SERPENTINIZATION HISTORY IN MANTLE SECTION FROM A FOSSIL SLOW-SPREADING RIDGE SEQUENCE: EVIDENCES FROM POMAIA QUARRY (SOUTHERN TUSCANY, ITALY)

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ABSTRACT

In the Pomaia quarry (Southern Tuscany, Italy) a mantle section consisting of peridotites belonging to the Internal Ligurian units is exposed. This mantle section, that is regarded as representative of the Jurassic oceanic lithosphere of the Ligure-Piemontese oceanic basin, provides the opportunity for a complete reconstruction of the serpentinization history of the peridotites by studying of the systems of serpentine-bearing veins.

The tectono-magmatic history reconstructed for the peridotites includes the development of tectonitic textures followed by the intrusion of gabbro dykes and stocks. Subsequently, the gabbros as well as their boundaries with the peridotites are cut by high-T mylonitic shear zones, and then by thick cataclastic shear zones. The peridotites are cut by several systems of serpentine-bearing veins originated in the host rocks after the intrusion of gabbroic melts. All the structural, petrographic and mineralogical data, indicate that in the studied mantle a sequence of veins sequence developed. This sequence includes: 1) veins filled by lizardite with blocky texture 2) veins filled by chrysotile with both blocky and fibrous texture and 3) veins filled by antigorite.

This paper provides for the first time the evidence that the serpentinization in the peridotites from the Internal Ligurian units is associated to a sequence of different events of veining. These events developed in response to a history dominated by alternance of tectonic-controlled and magmatic-controlled hydration of the peridotites in a slow-spreading ridge setting. According to this reconstruction, the Pomaia peridotites represents the core of a megamullion built-up during an oceanic extensional tectonic stage in in a slow-spreading ridge system.

INTRODUCTION

The slow- and ultra slow-spreading mid-oceanic ridges (< 20 mm/year) are characterized by extensional tectonics in order to balance the low amount of magmatic budget, as documented since long time (e.g., Cannat, 1993). The oceanic crust in these settings is characterized by large exposures of serpentinized mantle rocks accreted to the crust and exhumed up to seafloor as recognized, for instance, in the Mid-Atlantic Ridge (e.g., Canales et al., 2004) or in the South-West Indian Ridge (e.g., Dick, 1989). The exhumation history of the mantle and its accretion to the crust are associated to ductile to brittle deformation during massive hydration leading to pervasive serpentinization (e.g., Mével, 2003).

The ophiolite sequence of Internal Ligurian units from Northern Apennine is commonly regarded as the best fossil example of the modern oceanic crustal sequences generated at a slow- and ultra slow-spreading mid-oceanic ridge (e.g., Lagabrielle and Cannat, 1990 and Treves and Harper, 1994). As observed in modern analogues, the basement of the Northern Apennine ophiolite sequence is represented by peridotites that experienced a long magmatic, metamorphic and deformation history related to their unroofing and exposure at the seabottom as oceanic core complexes (Lagabrielle and Cannat, 1990; Treves and Harper, 1994; Lagabrielle and Lemoine, 1997; Tribuzio et al., 2000; 2004; Menna, 2009; Sanfilippo and Tribuzio, 2011). During their progressive unroofing, the peridotites are affected by multisteps long-lived serpentinization processes in both magmatic and non-magmatic stages.

Despite the importance of the peridotites for the reconstruction of the oceanic history of the Northern Apennine ophiolites, accurate and multidisciplinary description of the serpentinization history of the peridotites is lacking at all.

In this paper a serpentine-bearing vein sequence in the peridotites (Internal Ligurian units, Southern Tuscany, Italy) from the inactive Pomaia quarry (Fig. 1) has been investigated in order to provide a detailed reconstruction of the serpentinization history in a fossil analogue of a modern slow-spreading ridge.

THE INTERNAL LIGURIAN OPHIOLITES AS FOSSIL SLOW-SPREADING OCEANIC CRUST

The Internal Ligurian units (Fig. 1) occur in an uppermost structural position at the top of nappe pile cropping out along the western side of the Northern Apennine (Marroni et al., 2010) and in Corsica Island as well (Marroni and Pandolfi, 2003). They are regarded as representative of the oceanic crust issued from the Ligure-Piemontese basin, a small oceanic area opened in the Middle Jurassic time between the Europe and Adria continental margins and subsequently affected by convergence in the Late Cretaceous (Decandia and Elter, 1972). The convergence led to an intraoceanic subduction followed by a continental collision in the Middle Eocene when the oceanic area was completely consumed, at least in the northern domains of the Ligure-Piemontese basin (Marroni et al., 2010, and references therein). The Internal Ligurian units include (Fig. 2) a Middle to Late Jurassic ophiolite sequence covered by Jurassic to Paleocene pelagic to turbiditic deposits (e.g., Elter 1975). The sedimentary cover of the ophiolites displays evidence of a pre-Oligocene, polyphase structural evolution under metamorphic conditions ranging from very low-grade to blueschist facies (e.g., Marroni, 1991). This structural

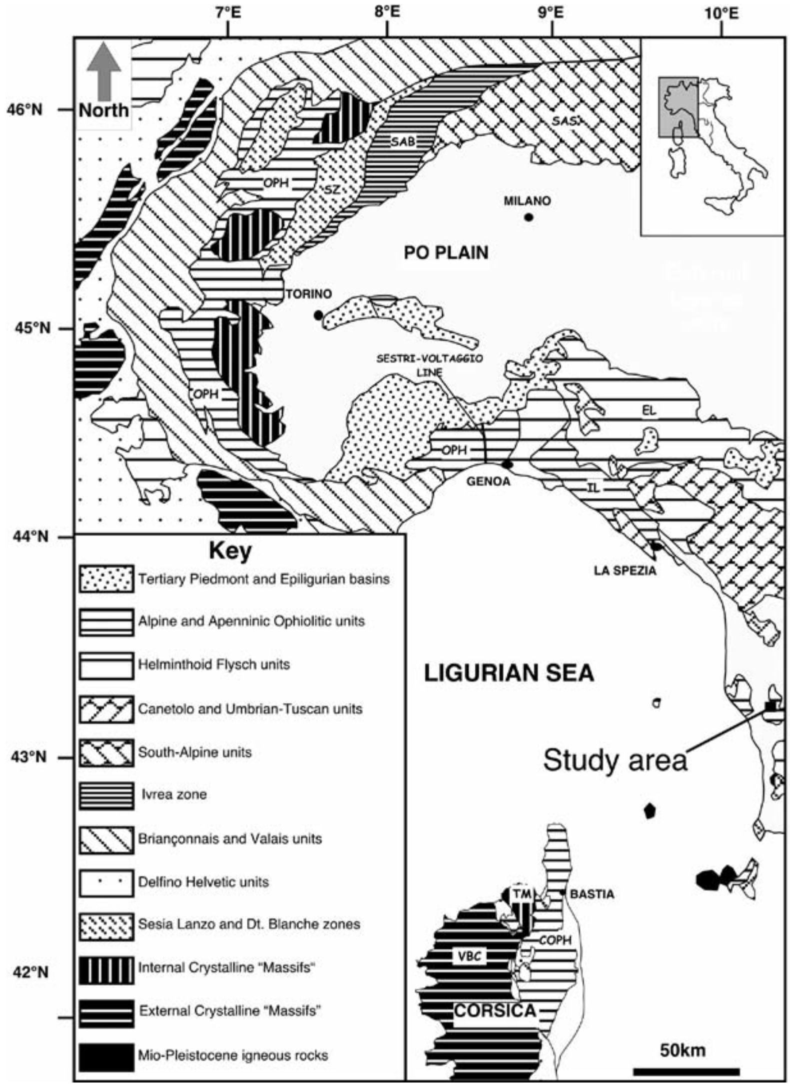

Fig. 1 - Tectonic sketch map of the Western Alps, Northern Apennine and Corsica. The location of the study areas is indicated. COPH: Schistés Lustrés of Corsica, EL: External Ligurian units, IL: Internal Ligurian units, OPH: Sestri Voltaggio, Voltri Group, Piemontese units, SAB: South Alpine basement, including Ivrea and Canavese zones, SAS: south Alpine sedimentary cover, SZ: Sesia zone, TM: Tenda Massif, VBC: Variscan basement of Corsica (from Marroni and Pandolfi, 2007).

evolution is assumed to reflect a deformation history that includes underthrusting, underplating and exhumation within the accretionary wedge associated with Alpine subduction (e.g., Marroni et al. 2004). In the Southern Tuscany, a well preserved ophiolite sequence crops out (Bortolotti, 1983), mainly in the Monti Livornesi and Monti of Castellina Marittima areas. In the latter area, the ophiolite sequence is affected by very-low grade metamorphism, with T estimated as ranging between 150° and 200°C by illite and chlorite crystallinity and by calcite twinning (Leoni and Marroni, unpublished data). The ophiolite sequence, reconstructed by an assemblage of the sequences cropping out in different areas, is less than 1 km thick (Cortesogno et al., 1987). It represents a relatively thin oceanic basement nappe, that includes serpentinized mantle peridotites intruded by gabbros and covered by a volcano-sedimentary complex consisting of basaltic flows, interfingering with ophiolitic breccias and sediments (Fig. 2). However remnants of sheeted dyke complex as well as occurrences of 1.5 km thick gabbroic sequence have been found, respectively, in the Elba Island (Bortolotti et al., 2001) and in the Corsica Island (Sanfilippo and Tribuzio, 2012).

The peridotites consist of moderately depleted clinopyroxene-poor spinel lherzolites, that underwent static recrystallization under spinel-facies conditions (T ranging from 1100 to 1250°C; Rampone et al., 1996). The mantle peridotites, characterized by pyroxenite layers and minor dunitic lenses, are intruded by a shallow-level gabbroic complex and cut by widespread gabbro dykes (Beccaluva et al., 1984; Rampone et al., 1998; Rampone and Piccardo, 2000; Piccardo et al., 2004). The gabbroic complex consists of large, up to several kilometre-wide bodies, volumetrically dominated by isotropic olivine-bearing gabbro showing small lenticular bodies of layered melatroctolites and troctolites (Tribuzio et al., 2000, and references therein). Chromitite layers or pockets also occur in the largest layered gabbros bodies. The gabbros as well as the serpentinites are cut by Fe-Ti-oxide gabbro, diorite and plagiogranite dykes and small stocks (Serri, 1980). A Sm/Nd age of 164±14 Ma on whole rock and clinopyroxene from gabbros, interpreted as the age of igneous crystallization, has been obtained by Rampone et al. (1998). In addition zircons separated from plagiogranites yielded an U/Pb age of 153±0.7 Ma (Borsi et al., 1996). Both mantle peridotites and gabbros are cut in turn by basaltic dykes showing a N-MORB geochemical signature (Cortesogno and Gaggero, 1992). The top of the peridotites is formed by ophicalcites (Levanto Breccia), regarded by Treves and Harper (1994) as a tectono-hydrothermally altered shear zone partly reworked at its top into a sedimentary breccia (Framura Breccia).

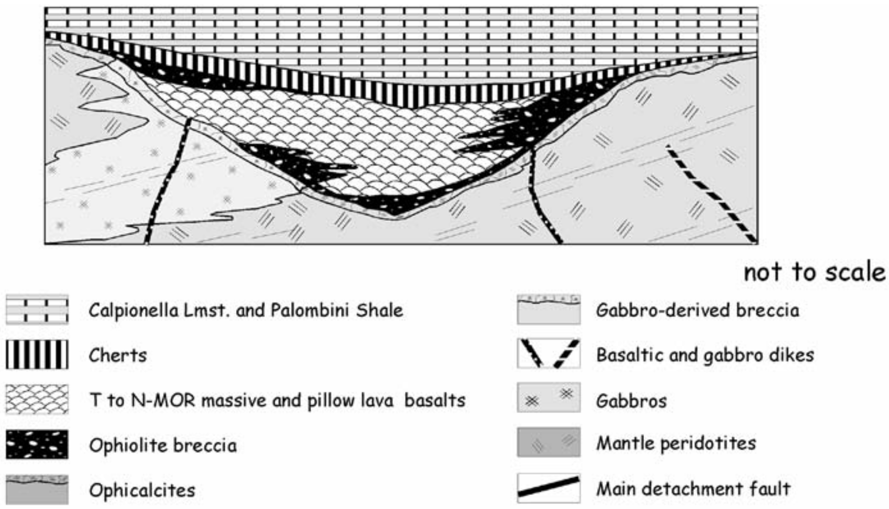

Fig. 2 - Reconstruction of the succession of the Internal Ligurian units (modified after Marroni and Pandolfi, 2007).

For the gabbros, a polyphase, ductile to brittle tectono-metamorphic history can be reconstructed for the time after their emplacement (Cortesogno et al., 1994). This history includes a first phase of ductile, localized deformation that produced flaser (gneissic) textures and folding in the gabbros and the host lherzolites (Molli, 1994; 1995). The second phase, represented by hornblende+plagioclase-filled fractures, is followed by a third phase during which brittle normal faults with the formation of cataclasites developed. Deformation was accompanied by retrograde metamorphism reflecting conditions from upper amphibolite (T ranging from 730°-660° to < 500° and P < 0.3 GPa) to lower amphibolite and upper greenschist (T < 300° and P < 0.1-0.2 GPa) facies (Messiga and Tribuzio, 1991; Riccardi et al., 1994, Tribuzio et al., 1997). Frequently, the contact between gabbro and serpentinite is a fault developed in the oceanic environment during the last phase (Cortesogno et al., 1987; Principi et al., 2004).

Where the ophiolite sequence is well developed, the basement is overlain by a volcano-sedimentary complex, up to 400 m thick, that generally includes the Lower and Upper Ophiolitic Breccias separated by basaltic flows (Cortesogno et al., 1987 and quoted references).

The Lower Ophiolitic Breccias are characterized by fragments of serpentinites (Framura Breccia and Casa Boeno Breccia) Fe-gabbros or diorites (Mt. Capra Breccia), interfingering with rare layers of pelagic sediment. The intervening basalts, up to 200 m thick, are mainly pillow-lavas and pillow breccias, but locally sills with a massive texture have been observed. The geochemical parametres indicate that also these basalts are of N-MORB type. The magmatic activity with its important advection of heat induced widespread hydrothermal metamorphism, reaching greenschist to lower amphibolite facies. The basalts are interlayered with or overlain by the Upper Ophiolitic Breccias characterized by fragments of flaser gabbro (Mt. Zenone Breccia) or serpentinite (Mt. Bianco Breccia); however, polymict breccias (Movea and Mt. Rossola Breccias) characterized by fragments of basalt, gabbro and peridotite also occur (Principi et al., 2004). The age of the volcano-sedimentary complex ranges from late Bajocian/early Bathonian to late Bathonian/early Callovian (e.g., Chiari et al. 2000 and references therein). The Upper Ophiolitic Breccias are directly overlain by pelagic deposits represented by cherts (Mt. Alpe Cherts, late Bajocian/early Bathonian to Tithonian), Calpionella Limestones (Early Cretaceous) or Palombini Shales (Early to Late Cretaceous) (Marroni and Perilli, 1990; Chiari et al. 2000; Perilli and Nannini, 1997). Locally, the thickness of the volcano-sedimentary sequence is reduced to a few metres or to zero. In this case, the ophicalcites or the gabbros are directly overlain by the sedimentary rocks.

THE PRE-OROGENIC TECTONO-MAGMATIC HISTORY OF THE INTERNAL LIGURIAN OPHIOLITES

The ophiolite sequence reconstructed in the Internal Ligurian units is regarded as a fossil oceanic sequence developed in a slow-spreading ridge.

The occurrence of peridotites and/or gabbros directly covered by pelagic sediments indicates structures that can be interpreted as fossil core complexes, analogous to those recognized in modern oceanic areas (e.g., Bonatti et al., 1971; Engel and Fisher, 1975; Karson, 1990; 1998). In these areas, these structures can be interpreted as developed at very slow-spreading ridges, where the intrusive and volcanic activities are spatially and temporally variable along ridge segments because of the low magma budget. This low magma supply may lead to increase tectonic partitioning of sea-floor spreading and significant thinning and denudation of oceanic crust that promotes the formation of core complexes (Sinton and Detrick, 1992; Tucholke and Lin, 1994; Tucholke et al., 2008; Blackman et al., 1998; Buck et al., 2005). As outlined by Michael et al. (2003), Dunn et al. (2005), Ildefonse et al. (2007), Tucholke et al. (2008) and Cipriani et al. (2009), the very slow-spreading ridge are thus dominated by a sequence of amagmatic and magmatic stages.

During the amagmatic stage (e.g., Michael et al., 2003; Dunn et al., 2005 and Ildefonse et al., 2007) the oceanic core complexes are represented by exhumed lower crustal and upper-mantle rocks, i.e., peridotites and gabbros, in the footwalls of extensional detachment faults. The extensive, exhumed footwall of these detachment faults rotates and flattens in response to isostatic forces, creating a cross-sectional profile like that of a rolling hinge. These large, exhumed footwalls, termed megamullions, represent poorly deformed bodies bounded by shear zones where the strain localization mechanisms lead to high temperature ductile fabrics in gabbros and peridotites. When the footwalls of extensional detachment faults are close to the exposure, the ductile deformation changes to brittle ones, with pervasive fractures that induce localised fluid circulation and vein opening. On the ocean floor, interaction of seawater with ultramafic rocks results in the incorporation of marine carbonate into the shallow oceanic lithosphere (Früh-Green et al., 2003; Kelley et al., 2001; 2005; Ludwig et al., 2006). In the following magmatic stage (e.g., Ildefonse et al., 2007; Tucholke et al., 2008 and Cipriani et al., 2009) the oceanic core complexes are intruded by new magma input with emplacement of basaltic flows and dykes.

This mechanism produces a lithospheric architecture that is distinct from the layered, Penrose-type ophiolite sequence (e.g., Dilek et al., 1998). Thus, the mid-ocean ridges with intermittent magma supply are characterized by a basement consisting of isolated gabbro intrusions within serpentinized peridotites exposed at the core of the megamullions and covered by discontinuous volcanic cover and widespread ophiolite breccias (e.g., Cannat, 1993; 1996).

This architecture is anologous to that reconstructed in the Internal Ligurian ophiolites (Lagabrielle and Cannat, 1990; Treves and Harper, 1994; Lagabrielle and Lemoine, 1997; Menna, 2009) where the basement, consisting of serpentinites with gabbro multiple intrusions, was exposed at the seafloor in correspondance of the center of megamullion. In this frame, the gabbros represent the remnants of the oldest magmatic phase before the inception of the extensional tectonics developed during the amagmatic phase (Fig. 3). The proofs of this phase is represented by the ophicalcites, found at the top of the serpentinites and regarded by Treves and Harper (1994) as a tectono-hydrothermal altered shear zone corresponding the extensional detachment fault. Also the ductile shear zones in gabbros (Cortesogno et al., 1994) showing an attitude like that of the layering and the magmatic foliation can be regarded as structures synthetic to the main detachement fault. After the development of the oceanic core complex, a new magmatic pulse occurred as testified by the occurrence of basaltic dykes in both peridotites and gabbros and by emplacement of magmatic flows over them (Cortesogno et al., 1987; Principi et al., 2004).

THE SERPENTINIZED MANTLE SECTION OF POMAIA QUARRY

Field data

The studied mantle section crops out in the Pomaia quarry that provides an exceptional exposures of the peridotites (Fig. 4a). This quarry is located in the western side of the Castellina Marittima Mts., Southern Tuscany (Fig. 4b). In this quarry the mantle rocks of the ophiolite sequence belong to Internal Ligurian units, that are well preserved in a horst-bounded by two north-south trending, high-angle normal fault developed during the Mio-Pliocene opening of the Tyrrhenian basin. In this area, the ophiolites, folded together with the sedimentary cover, are unconformably covered by Late Miocene, post-orogenic deposits. Westward of the Pomaia quarry, the mantle rocks are covered by basalts, but their relationships are not clear.

The mantle section consists of serpentinized peridotites showing tectonitic texture marked by oriented, mm-size pyroxene crystals (Fig. 5a). Bands of dunites as well as rare pyroxenites veinlets also occur. The serpentinization occurs over discontinuous patches with an increase toward the boundaries of the main body. However, the peridotites are not completely serpentinized with the total disappearance of primary minerals; the serpentinization extent is variable, with differences in the same lithotype over few meters.

The peridotites are cut by gabbro dykes (Fig. 4b) and intruded by a gabbro stock. The dykes consist of 5 to 30 cm thick bodies of fine- to medium-grained gabbro. These dykes show a NW-SE trend with subvertical attitude, even if subhorizontal dykes have been found (Fig. 6a). The persistence of these dykes clearly indicate that the orogenic deformation is poorly developed in the studied mantle section. The stock occurs as 50-60 m width lenticular bodies consisting of gabbro with medium- to coarse-grained texture. In its northern side, the gabbro stock is separated by peridotites by a shear zone developed under high-T conditions metamorphism. The

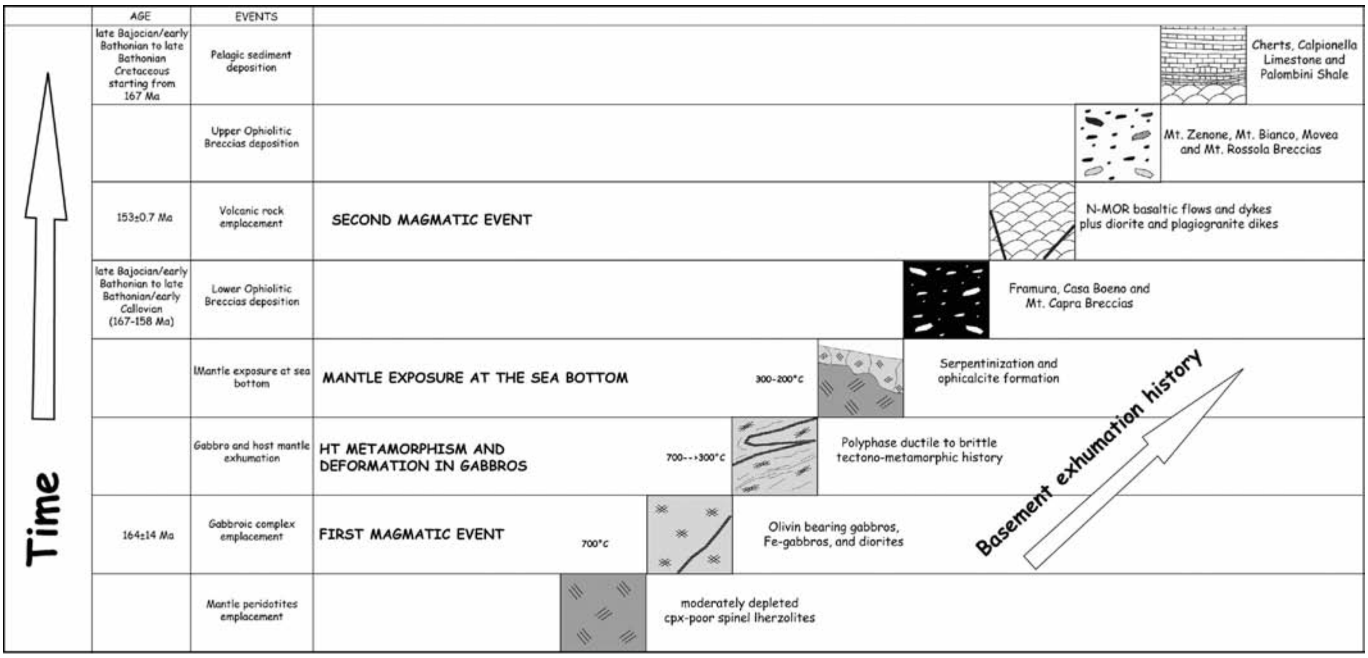

Fig. 3 - Simplified model of the oceanic domain based on data from the Internal Ligurian units and the Schistes Lustrés complex of Corsica. Observed field relationships are indicated by boxed areas (from Marroni and Pandolfi, 2007); d- Main tectono-metamorphic and sedimentary events recognized in the succession of the Internal Ligurian units. Age data from Borsi et al. (1996), Rampone et al. (1998), Chiari et al. (2000) and references therein.

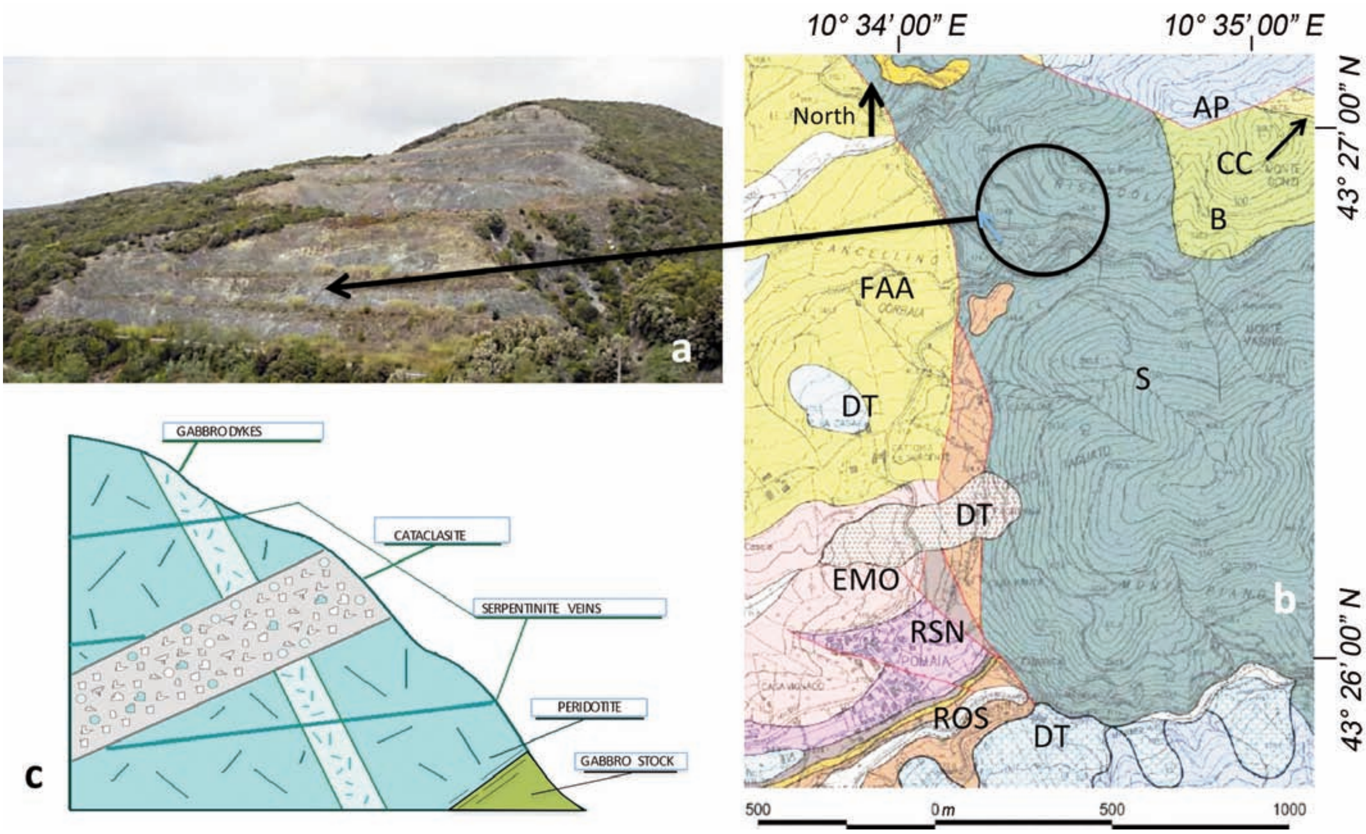

Fig. 4 - a) view of the Pomaia quarry; b) geological map of the area sorrounding the Pomaia quarry. The localization of the Pomaia quarry is evidenced by the circle (S- peridotites; B- basalts, CC- Calpionella Limestone (Berriasian-Valanginian), AP- Palombini Shales (Valanginian-Santonian); FAA- Shales (Pliocene); EMO- Shales and chalks (Miocene); RSN- Chalks (Miocene), ROS- Limestones (Miocene); DT- Debris and landslides; c) sketch of the relationships among the different lithotypes identified in the Pomaia quarry.

gneissic texture is highlighted by a well developed foliation consisting of elongated plagioclase and olivine, where porphyroclasts of pyroxene occur. In this lithotype the ductile deformation of plagioclase and amphibole indicate high-T conditions of metamorphism associated with ductile deformation. The peridotites as well as the gabbro dykes and stock are cut a complex network of veins (Fig. 5c) filled by serpentinite minerals. Finally, the peridotites, the gabbros and the serpentinite veins are cut by brittle shear zones consisting of up to 2-3 m thick cataclastic rocks made up of up to cm-sized angular fragments of peridotites and gabbros in a carbonate matrix (Fig. 5d). In the cataclastic rocks cm-size fragments of dark green fibrous serpentine minerals are found. These shear zones show evidence of rotated fragments, that in some places are arranged in aligned trains parallel to shear zone walls. The cataclastic shear zones show a main attitude with NW-SE trend and both subvertical and subhorizontal dipping (Fig. 6b). The whole mantle section is finally cut by a set of fractures without evidence of infilling or displacement along them. These fracture systems have been recognized also in the ophiolite sedimentary cover.

On the whole, the tectonomagmatic history reconstructed for the peridotites includes the development of tectonitic textures followed by the intrusion of gabbro dykes and stocks. Subsequently, the gabbros as well their boundaries with the peridotites are cut by high-T mylonitic shear zones, in turn deformed by thick cataclastic shear zones. Field data point out that the network of serpentine-bearing veins in the peridotites originated after the intrusion of gabbros and until the development of the cataclastic shear zone. This history can be compared to that reconstructed by Cortesogno et al. (1987) and Menna (2009) in the Bracco area (Fig. 3).

Vein sequence in the peridotites

The studied peridotites are cut by several systems of veins. Along the veins a dark halo where the serpentinization increases is common. All the vein types show good continuity with persistance up to several metres, whereas their termination occurs generally by a single tapering. The veins can be subdivided in the field according to the mesoscopic features of their infillings. Some veins show a blocky infilling (Fig. 5e) whereas the others are filled by fibers of serpentine minerals found at both high- or at low-angle to the walls (Fig. 5f). In the veins showing fibers subperpendicular of the vein wall, structures as median line or alignement of detached fragments parallel to the walls can be easily observed. In addition, veins showing a blocky-textured infilling coexisting with fibrous-rich wall are observed. The blocky vein systems show a scattered distribution even if a prevailing subhorizontal attitude can be identified (Fig. 6c). In contrast, the fibrous veins are arranged in three well distributed trends, respectively subhorizontal, NW-SE with NE dipping and NW-SE with SW dipping (Fig. 6c). The blocky veins range in colour from pale greenish to whitish, whereas the fibrous ones are whitish or grey-greenish. In summary, five types of veins have been sampled for petrographical and mineralogical analyses. According to crosscutting relationships a timeline of development of these veins has been reconstructed. This timeline, from the oldest to the youngest veins, is reported hereafter:

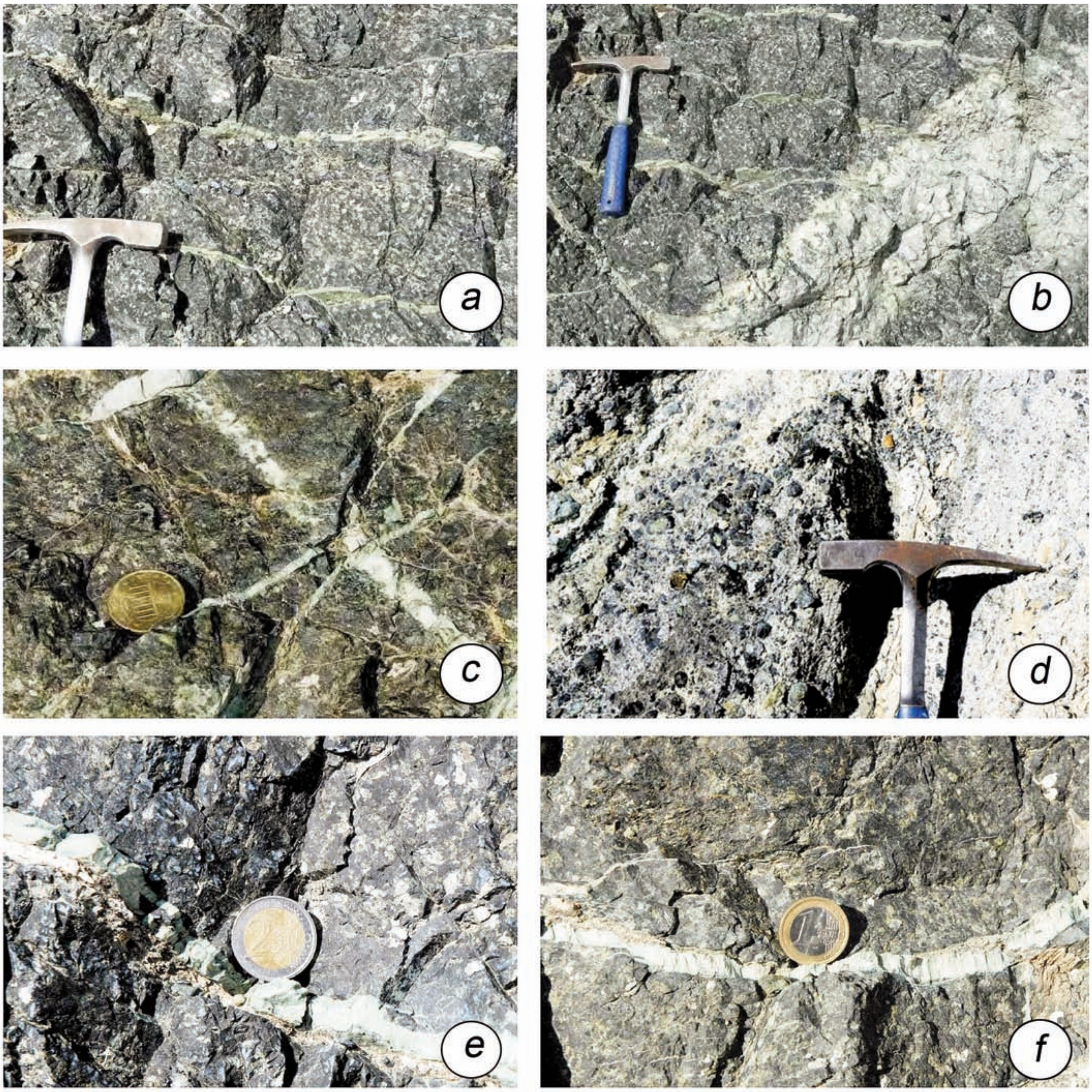

Fig. 5 - Mesoscale features of the main lithotypes from the Pomaia quarry: a) peridotites; b) peridotites cut by gabbro dykes; c) gabbro dykes cut by veins filled by serpentine veins; d) cataclasites, e) blocky veins; f) fibrous veins.

1) Type A (veins with pale greenish blocky infilling)
2) Type B (veins with whithish blocky infilling)
3) Type C (veins with whitish fibrous infilling)
4) Type D (veins with composite infilling consisting of pale greenish blocky core sorrounded by whitish fibrous boundaries)
5) Type E (veins with grey-greenish fibrous infilling)

Microscale features of the lithotypes

Peridotites

These rocks can be classified as lherzolites according to their primary assemblage consisting of olivine, orthopyoxene, clinopyroxene and spinel (Fig. 7a). Diffuse but not pervasive serpentinization phenomena determine a diffuse recrystallization of the lherzolites, mainly at the expenses of olivine and orthopyroxene. Based on their pseudomorphosic textures (Cortesogno et al., 1987; Tribuzio et al., 2004), our lherzolitic samples formed after the serpentinization of a mineral assemblage consisting olivine (50%), orthopyroxene (10-30%), clinopyroxene (0-20%), red-brown chromite and green aluminium spinel (< 4%). The primary texture was tectonitic with large, oriented porphyroclasts of orthopyroxene in fine-grained recrystallized granoblastic aggregated of pyroxene and olivine.

At the microscale, olivine is almost entirely transformed in serpentine minerals in the mesh, textured domains, whereas the pyroxenes are partially trasformed in bastites. Spinel remains unaltered also in the more serpentinized samples.

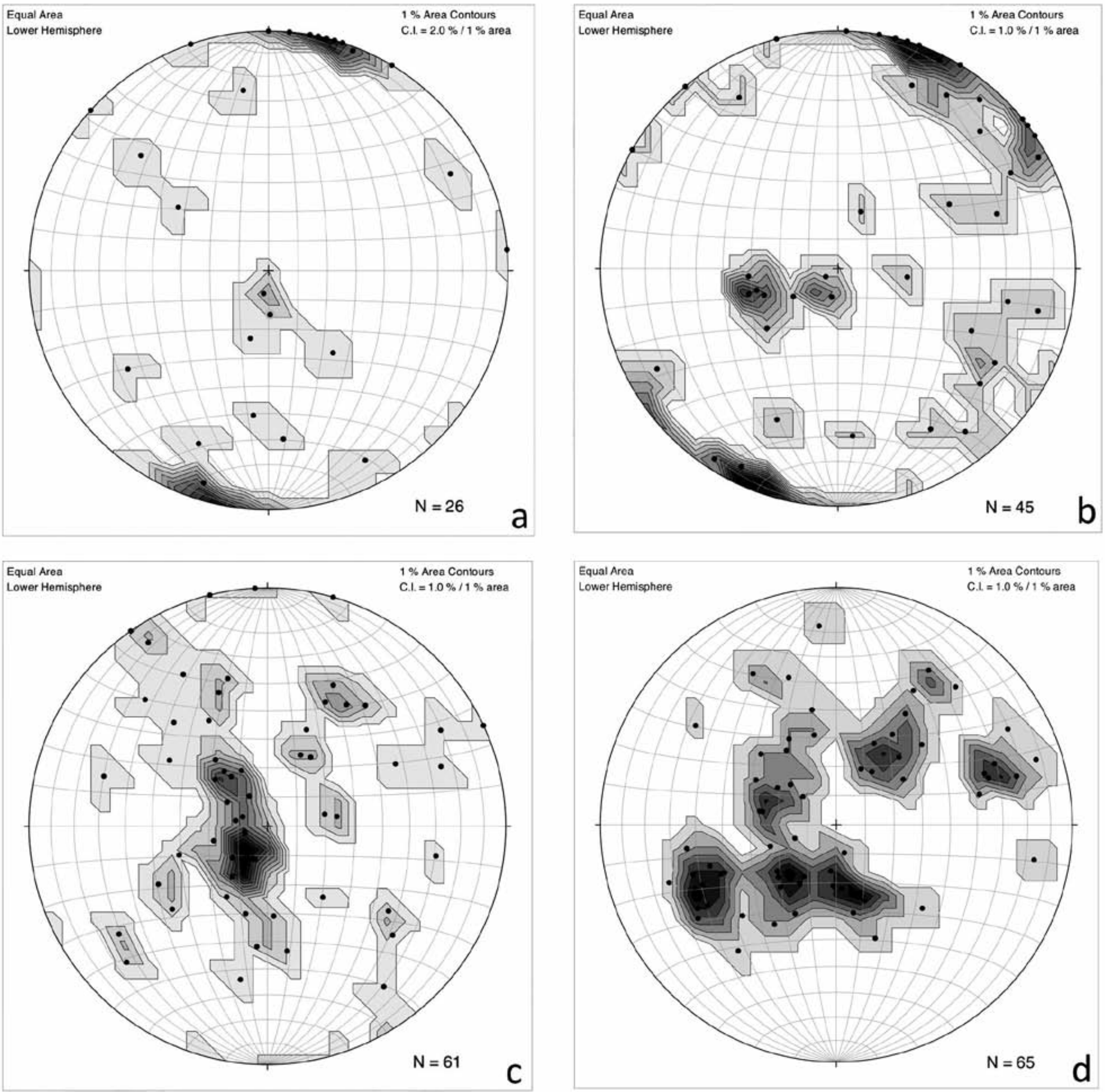

Fig. 6 - Stereographic projections (lower emisphere, Schmidt net) of the main structural elements from Pomaia quarry: a) gabbro dykes; b) cataclastic shear zones; c) blocky serpentine-bearing veins; d) fibrous serpentine-bearing veins.

Olivine is totally replaced by serpentine in the mesh-textured domains, whereas the pyroxenes are trasformed in bastite. In the typical mesh texture (Fig. 7b), the olivine is broken and replaced by concentric rims of serpentine aggregates (Fig. 7c); cores of olivine are still observable in the largest fragments. Bastite consists of fine-grained aggregates of serpentine fibers that replaced and mimicked the pyroxene.

Gabbros

These rocks can be defined as pyroxene-bearing gabbros consisting of plagioclase (about 70% of total rock), pyroxenes and minor olivine and Fe-oxides (Fig. 7d). The gabbros show coarse granular ipidiomorphic texture, with idiomorphic plagioclase and interstitial to poikilitic clinopyroxene. The plagioclases show anorthite to andesine-labradoritic composition, whereas the pyroxene (about 25%) is mainly represented by clinopyroxenes (diopside) with orthopyroxenes exsolutions. Rarely, small inclusions of red-brown amphiboles (Ti-pargasite) have been observed. Olivine (< 10%), is almost completely transformed to tremolite + talc, eventually with chlorite rims when in contact with plagioclase (Cortesogno et al., 1994; Cortesogno and Gaggero, 1997). Ilmenite, Ti-oxide, chromium spinel and rare apatite also occur.

Gneissic gabbros

These rocks represent gabbros affected by remarkable internal mineralogical and microstructural re-organization,

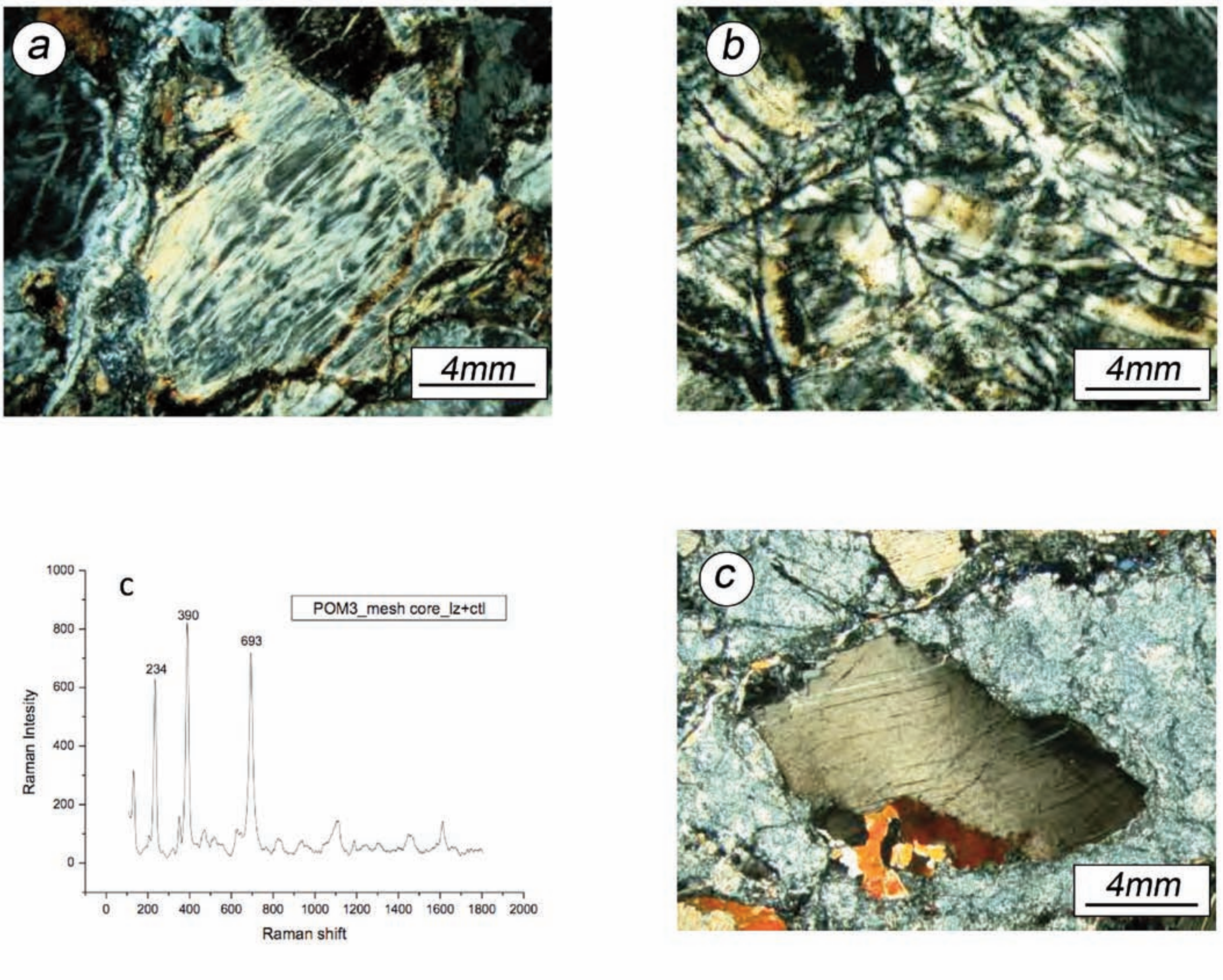

Fig. 7 - Microscale features of the main lithotypes from the Pomaia quarry: a) bastite from peridotite; b) mesh texture from peridotite; c) microRaman analyses of the peridotites showing the occurrence of lizardite and chrysotile; d) gabbro texture with a pyroxene relic.

attaining a well-defined mylonitic fabric. A decrease of the grain size, together with a progressive development of a more defined foliation can be observed in the core of the shear zone. The texture consists of an alternance of mm-sized plagioclase- and pyroxene-rich levels. Magmatic relics, mainly consisting of rounded pyroxene crystals, are often preserved from metamorphic recrystallization. In the plagioclase-rich levels the primary minerals underwent complete recrystallization, forming polygonal aggregates with 120° triple junctions. The pyroxene-rich levels, that are more or less continuous, are characterized by the presence of clinopyroxene porphyroclasts, surrounded by aggregates of new granoblastic clinopyroxenes (0.1-0.2 mm) growth in the pressure shadows. Brown hornblende is also present.

Cataclasites

In thin section the cataclasites occur as mm- to cm-sized fragments consisting of peridotites, gabbros and serpentine-rich veins showing both blocky and fibrous infillings. The matrix is represented by smaller fragments lithologically analogous to that of larger dimension. The cement is mainly represented by calcite, but preexisting fibrous serpentine minerals recrystallized around some peridotite fragments have been observed.

Microscale features of the vein systems

In the field, five types of veins have been detected according the features of the infilling (fibrous vs. blocky) and the related colour (pale-greenish vs. whithish vs. grey-greenish). These five types has been investigated by polarized-light microscopy, standard powder X-Ray diffraction (Philips PW-1830 at Dipartimento di Scienze, Università di Pisa), and microRamam spectrometry (Jobin Yvon LabRam with 632.8 nm laser, at Centro Interdipartimentale Scansetti, Università di Torino) in order to determine the mineralogy of the serpentine minerals. Fibers images have been acquired at scanning electron microscope (PHILIPS XL30 at Dipartimento di Scienze, Università di Pisa). These types are described herebelow according the timeline observed in the field:

Type A veins: in thin section these veins have a sub-mm thickness wickly changing across a single thin section, whereas their termination occurs as a single tapering (Fig. 8a). These veins are characterized by an infilling consisting of very fine-grained, isotropic homogenous network of minerals. MicroRamam spectrometry pointed out the lizardite nature of the vein mineral (Fig. 8b). These veins are cut by all the types of fibrous veins.

Type B veins: these types of veins range in thickness from few mm to 1-3 cm. They are characterized by a homogenous infilling characterized by high birifringence that observed at very high magnification appears as a continous network of crystals without any preferred orientation, that can be defined as blocky texture (Fig. 9a). The boundary of these veins are sharp without discontinuities. Fragments of the wall randomly enclosed in the infilling can be observed. XRD analysis show the serpentine peaks, and microRamam spectrometry reveal chrysotile peaks (Fig. 9b).

Type C veins: these veins are characterized by mm thickness and by a significant persistance with single tapering termination. At both macro- and microscopic scale, the thickness is variable, even on short distance. However, the most prominent feature of these veins, best seen at high magnification, is their infilling consisting of fibers arranged perpendicularly or subperpendicularly to vein walls (Fig. 10a) with fibers of micrometric thickness ten of micrometers long (Fig. 10c and d). These veins do not show crystallographic relationships with the vein walls and the veins can be defined as antitaxial type according to Ramsay (1980). Finely spaced banding parallel to vein walls are reproduced by the same chrystallographic orientation of the different segments of the fibers. In addition, all the fibrous veins are commonly characterized by median lines and bands of wall rock fragments parallel to the bands. No inclusions or second phases are observed within these trails so they are only extinction figures. The internal structure of the vein is often asymmetric close to the tip, where the bands appear discordant to one of the walls. Crack propagation is not guided by peridotite texture as demonstrated by bastite minerals crosscut by veins. These structures correspond to median line and inclusion bands of wall rock fragments described by Ramsay (1980) in calcite- and quartz-filled fibrous veins. All these features indicate that these veins were opened by crack-and-seal mechanism (e.g., Andreani et al., 2004). XRD analyses of the vein infilling show the serpentine peaks, which can be attributed to chrysotile polimorph after microRamam spectrometry investigations (Fig. 10b). These veins cut the chrysotile blocky veins, even if the latters cutting the fibrous ones are also recognized. Thus, crosscutting relationships between B blocky and C fibrous chrysotile veins can be etablished.

Type D: these veins are characterized by two different infillings (Fig. 11a). The core consists of blocky lizardite infilling whereas at the margins an infilling of fibrous chrysotile

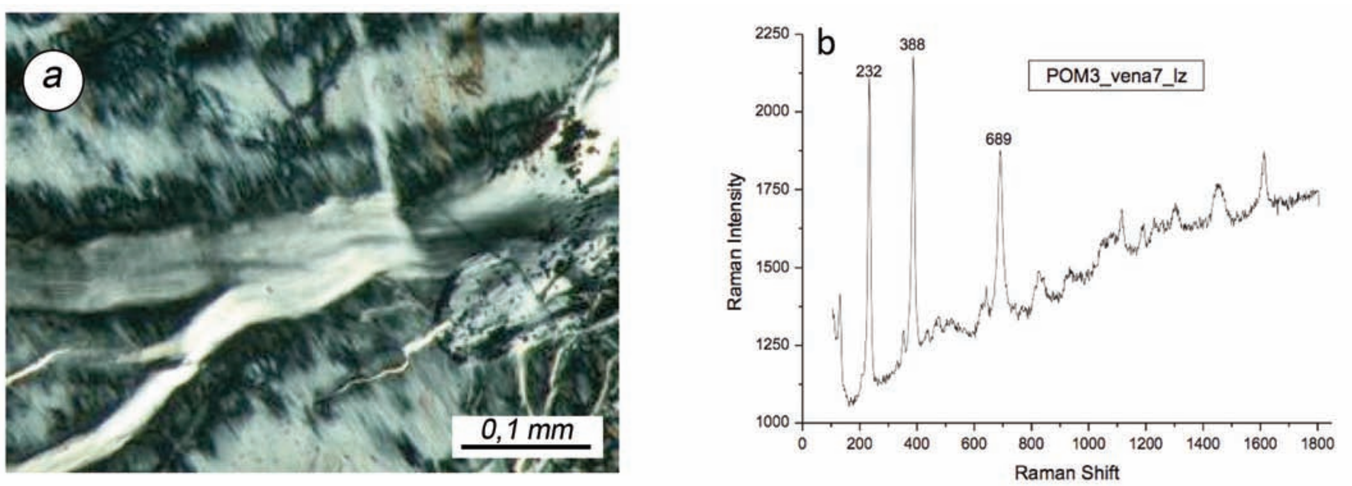

Fig. 8 - Type A lizardite blocky veins: a) features at the microscale; b) microRaman analyses.

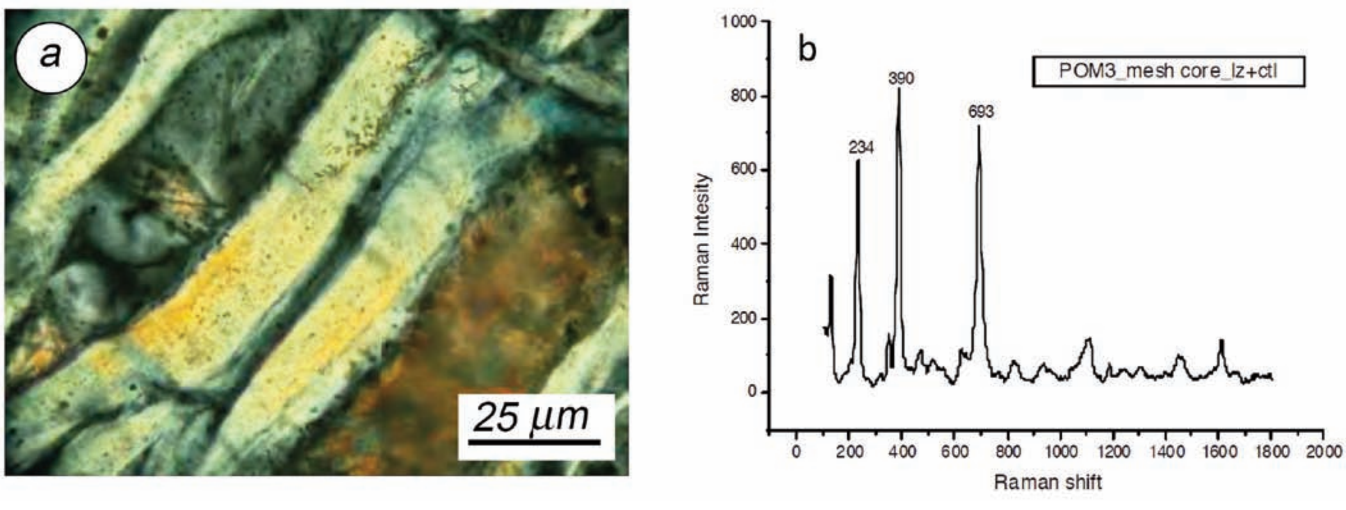

Fig. 9 - Type B chrysotile blocky veins: a) features at the microscale; b) microRaman analyses.

occur (Fig. 11b). These veins are interpreted as primary lizardite-rich veins re-opened during the further vein development with crystallization of chrysotile fibers.

Type E veins: according to the microstructural evidence, these veins are the youngest amongst the serpentine-rich veins system minerals. They occur in dilational jogs filled by fibrous-textured crystals oriented parallel or subparallel to the veins walls (Fig. 11a), generating fibers with sub-micrometric width (Fig. 12c and d). The thicknesses of these veins range from a few mm to 1-2 cm. Fragments consisting only by up to 10 cm long fibers of these veins have been found in the cataclasites. XRD analyses show the serpentine peaks, which can be attributed to antigorite after microRamam spectrometry investigations (Fig. 11b).

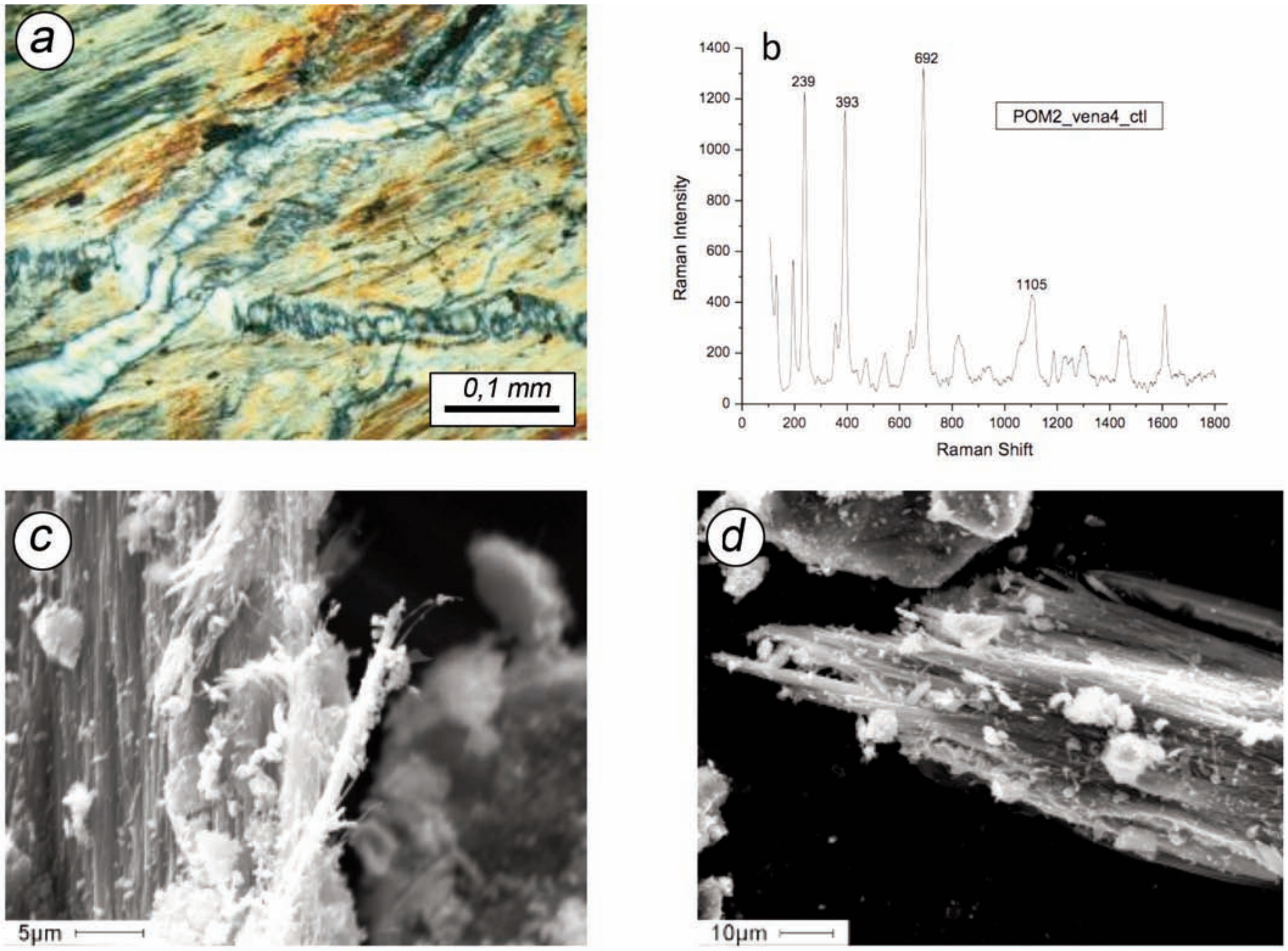

Fig. 10 - Type C chrysotile fibrous veins: a) features at the microscale; b) microRaman analyses; c and d) fibers images at SEM.

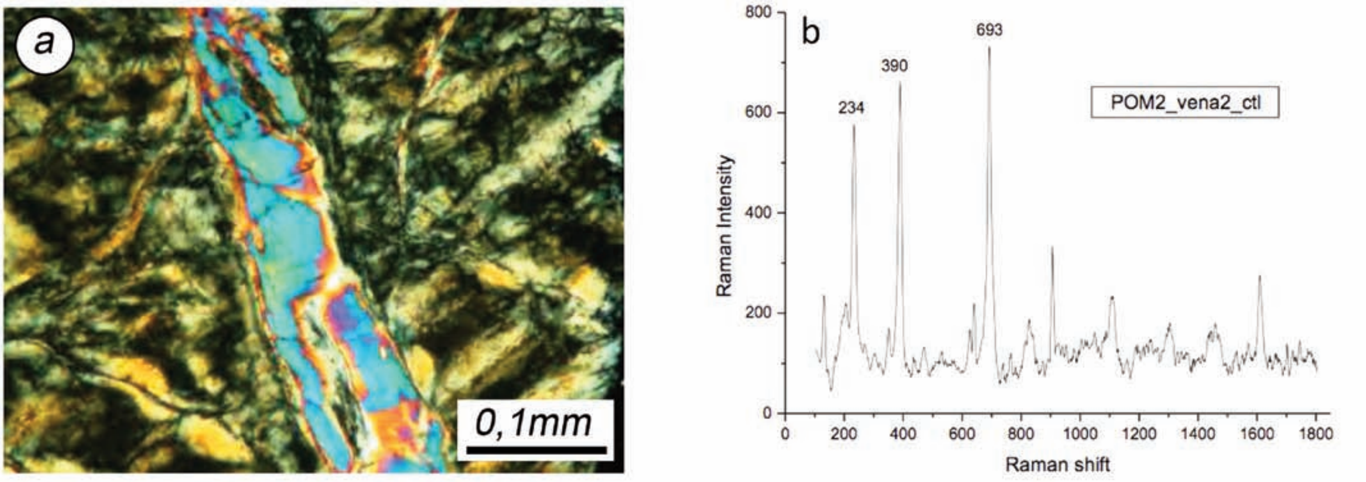

Fig. 11 - Type D composite veins: a) features at the microscale; b) microRaman analyses.

DISCUSSION

The structural, petrographic and mineralogical data of the studied mantle sequence indicate that during the serpentinization a crystallization sequence with lizardite (veins type A) followed by chrysotile (veins type B,C and D), then antigorite (veins type E). This crystallization sequence developed in an oceanic environment where pulses of magmatism and extensional tectonics were occurring. The veins are here regarded as main fluid pathways responsible for the serpentinization of the studied mantle sequence.

The field evidence indicates that the first event of the serpentinization-related veining includes the development of the lizardite blocky veins, followed by development of both blocky and fibrous chrysotile veins. The development of these veins started after the gabbro intrusion and before cataclastic events, according to the crosscutting relationships observed in the field. All these processese occurred a T below 500°C, maximum stability of serpentine minerals (Bowen and Tuttle, 1949; Evans, 2007).

Temperature-pressure stabilities of serpentine phases are not well constrained. Thermodynamic calculations predict that antigorite is the stable serpentine phase above 200°-300°C and pressures below 0.2 GPa and that chrysotile and lizardite form at temperature below 235°C (Wenner and Taylor, 1971). However, more recent stable isotope investigations (Agrinier and Cannat, 1997), field studies (Wicks and Whittaker, 1977; O'Hanley and Wicks, 1995), and hydrothermal experiments (Janecky and Seyfried, 1986; Normand et al., 2002; Allen and Seyfried, 2003) indicate that lizardite and chrysotile can form at temperatures of 350-400°C (Agrinier and Cannat, 1997).

Evans (2007) suggests that the lizardite and chrysotile occur in nature under virtually identical ranges of temperature and pressure, from surficial or near-surficial environments to temperatures possibly as high as 400°C. Laboratory evidence indicates that lizardite is more stable than chrysotile at low temperatures, but the difference in their Gibbs free energies is very modest in the 300-400°C range. Even if the lizardite makes its first appearance at temperatures lower than chrysotile (O'Hanley et al., 1989; Evans, 2007), the crystal structures of these two minerals lead to contrasting crystallization behaviors and hence modes of occurrence.

Lizardite and chrysotile are characterized by different chemical composition and, consequently their crystallization can be regarded as originated, respectively, from the alteration of olivine (that always contains 10% wt of Fe), and from late Mg-rich fluids circulating into the serpentinites, in the latest stages of their alteration (Evans et al., 2013). However, Evans (2007) suggested that chrysotile can be regarded as developed in tectonically active environments where its growth is favored under stress microenvironments

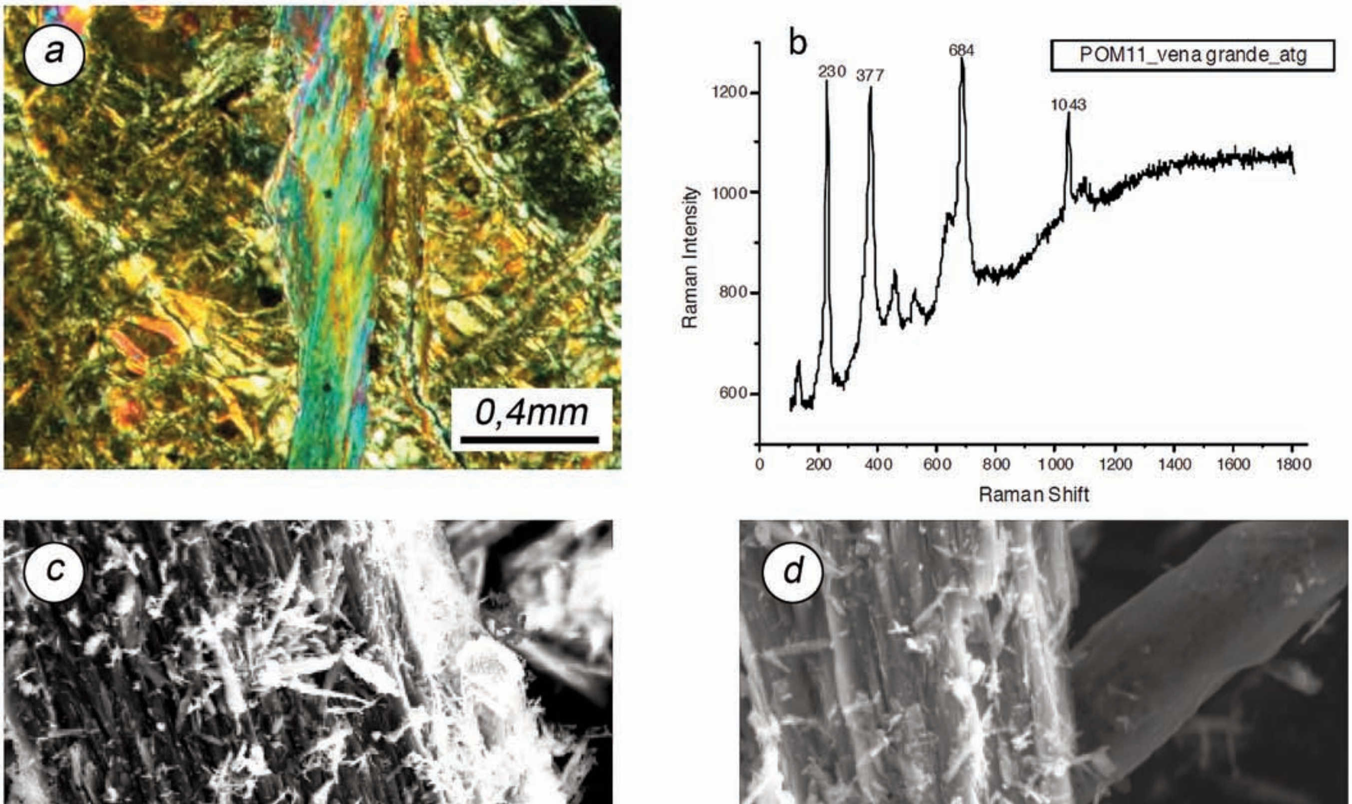

Fig. 12 - Type E antigorite fibrous veins: a) features at the microscale; b) microRaman analyses; c and d) fibers images at SEM.

of fluid-filled voids, pores and veins, generally after active hydration in the immediate surroundings has ceased. By contrast, the lizardite growth can be related to the hydration of peridotites in absence of tectonic stress-driven fluid circulation. The growth of lizardite produces relevant volume expansion that seems to be responsible of the stress associated with extreme flattening and shear in the serpentine bodies. This nevertheless do not excludes the simultaneous growth of lizardite and chrysotile in adjacent zone, where the influences of the stress is different or in the same zone, when subjected to stress regime change.

Thus, the switch of the nature of vein mineral from lizardite (veins type A) to chrysotile (vein types B and C) can be regarded as the result of transition to tectonics-controlled fluid circulation in the host peridotites during the transition from magmatic to amagmatic stage.

However, the development of chrysotile veins with different morphology (blocky vs. fibrous texture) can be regarded as the result of different ways of opening and subsequent sealing of these structures. The veins with blocky structure (veins type B) can be regarded, according to their overall features, as generated during fluctuation leading to alternating phases of dilation and collapse of the fracture walls (Sibson, 1990; 1992). The dilation can be easily originated when the hydrostatic pressure is greater than lithostatic one, allowing opening of fractures that become pathways for fluid expulsion. When the hydrostatic pressure decreases, crystallization starts and the fracture becomes filled by serpentine minerals. The blocky texture of the veins indicates growth at a rate slower than fracture opening, suggesting the instantaneous nature of hydrofacturing episodes. The fibrous veins (veins type C) can be instead related to a different mechanism, i.e., the crack-and-seal one (Ramsay, 1980). By this mechanism, the vein formation developed by crack opening, driven by stress associated to fluid pressure, immediately followed by fluid filling and then crystallization of the minerals with fiber shape. This mechanism replicating in time and space every time under active stress produces the observed fibrous structure of the veins. The multiple events driving the opening and maintenance of fluid pathways support a series of possible fluid-controlled pressure dilation and collapse events which took place in a setting of regional and/or local extension, consistent with near-surface brittle deformation. In this frame, the occurrence of composite veins (veins type D) where the infilling of blocky lizardite is replaced by fibrous chrysotile indicates the reuse of the same pathways by the fluids, along already etablished weakness structures.

Subsequently, the crystallization of fibrous antigorite occurred (veins type E). The crosscutting relationships of lizardite and chrysotile veins with that were filled by antigorite indicate that the latters are the youngest ones. The crystallization of antigorite indicates a re-heating with temperature above about 300°C whereas its morphology indicate stress-controlled crystallization.

Finally, the last event is represented by the development of the cataclastic shear zone in which fragments of peridotite and gabbros are cemented by calcite.

This history can be correlated with the tectonic evolution described by Cortesogno et al. (1987) and Menna (2009) in the Bracco area where different magmatic and amagmatic events have been described. In the Pomaia quarry the first event of lizardite veining (vein type A) can be connected with the hydration of peridotites in absence of tectonic stress-driven fluid circulation during a magmatic stage. The following second event is represented by the growth of both blocky (vein type B), fibrous (vein type C) and composite (vein type D) veins filled by chrysotile. The switch of the crystallization from lizardite to chrysotile in the veins can be regarded as result of the starting of tectonic-controlled fluid circulation in the host peridotites during the transition from magmatic to amagmatic stage. The transition from the magmatic to amagmatic stage can be hypothesized as gradual, with simultaneous growth of lizardite and chrysotile in adjacent zones, where the influence of the stress is different. The third event is represented by the growth of fibrous veins filled by antigorite (vein type E). This event is more puzzling, mainly because it represents a tectonic-controlled fluid circulation in the host peridotites under increasing temperature. A relationship of this event with a transition between the amagmatic and a new magmatic stage can be regarded as suitable hypothesis. The last event is represented by the development of cataclasites with matrix consisting of calcite and lizardite. This event cannot be safely assigned to oceanic tectonics, even if these cataclasites have never been identified in the overlying sedimentary cover.

CONCLUSIONS

This paper provides the first evidence that the serpentinization of the peridotites from the Internal Ligurian units is associated with a sequence of different serpentine-bearing veins. In the Pomaia quarry these events developed in response to an alternance of tectonic-controlled and magmatic-controlled hydration of the peridotites in a slow-spreading ridge setting. This reconstruction fits very well with the overall evidence collected in others areas where the Internal Ligurian units crop out. This evidence (i.e., Menna, 2009) strongly supports the same history reconstructed in the Pomaia quarry, i.e., an alternation of magmatic and amagmatic stages. However, the relationships of this history with the serpentinization process deserve more data that must be acquired by further investigations on several outcrops of Internal Ligurian peridotites.

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