

# FRESH, PSEUDOTACHYLYTE-BEARING MANTLE PERIDOTITES FROM THE LAWSONITE ECLOGITE-FACIES SAN PETRONE UNIT, ALPINE CORSICA

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## ABSTRACT

Mantle peridotites exhumed in mountain belts provide important insights on the composition and evolution of the upper mantle, and additionally inform on metamorphic, geochemical, and tectonic processes -including seismic activity- at convergent margins. In this contribution, we present field, microstructural, and mineralogical data of fresh, pseudotachylyte-bearing mantle peridotites from the lawsonite eclogite-facies San Petrone unit, Alpine Corsica, France. The present case study represents the first example of subducted fresh peridotite associated with fresh lawsonite eclogite-facies assemblages. Two bodies of fresh peridotite are embedded in fully serpentinized ultramafic rocks forming the substratum of a subducted ocean-continent transition of the Piemonte-Liguria Basin. Clinopyroxene and spinel mineral chemistry indicates that the investigated peridotite samples were part of a refertilized mantle and, therefore, the San Petrone unit likely belonged to the more distal part of the ocean-continent transition. Because small bodies of fresh peridotite embedded in fully serpentinized rocks can hardly be identified by means of geophysical investigations, this finding suggests that small, yet disseminated bodies of fresh mantle peridotite can potentially be more abundant than previously supposed at ocean-continent transition and, potentially, at mid-ocean ridges and in subduction zones. The preservation of fresh mantle peridotite bodies in subducting slabs is also discussed with respect to its potential implications on intermediate depth seismicity and geochemical cycling -including production of natural energy sources- from rifting to subduction.

## INTRODUCTION

Rifted margins are characterized by zones of exhumed crustal and mantle rocks, which separate continental from frankly oceanic domains (e.g., Decandia and Elter, 1972; Manatschal, 2004 and references therein). These zones are called ocean-continent transitions (OCT) and bear important information on how the strength of the lithosphere evolves during continental rifting, and on which factors control the rift architecture (Manatschal 2004; Peron-Pinvidic and Manatschal 2009; Brun et al., 2017). Ocean-continent transition zones are in a favourable position to reach high/ultra high-pressure conditions during subduction (Beltrando et al., 2010; Beltrando et al., 2014). Therefore, their study may provide important insights both on the rifting and oceanization stages as well as on the subsequent subduction zone evolution.

In the case of magma-poor margins, such as the Piemonte-Liguria Basin, rifting results in the exhumation, at the sea floor, of subcontinental mantle along lithospheric detachments. During extension, mantle rocks exposed at OCT zones may record complex melt-rock interactions related to both the onset and development of the oceanic lithosphere (Rampone et al., 2008; 2009; Müntener et al., 2010; Piccardo et al., 2010; Picazo et al., 2016). Petrography, major and trace element data can be used to infer the composition of mantle peridotites from OCT zones that are today exposed in mountain belts, including metamorphic belts. Spinel peridotites with pyroxenite veins, plagioclase-peridotites, and orthopyroxene-rich harzburgites are typical of OCT settings (Picazo et al., 2016 and references therein). The preservation of fresh oceanic/OCT peridotites in exhumed metamorphic units also

provides important insights on the evolution of rifted margins in subduction zones.

Fresh peridotites exposed in metamorphic belts may also provide insights on seismic processes occurring at convergent margins. Several studies over the last years have in fact focused on the formation of pseudotachylytes in some Alpine peridotite bodies as markers of subduction zone seismicity (Andersen and Austrheim, 2006; Austrheim and Andersen, 2004; Deseta et al., 2014a; 2014b; Magott et al., 2016; 2017; Scambelluri et al., 2017; Pennacchioni et al., 2020). Despite the attribution of ultramafic pseudotachylytes to high-pressure seismic events may be challenging, the local exceptional preservation of these structures in peridotite bodies has provided crucial information about the possible triggers of intermediate-depth earthquakes (e.g., Andersen et al., 2008; Scambelluri et al., 2017).

Lastly, peridotite bodies may also inform on the chemistry and redox state of subduction zone fluids. Fresh mantle assemblages may in fact be extremely reactive in the presence of aqueous fluids through the process of serpentization (e.g., Früh-Green et al., 2004; Seyfried et al., 2007; Andreani et al., 2013; Klein et al., 2014; Roumejon et al., 2015). During serpentization, either at the seafloor or in the subduction zone, iron oxidation and the formation of magnetite and Fe<sup>3+</sup>-bearing serpentine drive the production of molecular hydrogen and abiotic light hydrocarbons (e.g., Charlou and Donval, 1993; Mottl et al., 2003; Emmanuel and Ague, 2007; Cannat et al., 2010; Evans, 2010; Klein et al., 2013; Malvoisin, 2015; Plümper et al., 2017; Merdith et al., 2020 Vitale Brovarone et al., 2020). Additionally, the conditions at which serpentization takes place, and to what extent, may

ultimately influence geochemical fluxes and large-scale elemental recycling in subduction zones (e.g., Hacker, 2003; Padrón-Navarta et al., 2009; Kodolányi et al., 2012; Alt et al., 2013; Peters et al., 2017; Piccoli et al., 2019).

In this contribution, we present new data on a recently discovered occurrence of fresh, pseudotachylyte-bearing mantle peridotites preserved in the lawsonite eclogite-facies San Petrone unit, Alpine Corsica. With the aim of stimulating future work on these rocks, we present petrographic and major element data of the mantle peridotites and discuss the implications of this finding on: (i) the understanding of the pre-subduction ocean-continent transition setting; (ii) the formation of potential markers of intermediate depth seismicity in subduction zones, such as pseudotachylytes, and; (iii) subduction zone geochemistry, with particular focus on  $H_2$  and abiotic  $CH_4$  generation.

## GEOLOGIC SETTING

Alpine Corsica occupies the northeastern part of the island of Corsica, France. It represents a segment of the Alpine belt that was isolated from the European mainland by the opening of the Liguro-Provençal and Tyrrhenian basins (Jolivet et al., 1998; Molli and Malavieille 2010). The belt mainly consists of a stack of oceanic and transitional units of the Jurassic, slow-spreading Piemonte-Liguria Basin. Belt-scale, coherent tectono-metamorphic units underwent variable Alpine metamorphism ranging from sub-greenschist to lawsonite-eclogite facies conditions in the Late Eocene (Brunet et al., 2000; Martin et al., 2011; Vitale Brovarone et al., 2013 and references therein; Vitale Brovarone and Herwartz, 2013;). Four bodies containing fresh peridotite are documented within the Schistes Lustrés complex of Alpine Corsica (i.e., the metamorphosed remnants of the oceanic/transitional Piemonte-Liguria lithosphere; e.g., Lahondère, 1996; Vitale Brovarone et al., 2013 and references therein): (i) the mafic-ultramafic Pineto massif (Sanfilippo and Tribuzio, 2013), which belongs to the weakly metamorphosed Nappes Supérieures (280-310°C 0.3-0.4 GPa) (Vitale Brovarone et al., 2013); (ii) the Monte Maggiore ultramafic massif (e.g., Rampone et al., 2009; Piccardo and Guarnieri, 2010); (iii) Cima di Gratera (Austrheim and Andersen, 2004) mafic-ultramafic bodies, which both belong to lawsonite-blueschist facies unit and experienced metamorphic conditions in the range of 400-430°C 1-1.8 GPa (Vitale Brovarone et al., 2013; 2014b), and; (iv) the lawsonite eclogite-facies San Petrone ultramafic body, for which only a preliminary description is available (Vitale Brovarone et al., 2020). Among these bodies, the Monte Maggiore and Cima di Gratera bodies include ultramafic pseudotachylytes formation of which has been ascribed to high-pressure, subduction zone conditions (Austrheim and Andersen, 2004; Deseta et al., 2014a; 2014b; Magott et al., 2016; 2017; Fabbri et al., 2018). For the San Petrone body, similar interpretations were suggested by analogy with the Monte Maggiore, Gratera, and Lanzo pseudotachylytes (Vitale Brovarone et al., 2020; cf. Scambelluri et al., 2017, for Lanzo).

The lawsonite eclogite-facies San Petrone unit is interpreted to represent a segment of the ocean-continent transition involved in the Alpine subduction (Vitale Brovarone et al., 2011; Beltrando et al., 2014). The unit consists of a basal body of serpentinitized peridotites structurally overlain by a laterally variable tectonostratigraphy including metabasalts, metasedimentary rocks and isolated slivers of continental rocks -the so-called continental extensional al-

lochthons- characteristic of magma-poor ocean-continent transition (Manatschal et al., 2006; Beltrando et al., 2014). All lithologies of the San Petrone unit experienced a consistent structural and metamorphic evolution culminating at ~ 480-550°C and 2-2.2 GPa (Vitale Brovarone et al., 2011). The serpentinitization of the San Petrone ultramafic rocks has been interpreted to result from two main stages related to the rifting and oceanization of the Piemonte Liguria Basin (Vitale Brovarone et al., 2011; Beltrando et al., 2014) and to the high-pressure conditions in the Alpine subduction zone (Vitale Brovarone et al., 2020), respectively. The fresh peridotite bodies presented in this study represent relicts that fully or at least largely escaped fluid-rocks interactions and serpentinitization from rifting stage to subduction and exhumation.

## FIELD RELATIONSHIPS

The fresh mantle bodies presented in this study are located in the northern part of the San Petrone unit, close to Col de Prato pass (Fig. 1; 42° 25' 39'' N; 9° 19' 35'' E) and form two lenticular bodies inside weaker serpentinitized peridotites. The surface outcrop of the two peridotite boudins ranges from 50 to 200 m<sup>2</sup>. In both localities, several well-exposed outcrops define a core of fresh peridotite (Fig. 2a) surrounded by undeformed, partially to fully serpentinitized peridotite extending outward to foliated antigorite serpentinite. The undeformed serpentinitized peridotite includes statically serpentinitized pseudotachylytes (Vitale Brovarone et al., 2020). Metabasalts, metagabbros, and metasedimentary rocks are closely associated with the fresh peridotite bodies and exposed at a few tens of meters from them. In detail, in the northwestern locality, the peridotites are capped by a thin layer of serpentinite, followed upwards by foliated metabasalts, radiolarian metacherts (Fig. 2d), and calcschists. This lithological association, which extends southwards for at least ~ 10 km, locally includes slices of continental basement rocks directly juxtaposed on top of the serpentinitized peridotites and interpreted to reflect the primary tectonostratigraphy of the ocean-continent transition of the Piemonte-Liguria Basin (Vitale Brovarone et al., 2011; Beltrando et al., 2014).

Metasedimentary rocks are separated from the fresh peridotite bodies by 10 to 500 m of serpentinitized peridotites or metagabbros. Although at least some Alpine structural overprint on the original architecture of the unit cannot be excluded, the overall, exceptional structural preservation of the unit (Vitale Brovarone et al., 2011) suggests that the fresh peridotite bodies were originally close (tens of meters) to detachment fault responsible for the mantle unroofing. The presence of a rim of partially to fully serpentinitized peridotite formed at high-pressure conditions at the expense of the fresh peridotite bodies (Vitale Brovarone et al., 2020) suggests that the fresh peridotite bodies were bigger prior to subduction, and that the distance between the fresh peridotite and the Mesozoic cover rocks was originally shorter (see discussion).

In the field, the peridotite displays an isotropic to weakly anisotropic structure, defined by the distribution of coarse-grained mantle minerals such as olivine, clinopyroxene, orthopyroxene, and spinel. Based on field and microstructural observations, the rock composition is inferred to span from harzburgite to lherzolite. Locally, 5-10 cm wide dunite layers are also found and characterized by the presence of relatively large (> 0.5 cm) spinel crystals (Fig. 2b). Small (~ 10 cm wide) plagioclase-rich pods are locally found and interpreted as the result of peridotite impregnation, by analogy

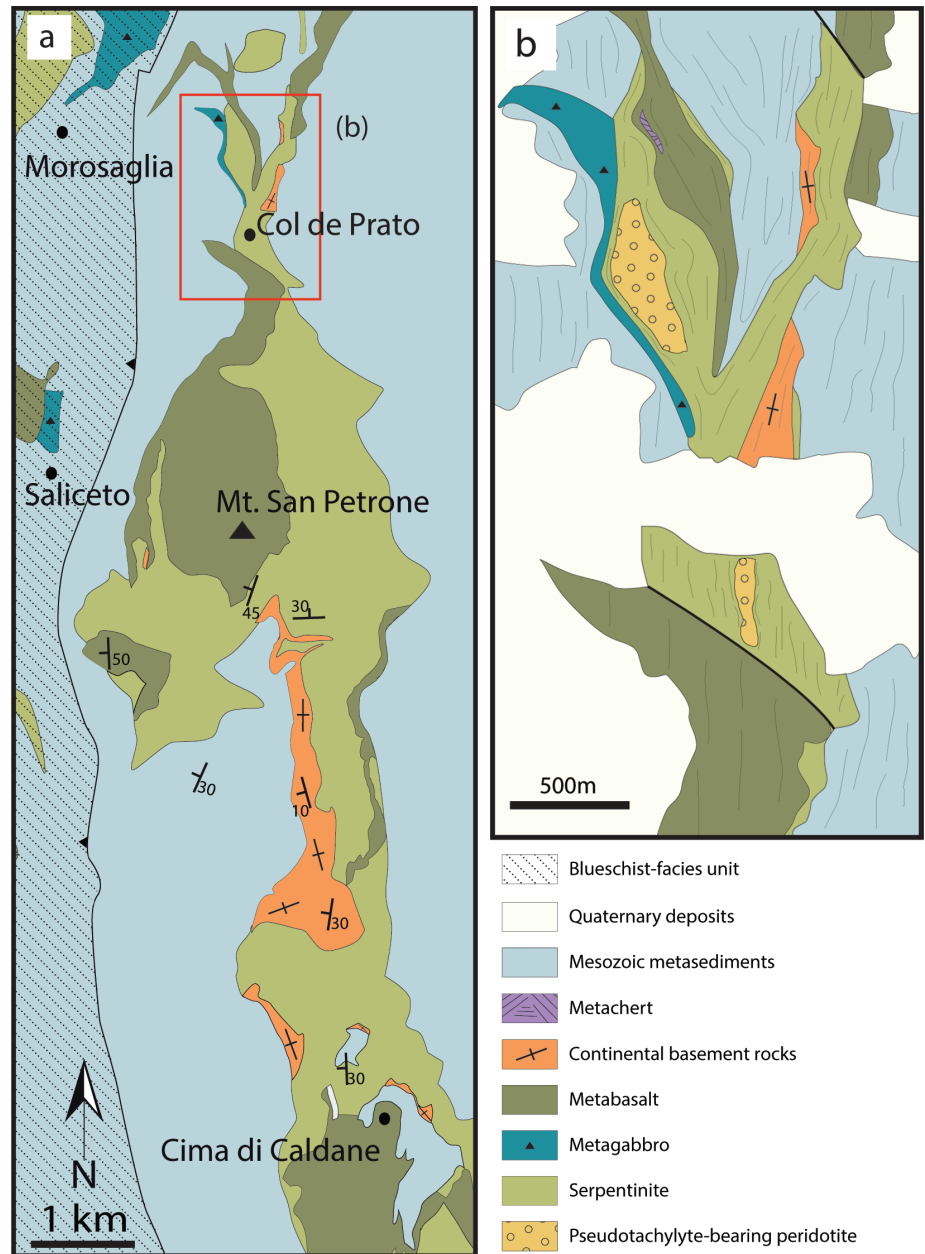


Fig. 1 - Interpreted geological map of the San Petrone unit. Modified after Rossi et al. (1994) and Vitale Brovarone et al. (2014). In (a), symbols for the general orientation of the Alpine foliation are shown. In (b), the main trend of the Alpine foliation is displayed on the map. The reader is referred to the PDF version of the article for a colour version.

with similar structures recognized in several slow-spreading and transitional ultramafic bodies (Müntener and Piccardo 2003; Piccardo and Guarnieri, 2010). Plagioclase is common in many of the collected samples and is found both fresh and fully converted into pseudomorphic products, as documented in thin section (see below). Nevertheless, plagioclase-rich domains and metagabbroic rocks within the San Petrone peridotite body appear to be less abundant compared to the Gratera and Monte Maggiore peridotites in Alpine Corsica. The majority of the metagabbro bodies was found inside or adjacent to the serpentinites surrounding the northern peridotite body (Fig. 1). These bodies appear intensely metamorphosed and variably deformed. Blue amphibole can be easily recognized on the hand specimen in Mg-Al-rich metagabbro, whereas omphacite, garnet and lawsonite can be identified in Fe-Ti-rich bodies.

The peridotites are crosscut by a multitude of pseudotachylyte veins, ranging from a few mm to several cm in thickness and from a few cm to at least 1 m in length (Fig.

2c). Pseudotachylyte veins are more abundant in the south-eastern locality, whereas only two outcrops containing a few pseudotachylyte veins were found in the northern body. Injection veins characteristic of pseudotachylytes are common at all scales.

## MICROSTRUCTURAL RELATIONSHIPS

The San Petrone peridotite exhibit various degrees of preservation, from fully preserved with minor serpentinization along veins and grain boundaries, to fully serpentinized through static replacement of the original mineralogy. In the latter case, even though the original structure of the peridotite is still recognized in this section, the only relicts of the precursor mineralogy are small cores of spinel embedded in serpentinization-related magnetite. Despite the intense brittle deformation and shuttering related to the pseudotachylyte-forming events that affecting several peridotite samples, the

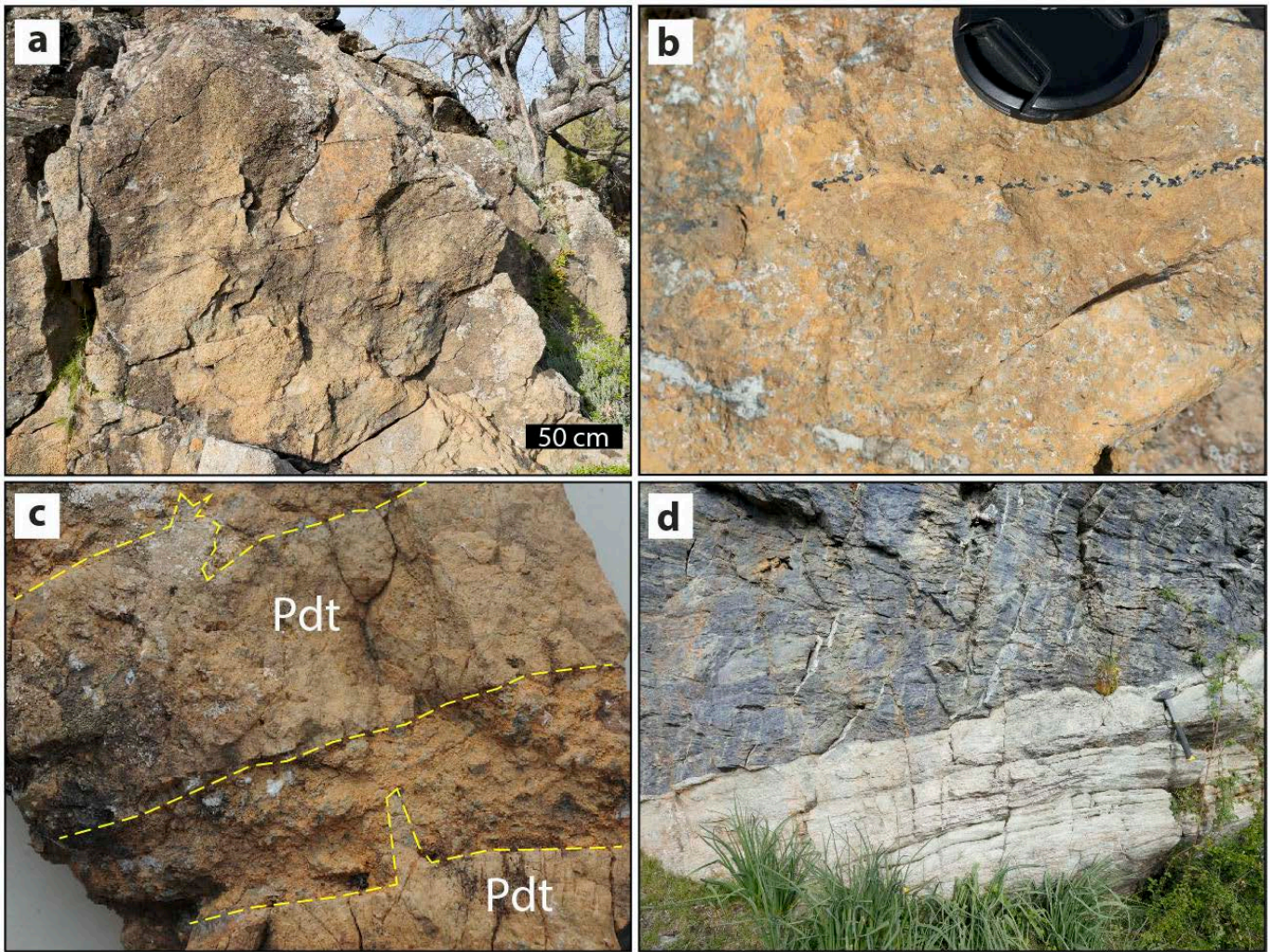


Fig. 2 - a) Field occurrence of the San Petrone fresh peridotite. b) Dunite channels within the San Petrone peridotite. Note the presence of coarse spinel crystals within the dunite. c) Sample of pseudotachylyte (Pdt) veins cutting the peridotite. The sample is about 15 cm wide. d) Contact separating metabasalt (bluish colour) from Mn-rich metachert. The outcrop is located at few tens of meters from the fresh peridotite to the N of the northern peridotite body (Fig. 1b).

mantle mineralogy is commonly very fresh (Fig. 3a-c). In this study, we present a preliminary petrographic investigation aimed at highlighting the similarity of the San Petrone peridotite with other well-studied Alpine peridotite bodies. A more detailed petrological-geochemical study will be required in the future.

Olivine is present as large (> 0.5 mm) crystals as well as smaller grain-size lobate crystals (Fig. 3d). The latter are found as partial replacement of large (> 0.5 mm) exsolved orthopyroxene crystals, as indicated by the lobate orthopyroxene grain boundaries (Fig. 3b). In some cases, the orthopyroxene shows extremely irregular outlines, including mouse tail-shaped extremities (white arrow in Fig. 3d) (see also Rampone et al., 2008 for equivalent microstructures). These microstructures suggest that the San Petrone peridotite recorded melt-rock interactions, by analogy with several Alpine peridotites (Rampone et al., 2008). Clinopyroxene is less abundant than orthopyroxene and is present as smaller crystals. Spinel is found both as individual crystals and as symplectites in association with orthopyroxene (Fig. 3e). The latter microstructure may testify to the reequilibration of former garnet in the spinel stability field (Morishita and Arai, 2003; Rampone et al., 2009; Piccardo and Guarnieri, 2010),

even though other interpretations are also possible (Secchiari et al., 2019). Despite the strong brittle deformation related to the pseudotachylyte formation in the spinel stability field (see below), fresh plagioclase was found in some peridotite samples, even in the close proximity of pseudotachylyte veins (Fig. 3f), whereas in other samples its former presence was inferred based on the presence of zoisite-rich pseudomorphoses.

Several samples are characterized by a remarkable abundance of pseudotachylyte veins cutting each other and resulting in networks overprinting the original structure of the host peridotite. Crosscutting relationships indicate the presence of multiple generations of pseudotachylyte veins, as already documented in the other known bodies of pseudotachylyte-bearing peridotites in Corsica and Lanzo Massif (e.g., Deseta et al., 2014a; 2014b; Magott et al., 2016; 2017; Scambelluri et al., 2017). In some cases, the injection veins propagate from sharp micro-fault zones free of any pseudotachylyte-type material. Marked strain gradients, including grain size reduction and fracturing, are observed from the host rock towards the pseudotachylytes (Fig. 3b). The pseudotachylyte microstructures generally vary with their thickness. Small veins are characterized by a fully recrystallized, dark-brown matrix including

variably deformed clasts of the host peridotite and commonly displaying flow structures (Fig. 4a, b). Large veins commonly exhibit spinifex structures (Fig. 4c-e), with individual rods up to ~ 1 cm long decreasing in size towards the vein selvages. As for most of the veins, the spinifex structures are completely

recrystallized into fine-grained granoblastic aggregates of the same mineralogy observed in the host peridotite, including olivine, ortho- and clinopyroxene, and spinel (Fig. 4e). The presence of spinel as a quench product of the pseudotachylyte indicates that the veins formed in the spinel stability field, as

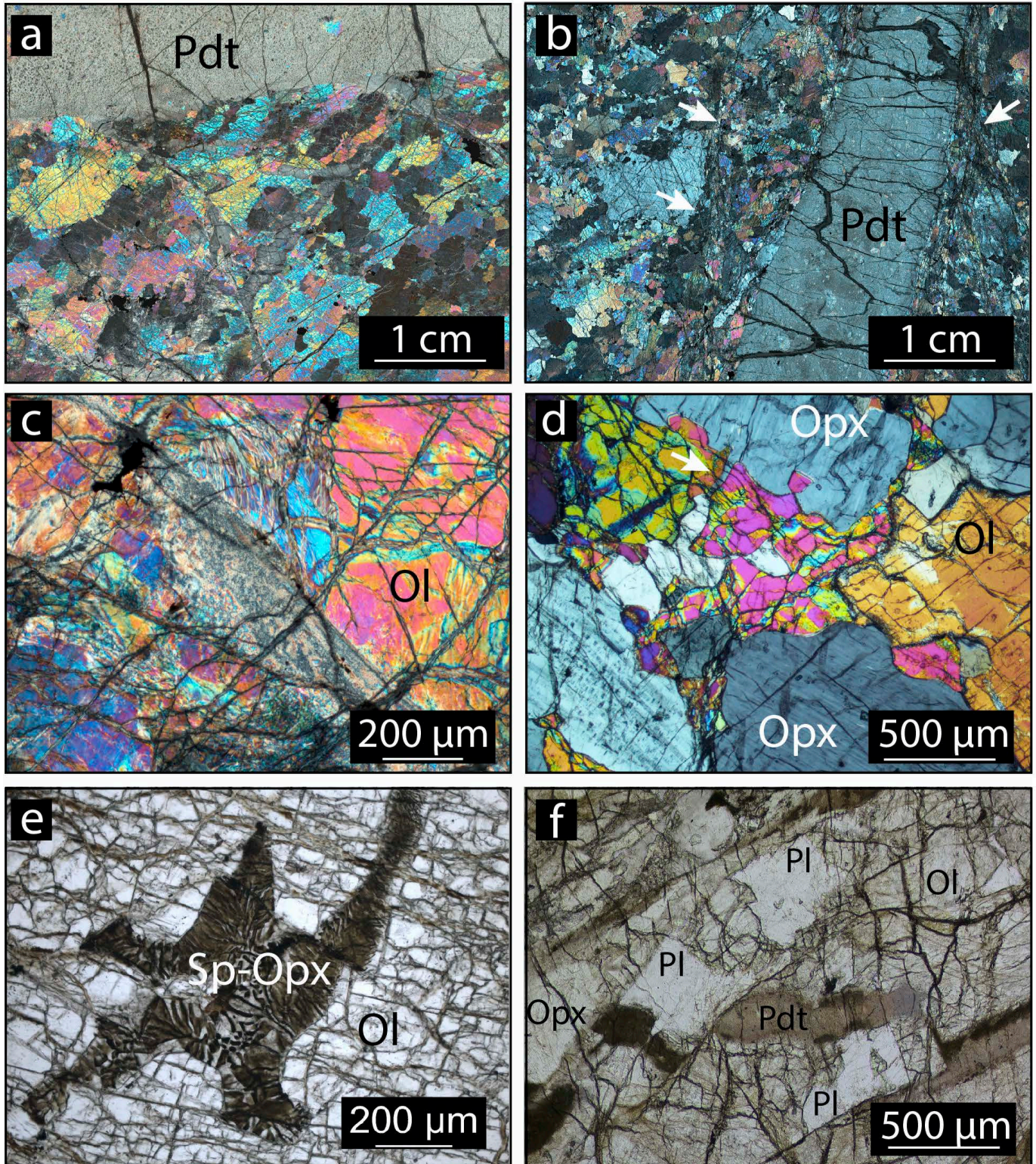


Fig. 3 - a-b) Cross-polarized light scans of thin sections of pseudotachylyte (Pdt)-bearing peridotite from the San Petrone unit. In (b), note the grain-size reduction in the proximity of the pseudotachylyte vein (white arrows). c) Intense brittle deformation and shattering of olivine related to the pseudotachylyte-forming event. d) Orthopyroxene (Opx) irregular outlines and lobate olivine (Ol) suggesting melt-rock interaction (see Rampone et al., 2008 for details). The white arrow indicates the position of a mouse tail-shaped orthopyroxene edge. e) Spinel (Spl)-orthopyroxene (Opx) symplectite suggesting the former presence of garnet. f) Preserved plagioclase (Pl) in pseudotachylyte-bearing peridotite. Plane-polarized light.

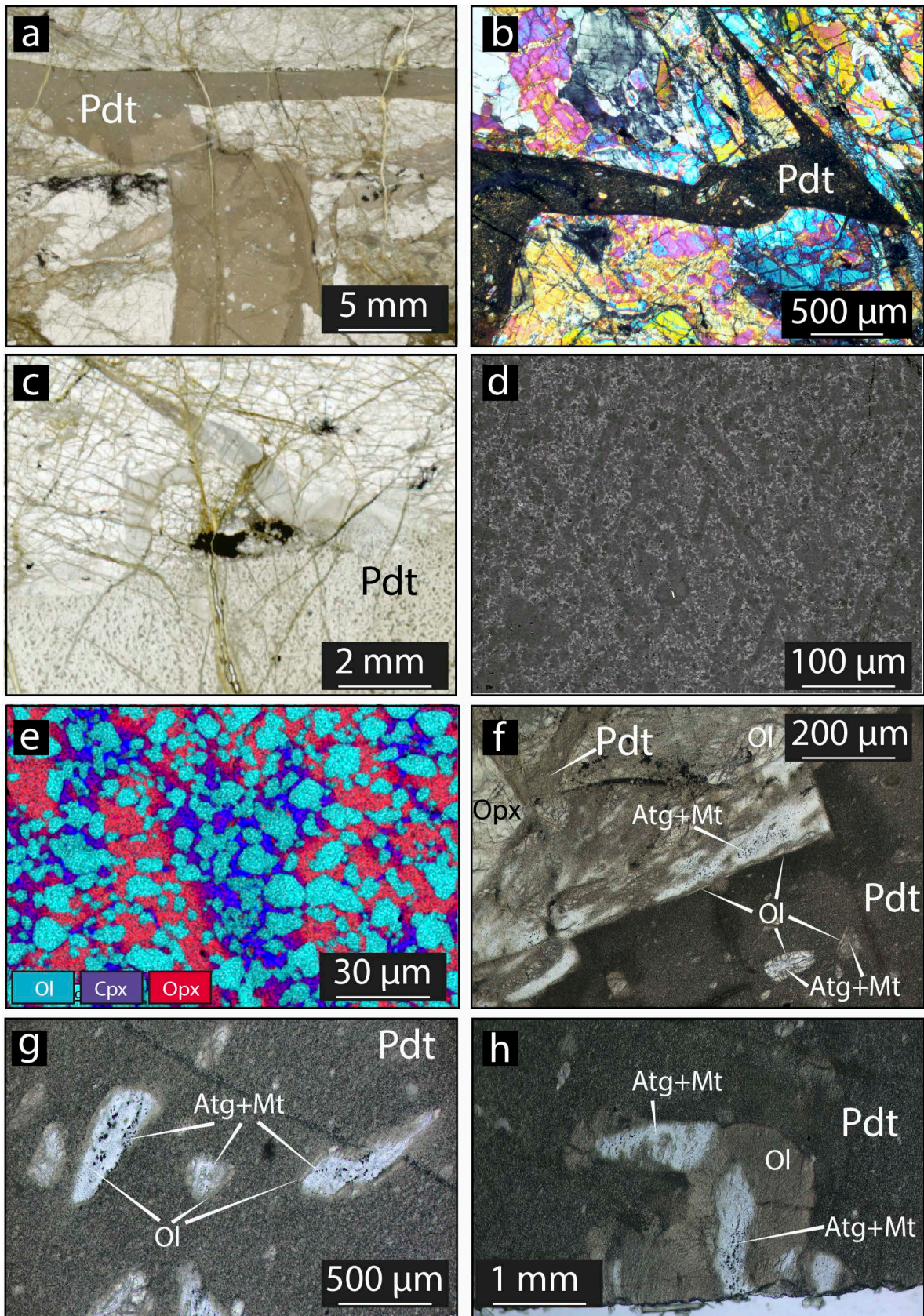


Fig. 4 - a-c) Examples of pseudotachylyte (Pdt) veins cutting across fresh mantle peridotite. (a, c: plane-polarized light, b. Cross-polarized light). d-e) Backscattered-electron image (d) and EDS-based X-ray composite (Al-Si-Mg) compositional map (e, close-up of d) of a recrystallized, spinifex-like pseudotachylyte. Note that the spinifex-like rods consist of fine-grained granoblastic aggregates of olivine (Ol), orthopyroxene (Opx) and clinopyroxene (Cpx) (+ spinel, not visible in this area). f-h) Example of pseudotachylyte (Pdt) hosted in a partially serpentinized peridotite; Atg = antigorite, Mt = magnetite. Although the timing of serpentinization relative to the pseudotachylyte formation is not clear, the formation of secondary olivine rims along the selvages of pseudotachylytes in contact with serpentine (f) and around serpentinite clasts within the pseudotachylyte (see also g-h) suggests that the seismic event formed after the partial serpentinization of the rock. Despite that, future work will be needed to confirm this hypothesis (see text for further discussion).

already documented in the Gratera and Lanzo pseudotachylytes (e.g., Andersen and Austrheim, 2006; Scambelluri et al., 2017). Talc and garnet were found in close association with the pseudotachylyte veins and typically formed as a replacement product of former orthopyroxene and plagioclase, as already documented in the Gratera (talc; e.g., Austrheim and Andersen, 2004) and Lanzo (talc and garnet; Scambelluri et al., 2017) pseudotachylytes. The presence of secondary garnet in the San Petrone plagioclase pseudomorphs is consistent with the eclogite-facies peak metamorphic conditions, as also documented in Lanzo (Scambelluri et al., 2017). In some cases, rather fresh pseudotachylyte veins are embedded in partially serpentinized peridotites and show secondary olivine formation along the vein selvages (Fig. 4f). Similar microstructures, interpreted as the result of thermal decomposition of matrix serpentine during the pseudotachylyte formation event, are documented in the Monte Maggiore peridotite and used to constrain the formation of the Monte Maggiore pseudotachylytes to high-pressure conditions in the Alpine subduction (Magott et al., 2020). Moreover, some pseudotachylyte veins include clasts of serpentinite (antigorite + magnetite) rimmed by secondary olivine. (Fig. 4f-h; cf. Fig. 3f in Austrheim and Andersen, 2004). Similar microstructures were described by Austrheim and Andersen (2004) and suggested to have formed by partial dehydration of antigorite during the pseudotachylyte formation.

## METHODS

Scanning Electron Microscopy (SEM) and Electron Dispersive X-ray Spectrometry (EDS) were performed with a Zeiss Ultra 55 field emission gun (FEG) SEM at IMPMC, Paris, France. The analyses were done with a working distance of 7.5 mm and operated at 15 kV with a 120  $\mu\text{m}$  aperture. Backscattered-electron (BSE) mode was used to investigate chemical heterogeneities using an Angle Selective Backscattered Detector (AsB) or an Energy Selective Backscattered Detector (EsB). Energy dispersive X-ray spectrometry (EDS) maps were acquired using an EDXS QUANTAX system equipped with a silicon drift detector XFlash 4010 (Bruker). Data were processed with the software Esprit (Bruker).

Mineral chemistry was determined by wavelength-dispersive spectrometry using a JEOL JXA 8200 superprobe at the Institute of Geological Sciences (University of Bern). Analytical conditions included 15KeV accelerating voltage, 20 nA specimen current, 40 s dwell times (including 2 x 10 s of background measurements), and a beam diameter of 2  $\mu\text{m}$ . Higher current and larger beam size were used for spinel measurements (50 nA and 5  $\mu\text{m}$ ). For silicate minerals, nine oxide compositions were measured, using synthetic and natural standards: wollastonite ( $\text{SiO}_2$ ), anorthite ( $\text{Al}_2\text{O}_3$ ), wollastonite (CaO), almandine (FeO), olivine (MgO), tephroite (MnO), bunsenite (NiO), rutile ( $\text{TiO}_2$ ), spinel ( $\text{Cr}_2\text{O}_3$ ). For oxide minerals, eight oxide compositions were measured, using synthetic and natural standards: almandine (FeO), spinel ( $\text{Al}_2\text{O}_3$ ), olivine (MgO), tephroite (MnO), bunsenite (NiO), rutile ( $\text{TiO}_2$ ), spinel ( $\text{Cr}_2\text{O}_3$ ), sphalerite (ZnO).

### Mineral chemistry

In this section, we provide major element analyses of the main mineral phases of the San Petrone peridotite. Mineral analyses are provided as supplementary material (Tables 1S-4S).

### Olivine

Coarse-grained primary mantle olivine in the host peridotite has average Mg number [ $\text{Mg\#} = \text{Mg}/(\text{Mg} + \text{Fe})$ ] of 0.90 (n. 166, SD = 0.01), and a relatively high  $\text{NiO}_2$  (0.39 wt.%; n. 166; SD = 0.03) and low MnO (0.14 wt.%; SD = 0.01) content (OL1 in Fig. 5a, b). Transects across individual olivine crystals do not show any significant variation from core to rim. Olivine recrystallized along deformation bands related to the pseudotachylyte events has  $\text{Mg\#} = 0.90$  (n. 3) and  $\text{NiO}_2$  content (0.36 wt.%, n. 5, SD = 0.02; OL2 in Fig. 5a,b) comparable to the coarse-grained olivine. Olivine in the pseudotachylytes (OL3 in Fig. 5a,b) includes clasts of mantle olivine, as well as a newly formed granoblastic metamorphic olivine formed during the quenching of the pseudotachylyte. MnO is 0.12 wt.% (SD = 0.02), consistently with crystallization together with pyroxenes.

Metamorphic olivine associated with HP serpentinization has  $\text{Mg\#} = 0.91$  (n. 29, SD = 0.01), slightly higher than the coarse olivine, a  $\text{NiO}_2$  content comparable with it (0.39 wt.%, n. 29, SD = 0.03), and high MnO (0.35 wt.%; SD = 0.06).

### Orthopyroxene

Coarse-grained mantle orthopyroxene in the host rock has  $\text{Mg\#} = 0.91$  (n. 80, SD = 0.01),  $\text{Cr\#}$  ( $\text{Cr\#} = \text{Cr}/(\text{Cr} + \text{Al}) * 100 = 13$  (n. 80, SD = 0.01), an average CaO content of 1 wt.% (n. 80, SD = 0.62), and an average  $\text{Al}_2\text{O}_3$  content of 3 wt.% (n. 80, SD = 0.64) (Fig. 5c,d). In the pseudotachylyte, the orthopyroxene formed during quenching has comparable  $\text{Mg\#}$  (0.90; n. 15, SD = 0.01) and  $\text{Al}_2\text{O}_3$  (2.8 wt.%, n. 80, SD = 0.48) to the host rock orthopyroxene, but higher  $\text{Cr\#}$  up to 27 (n. 15, SD = 0.03) and higher CaO (2.56 wt.%; n. 15, SD = 0.66),

### Clinopyroxene

Primary mantle clinopyroxene in the host rock has  $\text{Mg\#} = 0.91$  (n. 49; SD = 0.01),  $\text{Al}_2\text{O}_3 = 4.2$  wt.% (n.49, SD = 0.63),  $\text{TiO}_2 = 0.38$  wt.% (n. 49, SD= 0.17), and  $\text{Cr}_2\text{O}_3 = 1.19$  wt.% (n. 49, SD = 0.22) (Fig. 6a,b). Clinopyroxene formed after quenching of the pseudotachylyte has lower  $\text{Mg\#}$  (0.85; n. 13, SD = 0.02), much higher  $\text{Al}_2\text{O}_3$  (9.81 wt.%; n. 12, SD = 2.37), and lower  $\text{TiO}_2$  (0.3 wt.%; n. 12, SD = 0.12) and  $\text{Cr}_2\text{O}_3$  (0.52 wt.%; n. 12, SD = 0.46) compared to the primary clinopyroxene.

### Spinel

Spinel in the host peridotite has low  $\text{TiO}_2$  (median value of 0.06 wt.%; n. 8, SD = 0.18) and Cr number ( $\text{Cr\#} = \text{Cr}/(\text{Cr} + \text{Al}) = 0.38$  (n. 8, SD = 0.04) (Fig. 6c,d). In the pseudotachylyte, spinel displays variable  $\text{TiO}_2$  (0.57 and 0.12 wt.%) and  $\text{Cr\#}$  of 0.39 and 0.28, thus falling in the range of composition of primary mantle spinel.

## DISCUSSION

### Pre-subduction magmatic history of the San Petrone peridotite

The study of mantle peridotites provides important insights on the geodynamic evolution of the lithosphere in connection with slow to ultra-slow oceanization (Müntener and Piccardo, 2003; Rampone and Borghini, 2008; Müntener et al., 2010). The Alpine-Apennine ophiolites are fossil analogous of such geodynamic settings, though the Alpine overprint may hamper the investigation of the early magmatic evolution, and

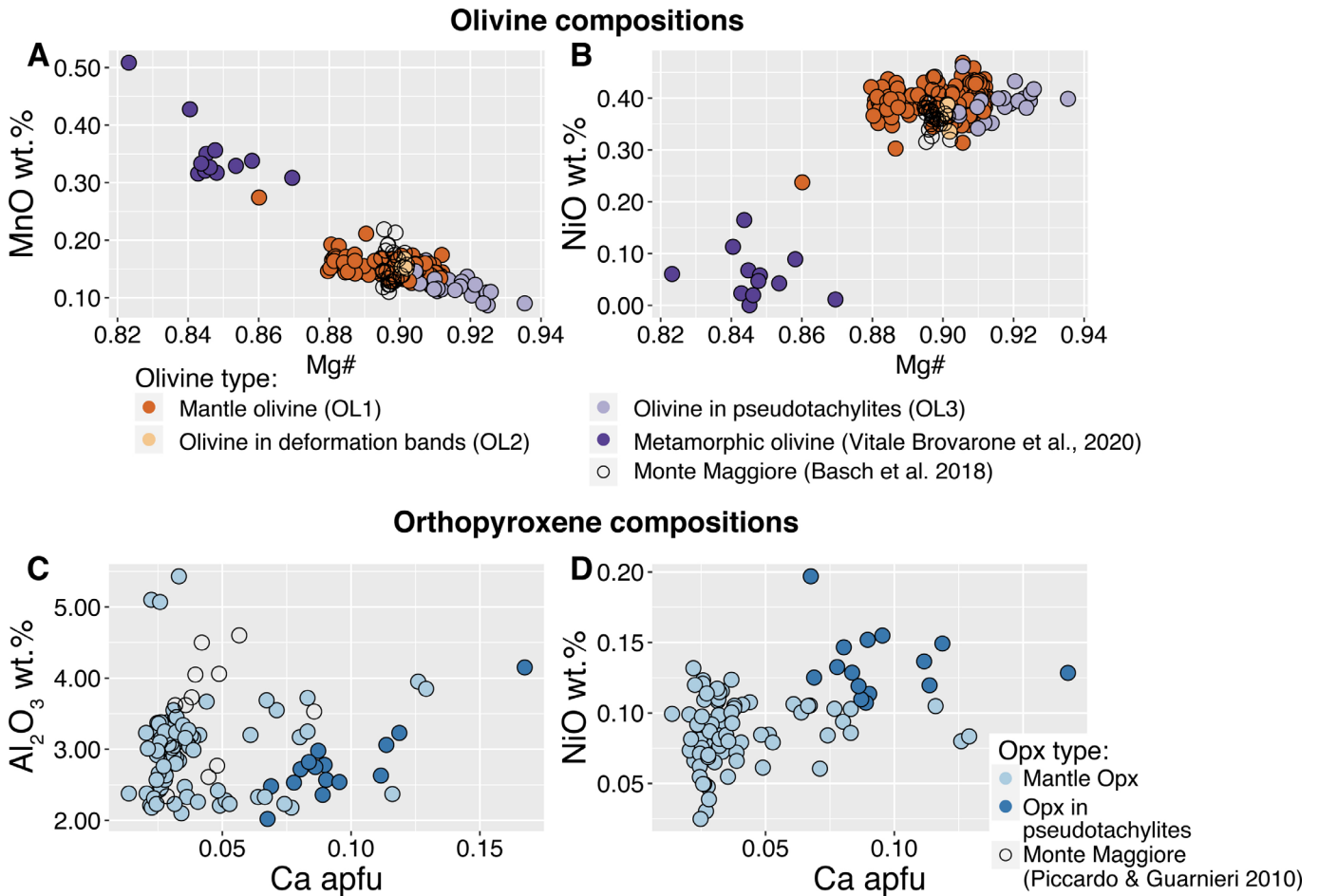


Fig. 5 - Major element compositional features of olivine and orthopyroxene from the San Petrone peridotite. Olivine compositions from Monte Maggiore spinel peridotite, plagioclase peridotite, spinel dunite, olivine-rich troctolite and troctolite are also reported (Basch et al., 2018). Orthopyroxene composition from spinel peridotite and plagioclase peridotite from Monte Maggiore are reported for comparison (Piccardo and Guarnieri 2010).

unaltered peridotites are only scattered and preserved in type localities through the Alpine-Apennine chain (Bezzi and Piccardo, 1971; Müntener and Piccardo, 2003; Müntener et al., 2004; 2010; Rampone et al., 2005; McCarthy and Müntener, 2015). Therefore, the finding of preserved fresh or even exceptionally fresh (fresh plagioclase) mantle rocks within the San Petrone unit provides new insights on the origin and evolution of the mantle lithosphere of a magma poor ocean-continent transition. Structural and petrologic studies of ophiolitic units of the Alpine-Apennine chain allowed classifying them between peri-continental and intra-oceanic settings (Marroni and Pandolfi, 2007; Manatschal and Müntener, 2009; Mohn et al., 2010; Picazo et al., 2016; Rampone et al., 2020). Recent works have proposed a simplified scheme to recognize different mantle domains and associated melt-related history on the basis of pyroxene and spinel mineral chemistry (Mohn et al., 2010; Picazo et al., 2016). Three main mantle-type were identified: (i) inherited subcontinental mantle, with a further subdivision in inherited (type 1a) vs. post-orogenic depleted mantle (type 1b) (see Fig. 9 in Picazo et al., 2016), (ii) refertilized mantle (type 2), and (iii) oceanic depleted mantle. Pitfalls of this approach include the fact that transition from inherited (1a) to infiltrated (1b) mantle domains are visible at the outcrop scale, and heterogeneities might be due to multiple processes, such as inheritance, pyroxenite-mantle interaction or subsolidus re-equilibration (Rampone et al., 1993;

2020). In such a case, a detailed geochemical and isotopic study is required. For the purpose of this study, the simplified scheme based on clinopyroxene and spinel composition of Picazo et al. (2016) was adopted. Fig. 6 displays the measured mantle clinopyroxene and spinel compositions from the San Petrone unit (this study), together with mineral chemistry data of the Monte Maggiore peridotite in Corsica (empty circles in Fig. 6 Basch et al., 2018) and of other Alpine and Apennines localities from Picazo et al. (2016). Clinopyroxene compositions display a very good match with expected compositions for refertilized mantle domains, with very depleted  $\text{Na}_2\text{O}$  and moderate  $\text{Al}_2\text{O}_3$  content (Fig. 6) and overlap with reported clinopyroxene compositions from Monte Maggiore (Basch et al., 2018). Comparable compositions of mantle olivine (OL1 and OL2 in Fig. 5) and orthopyroxene from San Petrone and Monte Maggiore are also observed (Piccardo and Guarnieri, 2010; Basch et al., 2018). Silicates in pseudotachylite are compositionally different from mantle relicts. Olivine has higher Mg#, orthopyroxene is more Ca-rich, and clinopyroxene has lower Cr and higher Al content. Spinel Mg#-Cr# composition is intermediate between refertilized mantle with important inheritance (type 1b) and refertilized mantle (type 2), and Ti content is lower compared to what reported by Picazo et al. (2016) for refertilized mantle samples. Nevertheless, low Ti content in spinel could be explained if melt impregnation occurred mainly by reactive porous flow



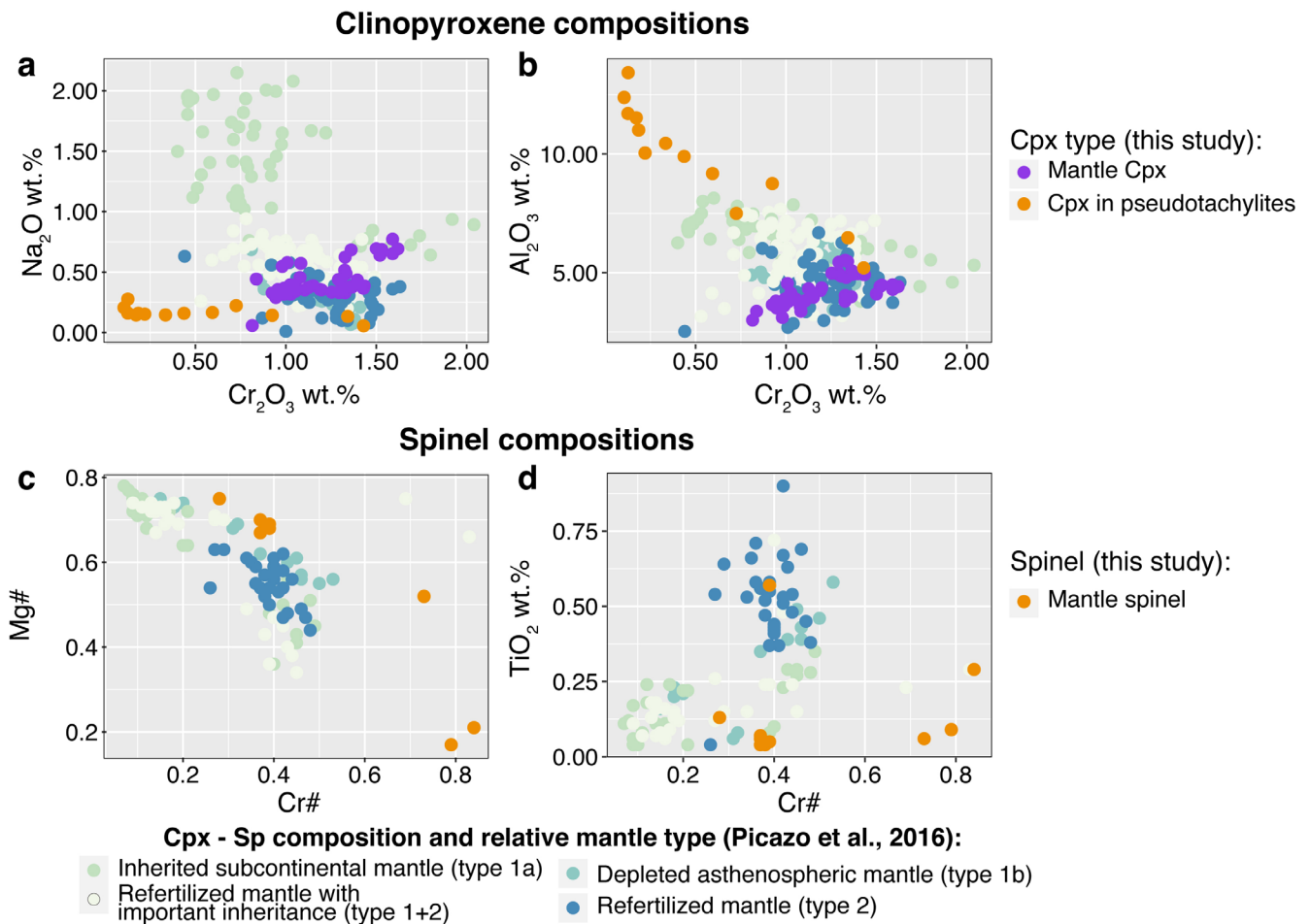


Fig. 6 - Major element compositional features of clinopyroxene and spinel from the San Petrone peridotite compared to literature data (Picazo et al., 2016).

at spinel facies conditions, which would be consistent with the observation of replacive dunite layers, scarcity of plagioclase, and Si depletion (inferred by the formation of brucite during HP serpentinization, Vitale Brovarone et al., 2020).

The intermediate composition might be explained by the original structural position of the peridotite body, considering that refertilization has been shown to increase towards the footwall of large mantle shear zone (Kaczmarek and Müntener, 2010), and that the amount of inheritance decreases towards the more distal parts of the ocean-continent transition (Picazo et al., 2016). In the case of the San Petrone unit, such an original transitional position (Fig. 7) is also consistent with previous paleogeographic reconstructions of the unit position in the Piemonte-Liguria Basin (Vitale Brovarone et al., 2011; Beltrando et al., 2014).

#### Preservation of peridotite bodies at exhumed mantle domains of a Tethyan fossil rifted margins

Despite the Alpine high-pressure metamorphic evolution, the San Petrone unit preserves the rift-related architecture of the Piemonte-Liguria ocean-continent transition (Vitale Brovarone et al., 2011). During the Mesozoic, subcontinental mantle rocks were unroofed along the Piemonte-Liguria Basin margins and covered by post-rift sediments (e.g., Manatschal, 2004; Beltrando et al., 2012; Ribes et al., 2019;

Epin et al., 2019). Mantle exhumation at rifted margins is typically accommodated by low-angle detachment faults or shear zones that also promote fluid infiltration and intense serpentinization of mantle rocks, as inferred from geophysical and drill core data, and from fossil analogous (Manatschal and Müntener, 2009; Pinto et al., 2015; Mateeva et al., 2017; Vieira Duarte et al., 2020). Along the Iberia margin, for example, the extent of serpentinization varies from 1 to 3 km of depth (Sutra et al., 2013; Stanton et al., 2016; Pinto et al., 2017). Serpentinization appears more intense when brittle lithosphere cools down and deformation localizes along high-angle normal faults (Bayrakci et al., 2016), as also preserved in fossil rifted margins such as the large peridotite body of Ronda, Spain (Frasca et al., 2016).

In the San Petrone unit, Mesozoic metasedimentary rocks, as well as slivers of continental basement rocks and Jurassic metabasalts, are directly juxtaposed onto serpentinized, refertilized subcontinental mantle rocks. The serpentinization of these rocks was initially interpreted to have happened during the formation of the Piemonte-Liguria Basin prior to subduction (Vitale Brovarone et al., 2011; Beltrando et al., 2014). Nevertheless, the identification of high-pressure serpentinization replacing at least a part of the San Petrone peridotite in the Alpine subduction zone (Vitale Brovarone et al., 2020) indicates that the size of the fresh mantle bodies was originally larger.

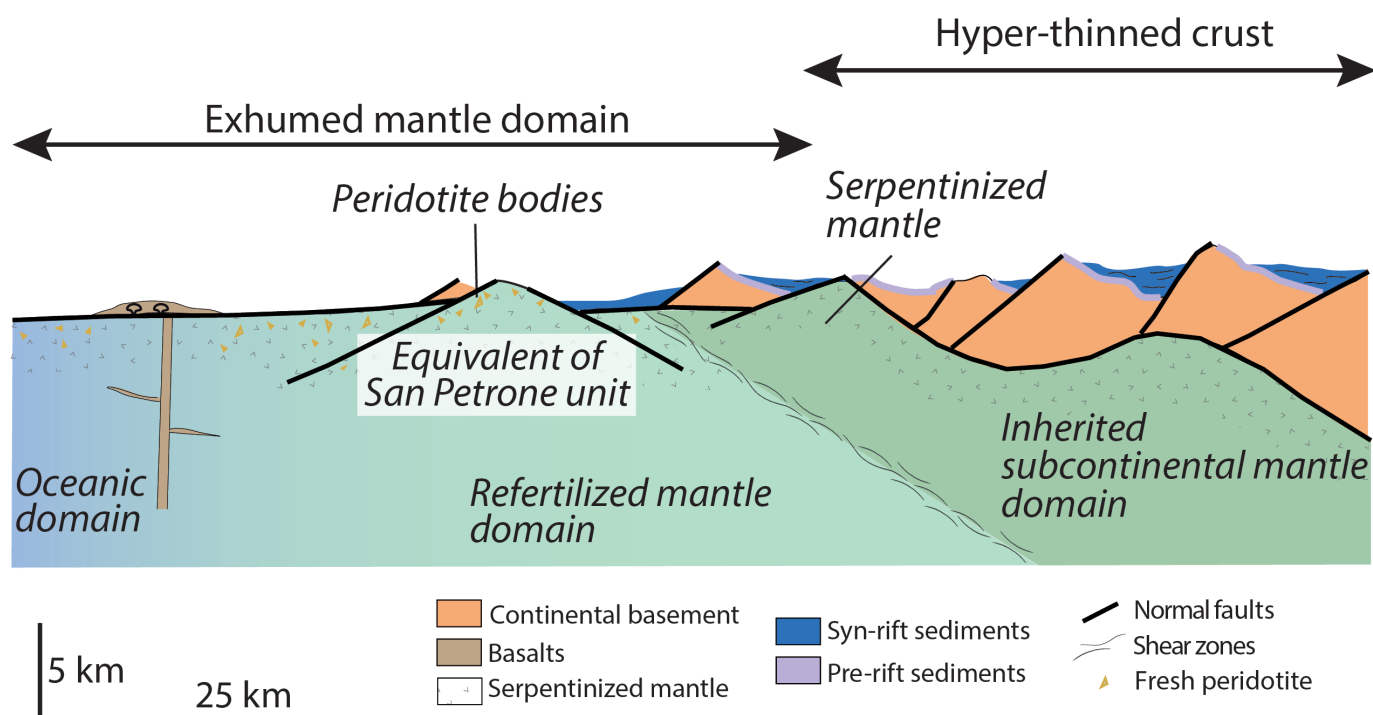


Fig. 7 - Conceptual sketch showing the architecture of an idealized magma-poor ocean-continent transition at the end of continental rifting. Modified after Sutra et al. (2013), Picazo et al. (2016) and Piccoli (2017).

Fresh mantle rocks are rarely preserved along oceanic/OCT detachment faults or in their direct proximity (e.g., Gakkell ridge; Michael et al., 2003; Lutz et al., 2018). Nevertheless, fresh peridotite bodies with sizes similar to San Petrone ones would be difficult to be detected by means of geophysical investigation in ultra-distal areas of rifted margins or along mid-ocean ridges. Moreover, the size of these bodies does not allow for direct comparison with large ultramafic massifs interpreted as subducted ultra-distal portions of rifted margins, like the Lanzo Massif in the Western Alps (Boudier, 1978; Pelletier and Müntener, 2006), or with obducted fossil continental rifted margin peridotites like the one exposed in the Ronda massif (Frasca et al., 2016). In particular, seismic velocities do not directly correlate with lithologies and derive from average of different lithologies, if no strong impedance contrast exists between them. For example, partially serpentinized peridotites may be indistinguishable from gabbros (Miller and Christensen, 1997; Carlson, 2001). Gabbros occur commonly as relatively small bodies within unroofed mantle sections in Alpine analogous, but these are usually complex to identify with seismic velocities in present-day slow-spreading ridges (Lagabrielle and Cannat, 1990; Manatschal et al., 2011 and references therein; Lagabrielle et al., 2015). The small size of peridotite bodies like those preserved in the San Petrone unit would make the recognition equally challenging with seismic velocities.

#### Pseudotachylyte formation conditions and analogies with other of peridotite-hosted examples

The newly discovered ultramafic pseudotachylytes exhibit remarkable structural and microstructural analogies with the four previously described peridotite-hosted pseudotachylytes within the Alpine realm: (i) the Balmuccia ultramafic body, which represents a lens of subcontinental mantle lithosphere

not involved in the Alpine subduction (Obata and Karato, 1995; Ueda et al., 2008; Souquière and Fabbri, 2010); (ii) the eclogite-facies Lanzo ultramafic massif, Italian Western Alps (Scambelluri et al., 2017; Piccardo et al., 2010); (iii) the blueschist-facies mafic-ultramafic body of Cima di Gratera (Austrheim and Andersen, 2004; Andersen and Austrheim, 2006; Deseta et al., 2014a; 2014b; Magott et al., 2016; 2017) and; (iv) the blueschist-facies Monte Maggiore ultramafic body (Fabbri et al., 2018; Magott et al., 2020), both in Alpine Corsica. Size, spatial distribution, and mineralogy are rather equivalent in all the above occurrences of ultramafic. Constraining the regional P-T conditions of pseudotachylyte formation in ultramafic rocks is challenging, owing to the little mineralogical variations expected in the rock. In all the above four cases, the pseudotachylyte assemblages include spinel, which constrain P to minimum values of 0.8 GPa.

However, inferences on the conditions and tectonic settings of formation of these rocks have required a combination of multiple lines of evidence. The formation conditions of the Balmuccia pseudotachylytes have been proposed to range from late Variscan (collision)/Early Permian (transtension) (“A-type” pseudotachylyte) to late Alpine (collision; “B-type”) (Souquière and Fabbri, 2010). In Lanzo, Monte Maggiore, and Cima di Gratera, previous works have constrained the formation of ultramafic pseudotachylytes to high-P conditions during the Alpine subduction (Andersen and Austrheim, 2006; Scambelluri et al., 2017; Magott et al., 2020;). The lines of evidence supporting the latter hypothesis include: (i) the presence of dendritic high-P minerals forming during the quenching of the pseudotachylyte in mafic rocks associated with the peridotite; (ii) the presence of antigorite (i.e. the serpentine polysome stable in subduction zone high-P conditions) veins crosscut by the pseudotachylytes; (iii) the presence of high-P pseudomorphic assemblages after mantle plagioclase corroded by the pseudotachylyte melt, and; (iv) the presence of rims of

metamorphic olivine formed at the expense of antigorite inside the pseudotachylytes or along their selvages.

The studied samples of ultramafic pseudotachylytes from the San Petrone unit exhibit some of the above features, such as the presence of olivine rims around serpentinite clasts inside the pseudotachylytes, and discontinuous rims of olivine separating rather fresh pseudotachylytes from intensely serpentinitized host rocks (Fig. 4f-h). Equivalent microstructures have been documented in the Gratera and Monte Maggiore pseudotachylytes and suggested to have formed through thermal breakdown of preexisting antigorite associated to the seismic event. This feature would constrain the formation of the San Petrone ultramafic pseudotachylytes to  $T \geq 400^\circ\text{C}$  (antigorite-in) during the Alpine subduction. However, future work will be needed to confirm this hypothesis.

In addition, a comparison between the distribution of ultramafic pseudotachylytes and mantle peridotites in Central and Western Europe suggests a tight link between the formation of these structures and the subduction of oceanic/transitional lithosphere to high-pressure conditions. Fig. 8 shows the distribution of peridotite bodies all over Central and Western Europe, and including present-day mid-ocean ridges (Mid Atlantic Ridge), present-day and fossil passive margins (Iberia; Central Alps), weakly metamorphosed Tethyan ophiolite suites (Liguria; Tuscany; Dinarides; Hellenides; Pineto), various orogenic peridotite massifs (Balmuccia, Finero, Betic-Rif), subducted passive margin or oceanic peridotites (Lanzo; Monte Maggiore; Cima di Gratera; San Petrone, Cima di Gagnone); mantle xenoliths are also included. From Fig. 8, it clearly emerges that all the documented cases of ultramafic pseudotachylyte are found in terranes related to compressional settings, and four out of five of them, including the San Petrone pseudotachylytes, are found in segments of rifted margin or oceanic lithosphere subducted to high-pressure conditions  $> 1$  GPa. The only ultramafic pseudotachylytes that do not follow this trend are from Balmuccia, which did not experience subduction zone metamorphism, but their formation is still referred to collisional stages (Souquière and Fabbri, 2010).

The Alpine belt seems to host the majority of ultramafic pseudotachylytes so far identified in Europe and worldwide, which calls for future investigations in other ultramafic massifs. For example, in the Erro-Tobbio ultramafic massif, Ligurian Alps, Italy, metric-size fresh peridotite lenses are embedded in mylonitic serpentinites (Scambelluri et al., 1991; Hermann et al., 2000), but pseudotachylytes have not been documented yet. In this case, however, the absence of pseudotachylytes may be explained by the preexisting partial serpentinitization of the massif, which has been shown to inhibit pseudotachylyte formations during subduction due to the formation of interconnected weaker antigorite network and more diffuse deformation (Ferrand et al., 2017).

### Implications of natural $\text{H}_2$ production through the Wilson cycle

The volume of fresh peridotite preserved along mid ocean ridges has recently been estimated for the last 200 Ma (Merdith et al., 2020). Fig. 9 shows the estimated amount of fresh peridotite unaffected by serpentinitization (referred to as residual fresh peridotite) along the Piemonte-Liguria Basin in the Jurassic (166 Ma), as well as a global plate reconstruction for reference (data from Merdith et al., 2020 courtesy of A. Merdith). The colour codes in Fig. 9 (see online version) refer to the estimated thickness, in km, of fresh peridotite unaffected by serpentinitization within the uppermost 4 km of oceanic lithosphere, which was calculated on the basis of geophysical data and their extrapolation to global scales (Merdith et al., 2020). Because the process of serpentinitization may be accompanied by iron oxidation and release of natural  $\text{H}_2$ , which in turn favours the conversion of dissolved [C] into abiogenic light hydrocarbons such as  $\text{CH}_4$ , Merdith et al. (2020) estimated global  $\text{H}_2$  fluxes related to serpentinitization along mid-ocean ridges for the last 200 Ma at  $0.2\text{--}14.1 \cdot 10^5$  Mt/Ma. The fact that small peridotite bodies, such as the San Petrone bodies, can hardly be detected by geophysical investigations at present-day mid-ocean ridges and passive margins, may suggest that assessments of the amount of residual peridotite

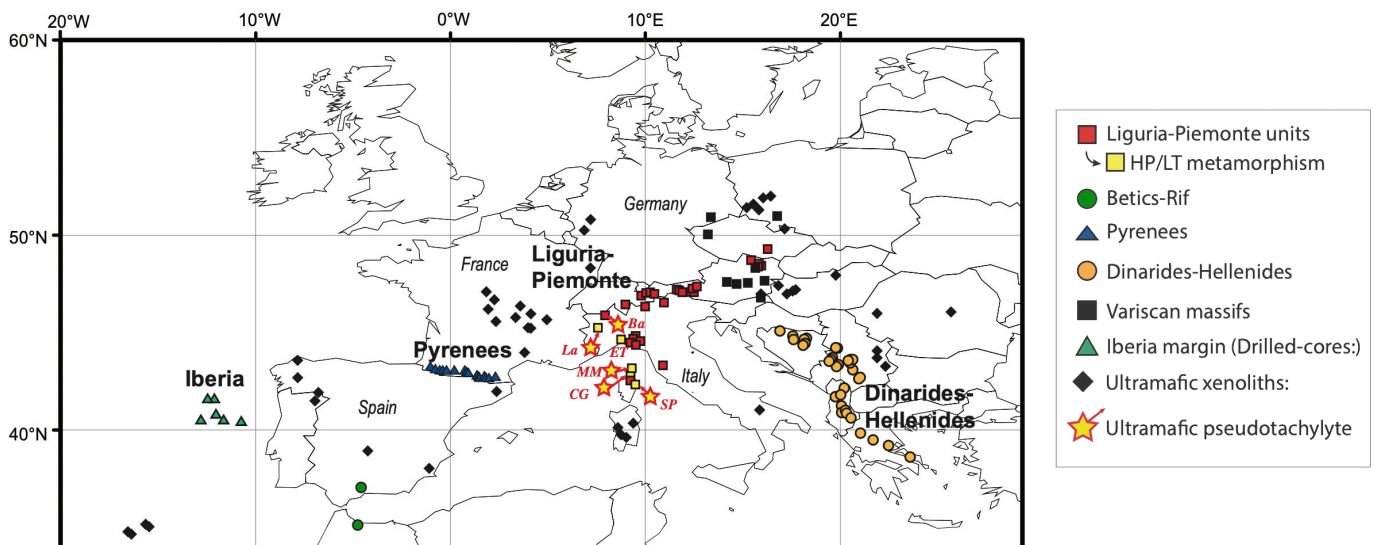


Fig. 8 - Present-day map location of outcrops, drill-cores and xenoliths of peridotitic composition (modified after Picazo et al., 2016). The distribution of lithospheric mantle peridotites having experienced high-pressure metamorphism is also shown, together with the documented occurrences of ultramafic pseudotachylytes.

in these settings may be conservative or, in other words, the extent of serpentinization may be lower than predicted by geophysical investigations. Thereby, the estimates of  $H_2$  production through serpentinization in these settings may potentially be overestimated.

In Fig. 9, the Jurassic Piemonte-Liguria Basin shows larger proportions of residual peridotite with respect to the coeval Neotethys and the Pacific Oceans mid-ocean ridges. However, only a relatively small number of fresh peridotite bodies are identified today in the Alpine orogenic system. This feature may result from the serpentinization events affecting the ultramafic rocks of the Piemonte-Liguria Basin later than the rifting-spreading stages (e.g., Ranero et al., 2003; Vitale Brovarone et al., 2020).

The possibility for serpentinization to happen during plate convergence bears important implications on the genesis of deep  $H_2$  and  $CH_4$  in subduction zones (Vitale Brovarone et al., 2017; 2020; Boutier et al., 2021). Data from the San Petrone, Gratera, and Lanzo peridotites constrain the serpentinization of large volumes of the subducted Piemonte-Liguria lithosphere to post-pseudotachylyte, antigorite grade high-pressure conditions ( $P > 1$  GPa;  $T \geq 400^\circ\text{C}$ ) (Vitale Brovarone et al., 2020). A quantitative assessment of the actual volumes of serpentinite formed at high-pressure conditions relative to the enclosing subducted oceanic serpentinite in the San Petrone unit was not possible for this study and would require future geochemical investigations. Nevertheless, the possibility for serpentinization to occur at high-pressure conditions increases the potential to generate  $H_2$  during subduction and calls for a possible reassessment of the context of formation of several serpentinite bodies exposed in metamorphic belts. Fig. 10 shows an idealized cartoon of a subducted oceanic to OCT lithosphere. The schematic representation of the distribution

of fresh peridotite bodies that escaped seafloor and trench serpentinization is also displayed. The effect of progressive hydration by aqueous metamorphic fluids and serpentinization is idealized by the decrease in size of the residual peridotite bodies with depth. This hypothetical cartoon aims at suggesting a potential pathway for deep  $H_2$  and  $CH_4$  formation through slab serpentinization, and the progressive disappearance of subducted peridotites in metamorphic terranes.

Potentially, many exhumed high-pressure serpentinite bodies are suitable to have formed during subduction from residual fresh peridotites. Future studies could identify the characteristic geochemical patterns of high-pressure serpentinization relative to its seafloor equivalents. Boron isotopes have been used to distinguish between subducted serpentinites and mantle wedge serpentinites (Scambelluri and Tonarini, 2012; Martin et al., 2016; 2020). The discovery of widespread slab mantle serpentinization may add additional complexity to the range of  $\delta^{11}\text{B}$  signatures of subduction zone serpentinites.

### Implications for deep seismicity in subduction zones

Previous work has suggested that subducted fresh peridotite bodies are suitable lithologies to favour the formation of seismic events through stress propagation from partially hydrated rocks and/or accumulation of large differential stress, leading to the formation of pseudotachylytes in ultramafic rocks and related lithologies (Scambelluri et al., 2017; Pennacchioni et al., 2020). The San Petrone peridotite bodies host ultramafic pseudotachylytes that, by analogy with several other equivalents in the Alpine belt (Austrheim and Andersen, 2004; Magott et al., 2016; Scambelluri et al., 2017), can be inferred to represent seismic events occurring during subduction. The preservation of small and potentially

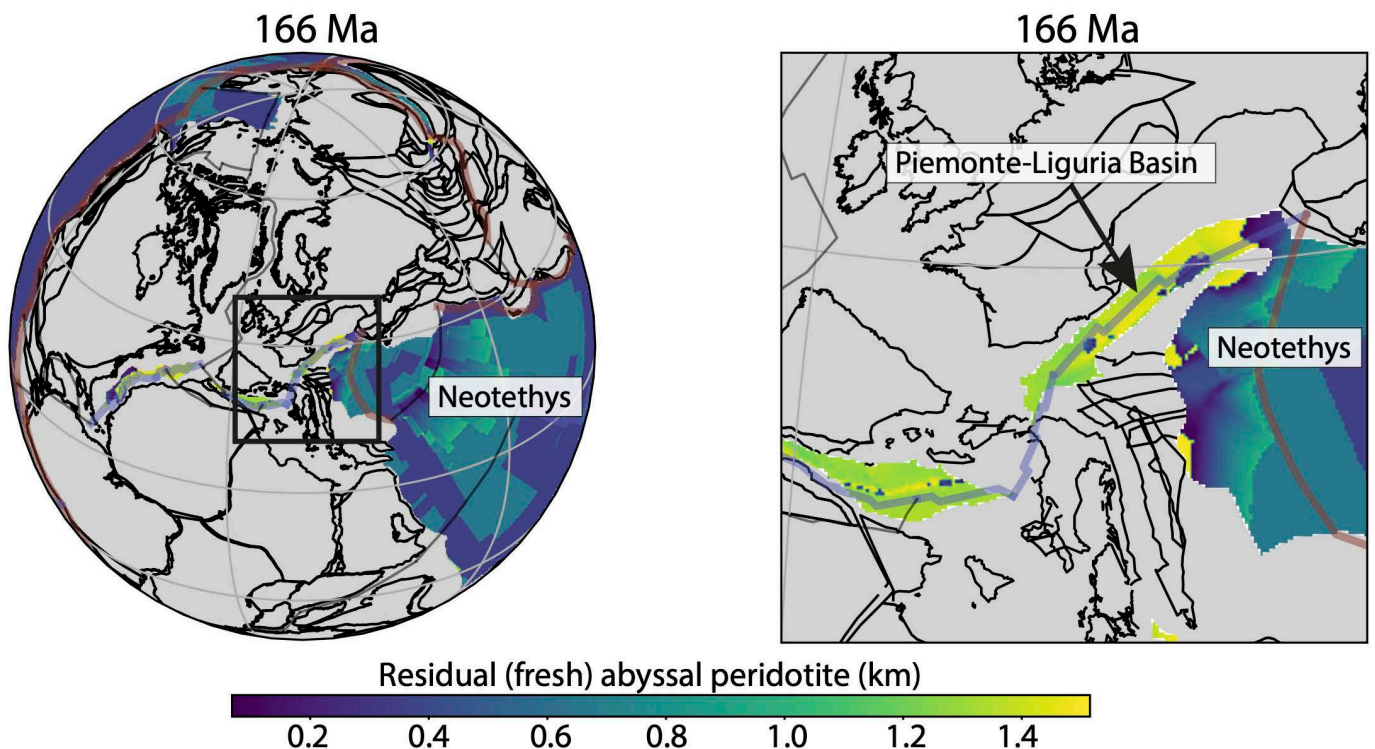


Fig. 9 - a, b) GPlates plate tectonics reconstruction and close up of the Piemonte-Liguria Basin at 166 Ma. The colour codes refer to the possible thickness in km of fresh peridotites unaffected by serpentinization within the uppermost 4 km of oceanic lithosphere. Based on Merdith et al. (2019). Courtesy of A. Merdith.

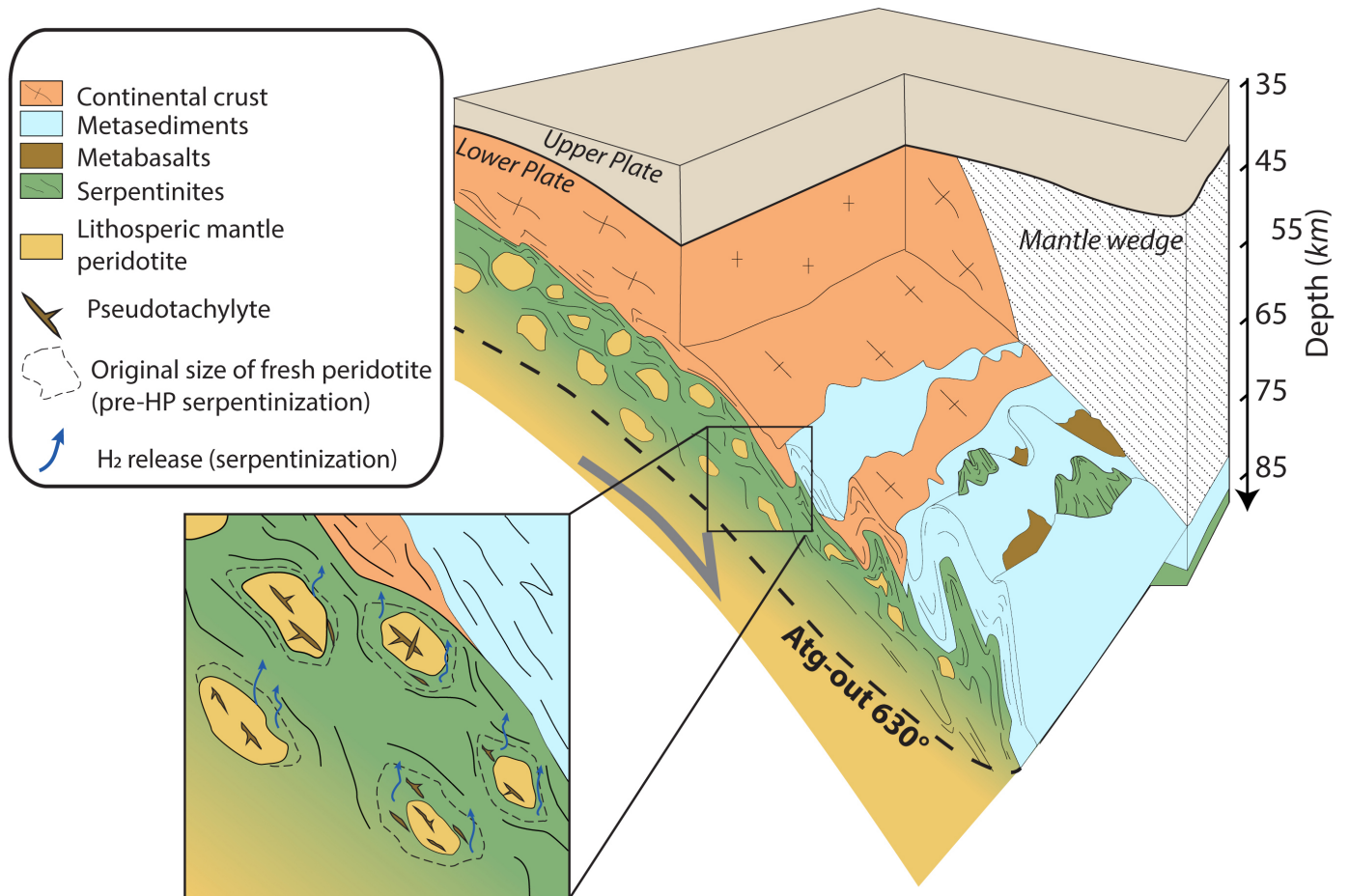


Fig. 10 - Conceptual reconstruction of the subduction of the oceanic to transitional Piemonte-Liguria lithosphere. The idealized distribution of fresh peridotite bodies is shown, according to the present study. As proposed by earlier work (Scambelluri et al., 2017; Pennacchioni et al., 2020) and supported by the present study, rigid blocks of fresh peridotite may localize the development of seismic events through stress propagation. The interaction of these bodies with circulating metamorphic aqueous fluids is suggested at the origin of high pressure serpentinization and the release of deep  $H_2$ -rich fluids. The antigorite-out curve (Atg-out) is shown for reference. Figure modified after Angiboust et al. (2012) and Piccoli et al. (2021).

widespread bodies of fresh peridotite as those presented in this study, may therefore have potential implications on the distribution of seismic events associated with stress propagation, including segments of subducting slabs expected to consist primarily of serpentinite. This survey summarized in Fig. 8 strongly supports the hypothesis that the preservation of small and potentially widespread bodies of fresh mantle peridotite embedded in the uppermost sections of subducting oceanic/transitional mantle lithosphere expected to consist primarily of serpentinite, may favour the developments of seismic events associated with stress propagation (Scambelluri et al., 2017; Pennacchioni et al., 2020). Moreover, during subduction competent peridotite bodies could experience seismic failure due to jamming, while the surrounding less competent serpentinitized shell could experience ductile deformation (Tarling et al., 2018; Beall et al., 2019).

The implications of the present study on subduction zone seismic events are not limited to processes taking place inside fresh peridotite bodies. Recent work has in fact shown that the release of  $H_2$ -rich fluid produces through high-pressure serpentinization reactions may affect the rheology of carbonate rocks, which may be abundant right above the subducting lithospheric mantle, and favour seismic activity (Giuntoli et al., 2020).

## CONCLUSIONS

This study provides field and preliminary petrographic, microstructural and geochemical data on two small bodies of fresh peridotite preserved in a subducted ocean-continent transition of the Piemonte-Liguria Basin. The San Petrone peridotite bodies give important insights on the preservation of dry mantle assemblages during a polyphase evolution started with subcontinental mantle unroofing and hydration along the Piemonte-Liguria margin, and followed by intense high-pressure metamorphism to about 2 GPa and 500°C in the Eocene, including hydration. Tracking the evolution of these bodies through the Wilson cycle also informs on the patterns of hydration and related geochemical cycling, notably the generation of  $H_2$  and abiotic  $CH_4$ , during the entire cycle. Based on the collected data, it is proposed that the presence of small bodies of fresh peridotite may affect the current estimates of mantle hydration within the first kilometers of transitional and slow to ultraslow oceanic lithosphere. Thereby, the related fluxes of  $H_2$  from serpentinization may be slightly overestimated. In turn, the preservation of peridotite bodies might increase the potential for  $H_2$  generation during subduction. Lastly, the good correlation between the occurrence of peridotite bodies and formation of high-pressure pseudotachylytes within the

Alpine belt, suggests that the preservation of fresh peridotite bodies potentially informs on the mechanisms and distribution of intermediate-depth seismicity in subduction zones.

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