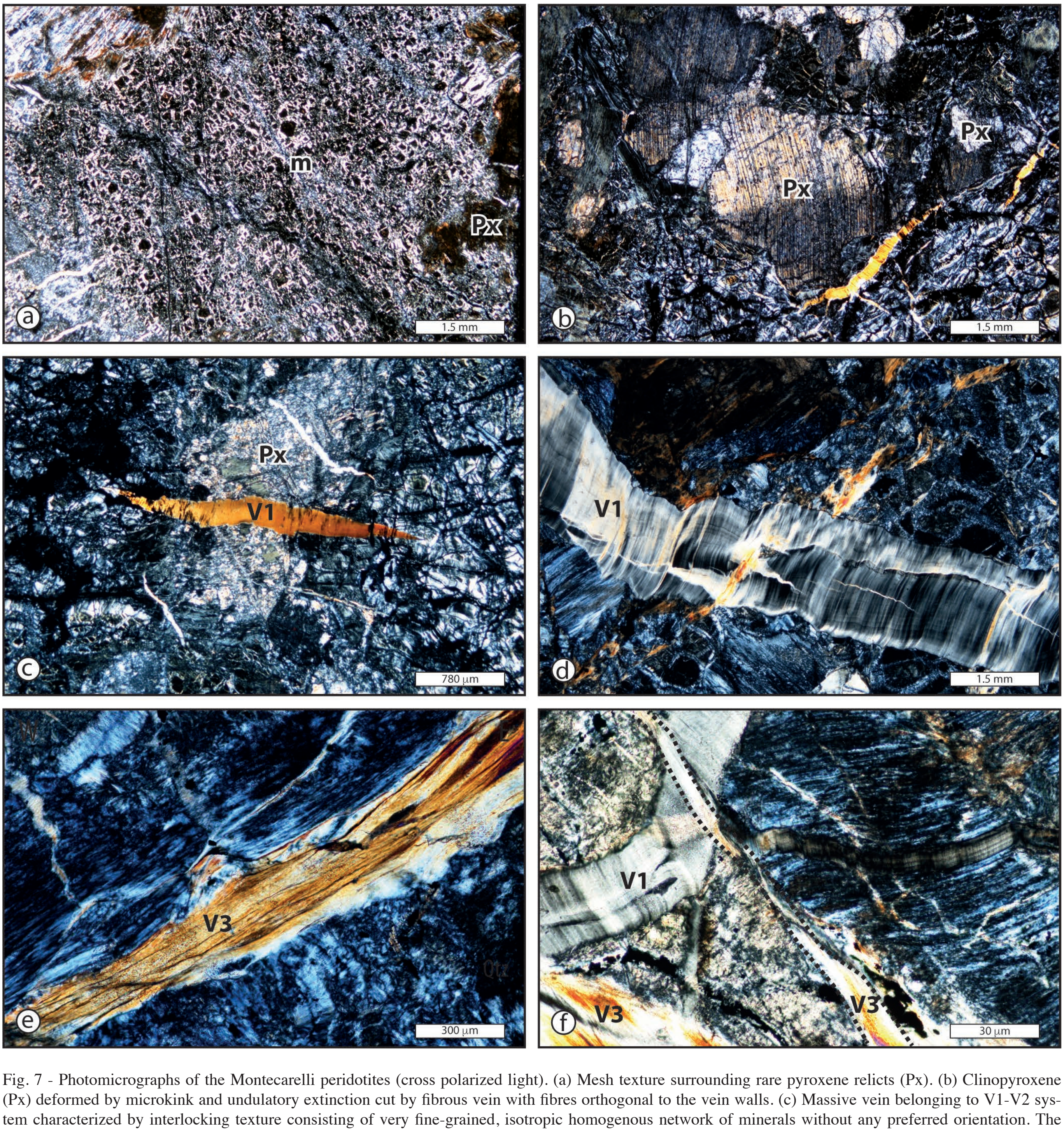

Fig. 7 - Photomicrographs of the Montecarelli peridotites (cross polarized light). (a) Mesh texture surrounding rare pyroxene relicts (Px). (b) Clinopyroxene (Px) deformed by microkink and undulatory extinction cut by fibrous vein with fibres orthogonal to the vein walls. (c) Massive vein belonging to V1-V2 system characterized by interlocking texture consisting of very fine-grained, isotropic homogenous network of minerals without any preferred orientation. The termination occurs as a single tapering. (d) Fibrous vein belonging to V1-V2 system characterized by fibres perpendicular to vein wall and by a well-developed median line. (e) Fibrous vein belonging to V3 system characterized by fibres parallel to vein wall. (f) Fibrous vein belonging to V3 system cutting across a fibrous vein belonging to V1-V2 system.

tip, where bands appear discordant to one of the walls. Crack propagation is not guided by peridotite texture as demonstrated by bastitic minerals crosscut by veins. All these features indicates that these veins were opened by a crack-and-seal mechanism (e.g., Andreani et al., 2004).

The shear veins belonging to V3 and V4 systems are characterized by fibrous infilling with fibres parallel to the vein walls (Fig. 7e, f). These veins are generally characterized by a thickness up to 1 mm but with a significant persistence with single tapering termination. They developed in dilational jogs where fibrous-texture crystals oriented parallel or sub parallel to the vein walls have grown. In several samples these dilational jogs are linked by a bridge of fibrous veins at higher angle with respect to the previous ones.

Mineralogy

X-ray powder diffraction patterns revealed that fibrous veins are mainly composed by antigorite, with only minor amounts of chrysotile, calcite and chlorite group minerals. Chlorite is particularly abundant in the host rocks. The V1-V2 veins are mainly filled by antigorite with minor occurrence of chrysotile and calcite. Only one of the sampled veins from V1-V2 system was found to be mainly formed by chrysotile. Also, the veins belonging to V3 and V4 systems are mainly characterized by antigorite with minor occurrence of chrysotile and calcite.

The identification of serpentine subgroup minerals through X-ray diffraction is based on the seminal paper by Whittaker and Zussman (1956). Fig. 8 shows a comparison between the X-ray diffraction patterns of antigorite and chrysotile from Montecarelli. Some differences can be observed. For instance, in the 2θ region between 33 and 39°, a strong reflection at 2.53 Å occurs in the pattern of antigorite, followed by a weaker reflection at 2.42 Å, whereas chrysotile is characterized by some weak reflections along with a strong reflection at 2.45 Å. According to Whittaker and Zussman (1956), another diagnostic region is that around 2θ = 60°. Indeed, the X-ray powder diffraction pattern of antigorite displays two reflections at 1.56 and 1.54 Å; on the contrary, only a reflection at 1.53 Å can be observed for chrysotile. Minor calcite and "chlorite" are associated with chrysotile (Fig. 8).

Micro-Raman spectroscopy confirmed and improved the results of X-ray diffraction. Indeed, it confirmed the identification of antigorite and chrysotile and allowed the finding of minor amounts of chrysotile in several antigorite-bearing samples, owing to the possibility of collecting data from a single fibre without a preliminary sample preparation (e.g., Bard et al., 1997; Rinaudo et al., 2003). Fig. 9 shows the Raman spectra of antigorite and chrysotile. Both spectra are in agreement with previous studies (e.g., Bard et al., 1997; Kloprogge et al., 1999; Rinaudo et al., 2003; Petriglieri et al., 2015) and allow an unambiguous distinction between these two mineral species, considering the spectral regions between 200 and 1200 cm^{-1} as well as that between 3000 and 3800 cm^{-1}. In particular, the O-H stretching modes occurring in this latter region are usually considered as playing a decisive role

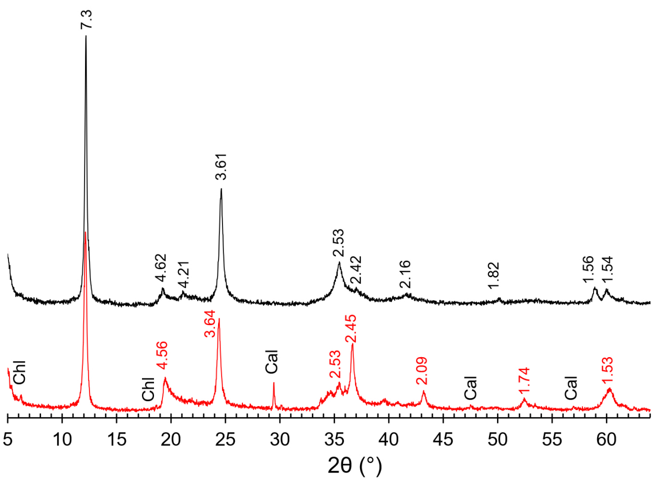

Fig. 8 - X-ray powder diffraction patterns of antigorite (black) and chrysotile (red) from the Montecarelli serpentinites. Both samples are from V3 veins. The *d* values (in Å) of the strongest reflections are shown. Chrysotile is associated with minor calcite (Cal) and chlorite (Chl).

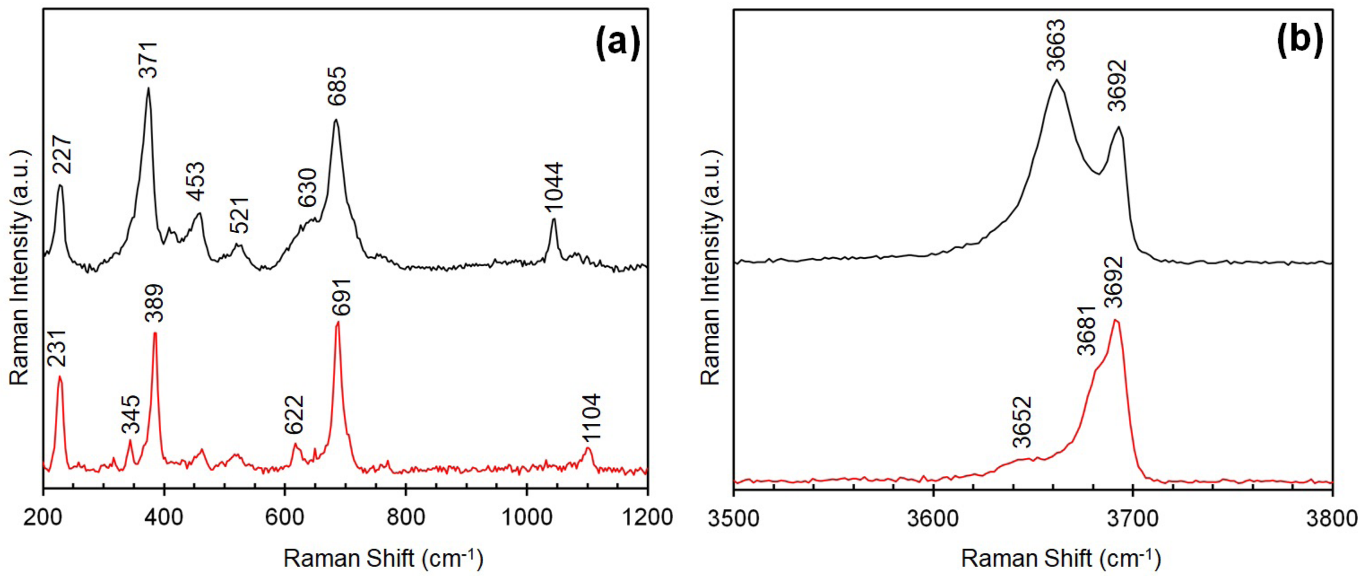

Fig. 9 - Micro-Raman spectra of antigorite (black) from V1-V2 veins and chrysotile (red) from V3 veins of the Montecarelli serpentinites. The position of the main Raman bands are reported (in cm^{-1}).

for a distinction between the different members of the serpentine subgroup (e.g., Petriglieri et al., 2015). In addition, a reliable identification of antigorite is also based on the band occurring at 1044 cm^{-1}, important for a discrimination of this phase from the other serpentine subgroup minerals (Petriglieri et al., 2015).

Electron microprobe analyses were performed on selected samples of antigorite and chrysotile from Montecarelli. The chemical composition of antigorite (in wt% - average of 18 spot analyses) is MgO 40.74(59), SiO_2 40.31(43), FeO_{tot} 2.56(9), NiO 0.05(2), Al_2O_3 0.67(4), MnO 0.06(2), total 84.39, whereas chrysotile has the following chemistry (in wt% - average of 10 spot analyses): MgO 39.49(68), SiO_2 40.43(43), FeO_{tot} 3.93(13), NiO 0.10(2), Al_2O_3 0.82(2), MnO 0.06(2), total 84.83. Assuming the occurrence of an amount of H_2O corresponding to 4 (OH) groups per formula unit and recalculating the Fe^{2+}/Fe^{3+} atomic ratio according to the heterovalent substitution $^{VI}(Mg,Fe)^{2+} + {}^{IV}Si^{4+} = {}^{VI}Fe^{3+} + {}^{IV}Al^{3+}$, the chemical formulae of antigorite and chrysotile are $(Mg_{2.93}Fe^{2+}_{0.07}Fe^{3+}_{0.04})_{\Sigma 3.04}(Si_{1.94}Al_{0.04})_{\Sigma 1.98}O_5(OH)_4$ and $(Mg_{2.84}Fe^{2+}_{0.11}Fe^{3+}_{0.05})_{\Sigma 3.00}(Si_{1.95}Al_{0.05})_{\Sigma 2.00}O_5(OH)_4$, respectively.

DISCUSSION

In the Northern Apennines, both Internal and External Ligurian peridotites are mainly characterized by the widespread crystallization of serpentine minerals such as lizardite and chrysotile. The same picture arises from peridotites of the other areas of the Apennine belt as those detected in the Southern Apennine (Punturo et al., 2015; Bloise et al., 2019). Moreover, in the Internal Ligurian peridotites some minor occurrences of antigorite have been reported (Donatio et al., 2013; Gaggero et al., 2013) whereas in the External Ligurian peridotites this mineral has never been described. The data provided in this paper clearly indicate that the Montecarelli peridotites are characterized by a massive crystallization of antigorite within veins belonging to different systems.

It is important to outline that the peridotites of External Ligurian Units derived from a geodynamic setting completely different to that of Internal Ligurian ones. While the Internal Ligurian peridotites are interpreted as sub-oceanic mantle exhumed in a slow-spreading ridge (e.g., Menna, 2009; Sanfilippo and Tribuzio, 2011; Donatio et al., 2013), the External Ligurian ones represent in fact a subcontinental mantle exhumed at continental margin and exposed at the seafloor during the late stage of rifting (Fig. 10), immediately prior to the opening of the Ligure-Piemontese oceanic basin (e.g., Piccardo et al., 1993; 2002; Rampone and Piccardo, 2000). This exhumation is achieved by extension leading to tectonic denudation of the mantle by lithospheric detachment faults (e.g., Marroni et al., 1998; Marroni and Pandolfi, 2007). This exhumation was also associated to an increase of the magmatic activity leading to localized re-heating of the peridotites by intrusive emplacement of minor gabbroic bodies and extrusion of basaltic flows. These events are associated to pervasive fracturing associated to water circulation leading to crystallization of serpentine minerals into the peridotites, mainly as vein filling (e.g., Picazo et al., 2013).

As indicated by the collected data, the Montecarelli peridotites are characterized by a sequence of veining during which the crystallization of antigorite is largely prevailing. It is important to outline that only a single vein is made up of chrysotile whereas in all the other veins the infilling is represented by antigorite (along with rare chrysotile). These veins belong to several systems, each characterized by geometrical features indicating a stress-controlled origin. Also, the fibrous antigorite detected parallel and perpendicular to vein walls suggests a stress-controlled crystallization of these minerals. No evidence of the age of this crystallization

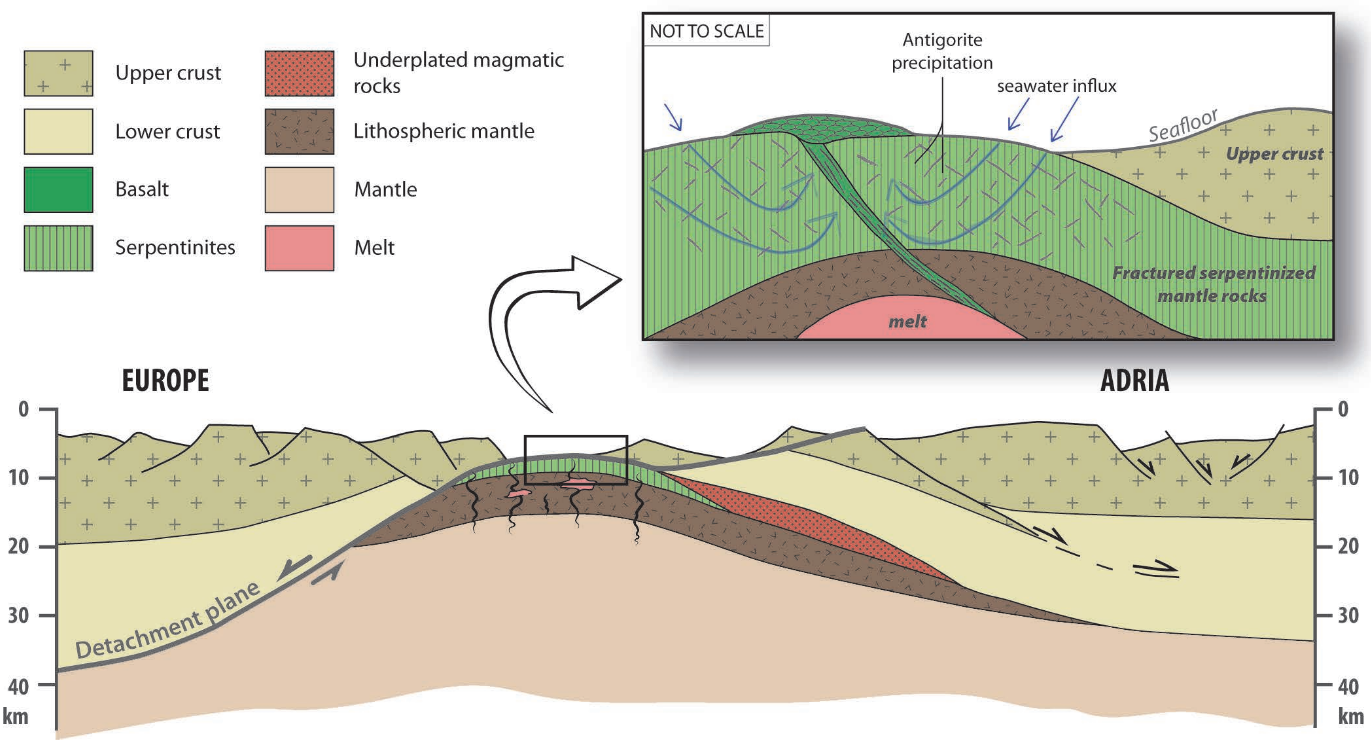

Fig. 10 - Schematic section showing the hypothetic scenario responsible of antigorite crystallization in the Montecarelli peridotite. See text for further discussion.

can be determined in the Montecarelli peridotites, which belong to a slide block without relationships with other lithologies as basaltic dykes or plagiogranite stocks able to provide valuable insights for their age. The crystallization of antigorite cannot however be related to HP-LT metamorphism, as for Alpine one, mainly because the studied peridotites are not affected by deformations (foliation or folds) that are expected in a rock that experienced burial and exhumation in a subduction setting. In the Montecarelli peridotites, the crystallization of the serpentine minerals can be likely interpreted as connected with the late stage of the rifting phase when peridotites were exposed at the surface, intruded by gabbro bodies and cut by basaltic dykes. However, the significance of the crystallization of antigorite in the Montecarelli peridotites remains undetermined.

In the oceanic peridotites several factors have been invoked to explain the presence of antigorite in abyssal samples (e.g., Rouméjon et al., 2019). These factors are: (1) high or increasing temperatures (e.g., Beard et al., 2009; Kodolányi et al., 2012), (2) deformation (e.g., Miyashiro et al. 1969; Ribeiro da Costa et al., 2008), or (3) an addition of dissolved silica (e.g., Rouméjon et al., 2015; Klein et al., 2017).

For the Montecarelli peridotites it is difficult to identify what of these factors was active or if these factors were all effective. The occurrence of antigorite within veins with fibres both perpendicular and parallel to the vein walls indicates a stress-controlled crystallization. A valuable suggestion is represented by a picture where the antigorite crystallization occurred during a tectonic event probably concurrent with an increase of temperature and/or a change in fluid-chemistry that became enriched in SiO_2. The relationships between the crystallization of chrysotile and antigorite are also very difficult to assess, mainly because in thin section these minerals cannot be distinguished. The very scarce occurrence of chrysotile seems to suggest its replacement by antigorite. This hypothesis is coherent with the replacement occurring within the veins that represented permeability pathways where the fluid flow in the serpentinized peridotite is preferentially localized.

We therefore propose with all possible caution a picture where the development of antigorite can be related to the intrusion of gabbro bodies that produced not only a temperature increase but also the circulation of abundant SiO_2-enriched fluids. These fluids can pervasively flow using the existing permeability (i.e., the veins) thus producing the crystallization of antigorite as replacement of chrysotile. Since the small exposure of Montecarelli peridotite, more data collected from other slide blocks of External Ligurian peridotites are necessary to confirm this reconstruction.

CONCLUSIONS

In Northern Apennines, the peridotites from External Ligurian represent subcontinental mantle exhumed at continental margin during the Jurassic rifting. These peridotites are generally highly serpentinized with development of chrysotile and lizardite found into both rockmass and veins. In this paper we provide, for the first time, the proofs of a massive recrystallization of antigorite within the peridotites of Montecarelli from the Leo Unit (cf. Pietra Parcellara Complex by Marroni et al., 2001) belonging to the External Ligurian Units. Antigorite has been found within veins belonging to four systems, from V1 to V4, each characterized by different attitude, and texture. The texture of the veins ranges from massive to fibrous, with the latter characterized by fibres both parallel and perpendiculars to the vein walls. The crystallization of the serpentine minerals cannot be interpreted as related to an orogenic high-pressure metamorphism but most likely can be regarded as developed at shallow structural level in the late stage of the rifting phase, when peridotites were progressively exposed at the surface, intruded by gabbro bodies and cut by basaltic dykes. The increase of temperature is here regarded as responsible of crystallization of antigorite, as detected, for instance, in the peridotites sampled in the modern oceanic basins.

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