ALPINE SERPENTINITE: A KEY TO UNRAVEL SUBDUCTION ACCRETION AT THE PLATE INTERFACE

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THE ROLE OF SERPENTINITE IN ELEMENT EXCHANGE IN SUBDUCTION ZONE SETTINGS

In the last decade, an increasing number of studies has dealt with the role of serpentinite as trace element repositories in subduction zones. Hattori & Guillot (2007) and Scambelluri *et al*. (2004, 2014) showed that serpentinite systems uptake fluid mobile elements like As, Sb, U, Th, Pb, Sr, W, B, and Cl from different reservoirs and release them in subduction zone fluids at sub-arc conditions. Recent analytical work on oceanic (Deschamps *et al.*, 2011; Kodolányi *et al*., 2012; Vils *et al.*, 2009), forearcs (Savov *et al.*, 2005), and subduction-zone (Cannaò *et al.*, 2015, 2016; Debret *et al.*, 2013; Hattori & Guillot, 2007; Lafay *et al.*, 2013; Scambelluri & Tonarini, 2012) serpentinites defined an inventory of elements up-taken by serpentinites during interactions with oceanic and with subduction zone fluids. This inventory led Deschamps *et al.* (2011) to define serpentinites as "*sponges*" for fluid-mobile elements (FMEs). Clearly, a different task is assessing the provenance of this FME-rich fluids and the timing of uptake by serpentinite. Several works tried to attribute serpentinites to a given geodynamic environment, based on their composition (Deschamps *et al.*, 2013) or using field, petrologic and geochemical constraints (Cannaò *et al.*, 2016; Lafay *et al.*, 2013; Scambelluri & Tonarini, 2012).

Insights on FMEs (B, Pb, As, Sb, Be, Li, U, Th, Cs, and W) and isotopes (B, Sr, and Pb) cycling in subduction zones and on serpentinization environment help understanding subduction dynamics. For instance, by comparing the U, Pb, B, Li and Sr and the isotopic imprints of de-serpentinized eclogitic meta-peridotite (Cima di Gagnone) with present-day abyssal serpentinite, Scambelluri *et al.* (2014) and Cannaò *et al.* (2015) defined the timing and the environment for hydration of such high-pressure metaperidotite. These authors concluded that high concentrations in Be, As, Sb, radiogenic Sr, and Pb (approaching the composition of associated paragneiss) suggested crust-derived FMEs percolated the oceanic serpentinites during the prograde subduction history. Lafay *et al.* (2013) reached similar conclusions by studying serpentinite olistoliths embedded in blueschist-facies accretionary metasediments in the French Queyras. Moreover, Cannaò *et al.* (2016) documented crust-derived subduction fluids introduced As and Sb and reset B and Sr isotope of original oceanic serpentinite in the Voltri Massif.

These studies on subduction serpentinites set the geochemical background knowledge, serving as guidelines for future studies aiming to assess the timing of serpentinite-fluid interactions and define lithologies and architecture of subduction plate interface. Geophysical seismic tomographies of present-day subduction zones image the plate interface as a km-thick layer atop the slab consisting of hydrated rocks hosting pressurized pore fluids (Audet *et al.*, 2009; Bostock, 2013; Hacker *et al.*, 2003; Van Keken *et al.*, 2002; Wada & Wang, 2009). Moreover, most subduction zone seismic activity occurs within this layer or in the mantle below (Bostock, 2013; Kita *et al.*, 2006). Several works discussed the tectonic accretion of subduction oceanic slices to the plate interface (Angiboust & Agard, 2010; Angiboust *et al.*, 2012c; Guillot *et al.*, 2015), suggesting that serpentinite-bearing oceanic slices of variable size accrete atop the slab, *i.e.* above crustal and sedimentary rocks. This accretion might trigger seismic activity (Angiboust *et al.*, 2012a) and crust-derived element influx in serpentinite (Cannaò *et al.*, 2016, Angiboust *et al.*, 2012c).

As such, petrological and geochemical studies of subduction serpentinites help monitoring the evolution and timing of accretion at the plate interface of large ophiolitic unit. This major task was the main subject of my PhD study, in the frame of the "Zooming In between Plates" program (ZIP; the Marie Curie Actions network of my PhD), achieved through a detailed geochemical analysis of the Zermatt-Saas, Lago di Cignana, Monviso and

Lanzo Serpentinite. Here, I summarize my work and I integrate my results with previous studies to unravel the potential architecture of the fossil Alpine plate interface.

THE LAGO DI CIGNANA UNIT

The Lago di Cignana Unit is a coesite- (Reinecke, 1998) and diamond-bearing (Frezzotti *et al.*, 2011) slice of oceanic-derived eclogites and metasediments recording Alpine UHP metamorphism at 600 °C - 3.2 GPa (110 km depth; Groppo *et al.*, 2009). This Unit is tectonically sandwiched between two ophiolitic units, the eclogitic Zermatt-Saas Zone (540 °C - 2.5 GPa; Angiboust *et al.*, 2009) and the blueschist Combin Zone (400 °C - 0.9 GPa; Reddy *et al.*, 1999), along a tectonic structure joining HP units recording a 1.2 GPa (40 km) pressure difference. So far, the Zermatt-Saas Zone has been attributed to normal HP conditions and the mechanism driving exhumation and accretion of the Lago di Cignana Unit in its present structural position is still unclear.

Petrologic and bulk-rock trace element analyses were performed on rocks from Lago di Cignana Unit and Zermatt-Saas Zone serpentinites. It was observed that, while serpentinites in the core of the Zermatt-Saas Zone show normal subduction-zone trace elements and REEs compositions, the serpentinite (hosting olivine + Ti-chondrodite + chlorite veins) enveloping the Lago di Cignana Unit is strongly enriched in sediment-derived fluid-mobile elements (U, Th, Nb, Ta, Ce, Y, As, Sb) and REEs. Its composition matches those of the closely associated Lago di Cignana Unit UHP eclogites and metasediments. The presence of extremely enriched olivine + Ti-chondrodite + chlorite veins in the serpentinites at direct contact with the UHP Lago di Cignana Unit suggests that fluid exchange and, therefore, coupling between serpentinite and crustal rocks occurred at peak metamorphic conditions. As such, the buoyancy force originating from the relatively light serpentinites fuelled the exhumation of the Lago di Cignana Unit. In this contest, the tectonic contact between the Zermatt-Saas Zone and the Combin Zone evolved into a true tectonic plate interface surface.

THE MONVISO OPHIOLITE

The Lago Superiore Unit at Monviso is one of the best-preserved sections of oceanic lithosphere in the Alpine ophiolites (Lombardo *et al.*, 1978; Angiboust *et al.* 2012b, 2014). It consists of metabasalts, metababbros, metasediments, and serpentine equilibrated in eclogite-facies condition during the Alpine subduction. The Lago Superiore Unit (LSU) is in contact with the Monviso Unit via the Upper Shear Zone and, in turn, cut by two major serpentinite shear zones, the Intermediate Shear Zone (ISZ) and Lower Shear Zone (LSZ). Below the LSZ, a lower section of the LSU, the so-called Basal Serpentinite, is in contact with the underlying Dora-Maira Unit. The LSU is a key example of HP ophiolite in which serpentinite shear zones played an essential role during their tectonic history, driving fluid fluxes and metasomatism, and localizing stresses and deformation (Schwartz *et al.*, 2001; Guillot *et al.*, 2004; Angiboust *et al.*, 2014). The basal section of the LSU consists of oceanic serpentinite that locally exchanged with fluids of metasedimentary origin (rich in As, Sb and radiogenic Sr, and Pb) along HP shear zones. The basal serpentinite is an analogous of the Voltri serpentinite described in Cannaò *et al*. (2016). In fact, while undeformed sections of the Basal Serpentinite still retain an oceanic serpentinization signature, crustal fluids enriched the serpentinite in As, Sb, and radiogenic isotopes (Sr, Pb) along prograde, olivine-bearing, shear-zones. During eclogite facies conditions, seismic rupture of the downgoing slab occurred, producing eclogite-facies breccia blocks (Angiboust *et al.*, 2012a). This resulted in a progressive deformation channelling along the top section of the serpentinite, thus creating the Lower Shear Zone. During exhumation, most deformation and mineral re-equilibration was localized in the LSZ, near the base of the Mg-Al gabbro blocks. This resulted in the destabilization of HP mineral phases (olivine and/or Ti-clinohumite) within the LSZ. Moreover, mechanical mixing and/or late fluid percolation chemically re-homogenized the TE and isotopic composition of the serpentinites in the LSZ serpentinite, which retain its HP geochemical composition and mineralogy only within deformed HP magnesite veins. While most deformation during the peak eclogite-facies metamorphism and during the retrograde history localized along the Lower Shear

Zone, the underlying Basal Serpentinite largely escaped the retrograde deformation and fluid infiltration event, and still records sections of the prograde history, from oceanization to HP metamorphic conditions.

THE LANZO ULTRAMAFIC MASSIF

The Lanzo Ultramafic Massif is a remarkable example of preserved subcontinental lithospheric mantle well preserving all evolutionary steps of a long tectonic history: from mantle upwelling (Piccardo *et al.*, 2007) to oceanization (Debret *et al.*, 2013) to subduction at eclogite-facies conditions and exhumation (Kienast & Pognante, 1988; Pelletier & Müntener, 2006; Debret *et al.*, 2013). In both the Lago di Cignana Unit and the Monviso ophiolite, mass transfer and fluid-rock interactions during oceanic hydration and during subduction largely modified the geochemical and isotopic composition of initial oceanic serpentinites. The Lanzo Ultramafic Massif differs from the above ophiolites in several aspects (Debret *et al.*, 2013). First, it preserves fresh Tethyan sub-continental lithospheric mantle (serpentinization < 1%) that is extremely rare in the Western Alps, which allows investigating the geochemical variability of an Alpine serpentinites protolith. Secondly, it shows a progressive oceanic serpentinization, from fresh peridotite to 100% static, oceanic, serpentinization. Moreover, HP olivine + antigorite foliation and Ti-clinohumite veins indicate fluid release and circulation during the HP event. Due to oceanic seawater hydration, the Lanzo serpentinized mantle acquires a distinct geochemical and isotopic imprint characterized by a strong enrichment in B and W, a moderate enrichment in As, Sb, and Pb, and a partial reset of Sr and Pb isotope ratio, tending towards Jurassic seawater values. During subduction, limited interaction with fluid mobile elements locally increased the Cs levels and Sr isotopes of static serpentinites, toward metasedimentary values. HP mylonite serpentinites show higher levels of reset and As-Sb enrichment, as probably accommodated a larger fluid flux during HP deformation.

Subduction recrystallization and deformation strongly affected the serpentinized sections encompassing the Lanzo peridotite and gabbro. In contrast, the fresh mafic and ultramafic cores still preserve the pristine pre-oceanic and pre-subduction structures and mineral associations. During subduction, the dry Lanzo peridotite and gabbro accumulated large differential stresses, released along active seismic structures such as pseudotachylytes. The dry sections of the Lanzo Ultramafic Massif, together with partially hydrated-eclogitized domains contain abundant sin-eclogitic pseudotachylyte. From fine-scale textural observations, in this work it was determined that co-seismic faulting leading pseudotachylyte formation formed during eclogite-facies conditions (2-2.5 GPa; 550-620 °C) within ophiolitic gabbro-peridotite of the Alps, an exhumed fossil remnant of subducted cold oceanic lithosphere. As proxy of cold subducting slabs, this field laboratory shows that dry, metastable rocks are unable to flow and concentrate stress to generate large subduction earthquakes without much involvement of free aqueous fluid.

DISCUSSION

Alpine serpentinite: a key to unravel subduction accretion at the plate interface

In this work, the petrologic evolution and the geochemical features of serpentinites from Zermatt-Saas Zone and Monviso and of peridotites and serpentinites from the Lanzo Ultramafic Massif were examined. These rocks underwent Alpine subduction to eclogite-facies HP (ZSZ, Monviso and Lanzo) and UHP (Cignana) conditions. The studied serpentinites record steps of the prograde subduction history, when antigorite and brucite break down to olivine + H_2O ad when olivine + Ti-clinohumite assemblages crystallize as rock-forming and as vein-forming (fluid related) phases. Serpentinite from Cignana, from Lanzo, and from the Basal thrust at Monviso well preserve this prograde to peak stage and point to PT conditions in a range of 2.0 - 2.5 GPa. Higher P conditions, suggested by the occurrence of Ti-chondrodite bearing veins from Cignana indicate burial to P > 2.8 GPa (Shen *et al.*, 2015). Similarly, occurrence of Ti-chondrodite in the Monviso Basal Serpentinite suggests that pressures as high as 2.7-2.8 GPa (Angiboust *et al.*, 2012b). Fig. 1 shows all PT path and peak equilibration conditions of the studied serpentinite. The above metamorphic units underwent similar subduction

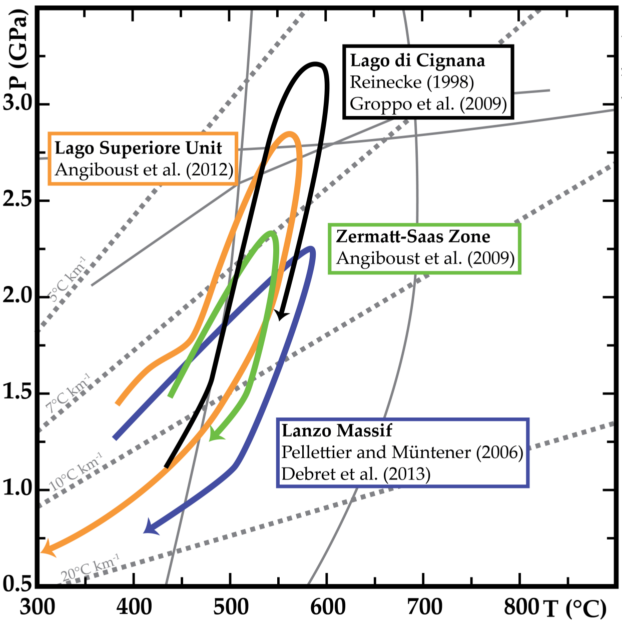

Fig. 1 - PT paths for the Zermatt-Saas Zone in green (after Angiboust *et al*., 2009), the Lago di Cignana Unit in black (after Reinecke, 1998 and Groppo *et al*., 2009), the Lago Superiore Unit in orange (after Angiboust *et al*., 2012b), and the Lanzo Ultramafic Massif in blue (after Pelletier & Müntener, 2006 and Debret *et al*., 2013).

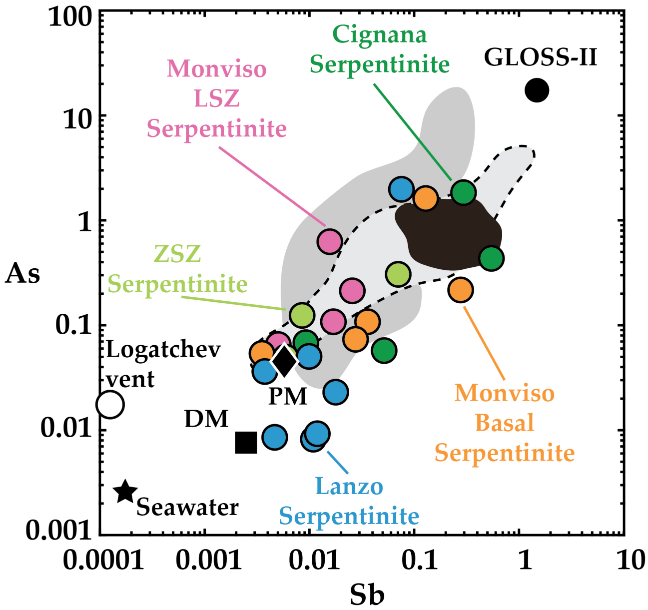

Fig. 2 - As *vs*. Sb plot for Zermatt and Cignana serpentinites, LSZ and Basal Serpentinites and Lanzo serpentinite. Light grey field: Cima di Gagnone metaperidotite (Cannaò *et al*., 2015); black field: Voltri serpentinite (Cannaò *et al*., 2016); dark grey field: Queyras serpentinite (Lafay *et al*., 2013). Depleted Mantle (DM), Primitive Mantle (PM), sea-water and Longachev vents and GLOSS-II are plotted for comparison.

histories but different peak equilibration conditions in their subduction pathway. My geochemical study shows that most serpentinites (Cignana, Monviso) reset their mantle and oceanic imprint and increasing their FME (As, Sb, U, Th) and radiogenic isotope (Sr and Pb) budgets during subduction.

Fig. 2 reports the As-Sb composition of the Cignana, Zermatt, Monviso and Lanzo ultramafic rocks, compared to previous work on Alpine serpentinites (Cima di Gagnone, Voltri Massif, Queyras). Most Cignana and Monviso serpentinites display enrichments in As and Sb due to fluid-mediated exchange with external crustal reservoirs. Similarly, to what observed in the Voltri static serpentinite by Cannaò *et al.* (2016), some serpentinites from Zermatt and Monviso still retain compositions acquired during their oceanic serpentinization and characterized by low As and Sb, similar in composition to the Depleted Mantle (DM) and Primitive Mantle (PM). This inheritance mostly pertains to undeformed rocks, like static serpentinite form the Basal Serpentinite at Monviso and undeformed serpentinites from Voltri Massif (Cannaò *et al.*, 2016). Nevertheless, most serpentinites records infiltrations of externally-derived subduction fluids carrying FMEs.

The isotopic composition of serpentinites also records this cryptic metasomatism (Fig. 3). The isotopic composition of serpentinite from Zermatt (light green circles), Lanzo and Monviso (blue and orange circles, respectively) fall on a mixing line (line 1) between the pristine mantle peridotite (blue square) and Jurassic seawater (light blue star). The green field in Fig. 3 thus represents the starting isotopic composition of oceanic serpentinite, before interaction with externally derived subduction fluids, which have a distinct isotopic signature, depending of their crustal source, whether MORB, or metasedimentary, (GLOSS-II; Plank, 2014).

Serpentinite interaction with these fluids produced a characteristic isotopic imprint in serpentinites. Serpentinite from the Lago di

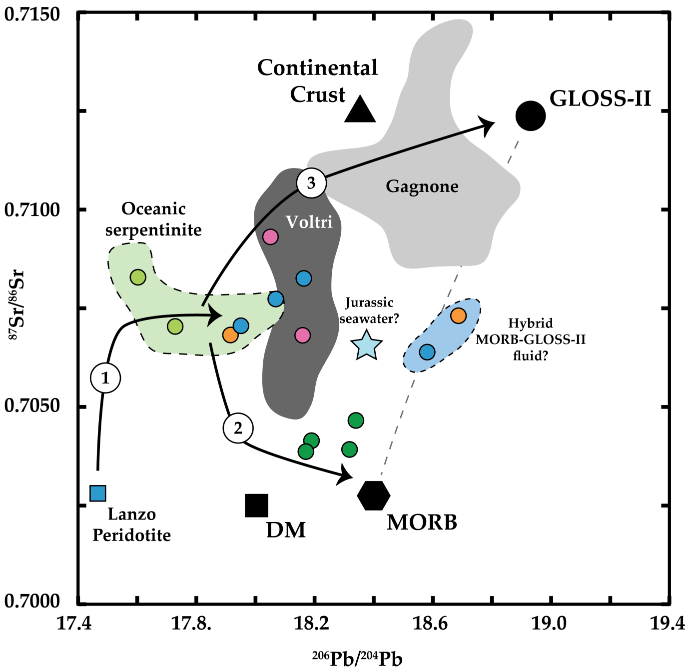

Fig. 3 - $^{206}Pb/^{204}Pb$ *vs.* $^{87}Sr/^{86}Sr$ plot of serpentinite from the Lago di Cignana Unit (dark green circles), the Zermatt-Saas Zone (light green circles), the Lanzo Ultramafic Massif (blue circles), and the Lower Shear Zone (pink circles) and Basal serpentinite (orange circles) from the Lago Superiore Unit. Colours and symbols are from Fig. 2. The sample LM1306 (blue square) represents the isotopic composition of pristine mantle peridotite. The sample LM1301 (lizardite veins at Mt. Musinè; light blue star) represents the isotopic composition of Jurassic seawater. Fields for Voltri serpentinite (dark grey) and Cima di Gagnone metaperidotite (light grey) are from Cannaò *et al.* (2016) and Cannaò *et al.* (2015) respectively. Values from GLOSS-II, depleted mantle, and average continental crust are reported for comparison. Mixing lines for peridotite-seawater (line 1), and oceanic serpentinite-MORB (line 2) and -GLOSS-II (line 3) are added to the figure. The mixing line between MORB and GLOSS-II is represented by the dashed line.

Cignana Unit (dark green circles) is compatible with a crust-derived fluid, along mixing line 2. Instead, serpentinites from the LSZ and, to a lesser extent, from Lanzo, follow mixing line 3, together with serpentinites from Voltri Massif (Cannaò *et al.*, 2016) and Cima di Gagnone (Cannaò *et al.*, 2015), suggesting a metasedimentary origin of the fluid. A few samples from Lanzo and the Basal serpentinite (namely samples LM1307 and GLSZ1417) fall off trend, along a mixing line between MORB and GLOSS-II (dashed line). This anomalous composition might result from fluids with hybrid, MORB-GLOSS-II, subduction fluid composition. As shown in Fig. 3, the isotope systematics helps to unravel the provenance of externally derived subduction fluids, which reacted with serpentinites.

The geochemical approach involving fluid-mobile trace elements and crust-derived radiogenic isotopes in serpentinite is a novel method to unravel the exchanges affecting serpentinites during subduction-zone metamorphism and to identify the rock sources of the fluid. Since fluids generally move upward during subduction metamorphism, this way-up criterion suggest that, to uptake the crust-derived fluids, the serpentinite should over-thrust, or accrete above the crustal and sedimentary rocks releasing FMEs and radiogenic isotopes to the fluid. Therefore, the above criteria are suggested as guidelines to unravel the timing of serpentinite accretion to the plate interface and to define its architecture. Fig. 4 shows the tectonic reconstruction of the Alpine plate interface and identifies serpentinite accreting at different depths to the plate interface.

Interestingly, the Lanzo Massif is the only ultramafic Alpine massif that did not record significant influx of sediment- and crust-derived components. This peridotite was largely preserved unaltered during the entire oceanic and subduction cycle. The serpentinized sections of the Lanzo peridotite show FME enrichments and Sr isotopic compositions compatible with serpentinization by Jurassic seawater. As such, despite experiencing subduction to eclogite-facies condition, the Lanzo serpentinite fully preserved its mantle and oceanic signature. This implies it experienced closed-system behaviour and no fluid mediated influx of sedimentary and crustal components during subduction. I therefore interpret the Lanzo Massif as a true remnant of oceanic slab within the Alpine nappe pile. All other Alpine serpentinite and ophiolite complexes experienced tectonic detachment from the slab, accretion to the plate interface and exchange with slab-derived fluids, which caused the cryptic subduction zone imprint.

The new geochemical approach enabled to distinguish the provenance of the various ophiolite slices now exposed in the Alps (slab *vs*. plate interface) and to define the architecture of the Alpine plate interface (Fig. 4).

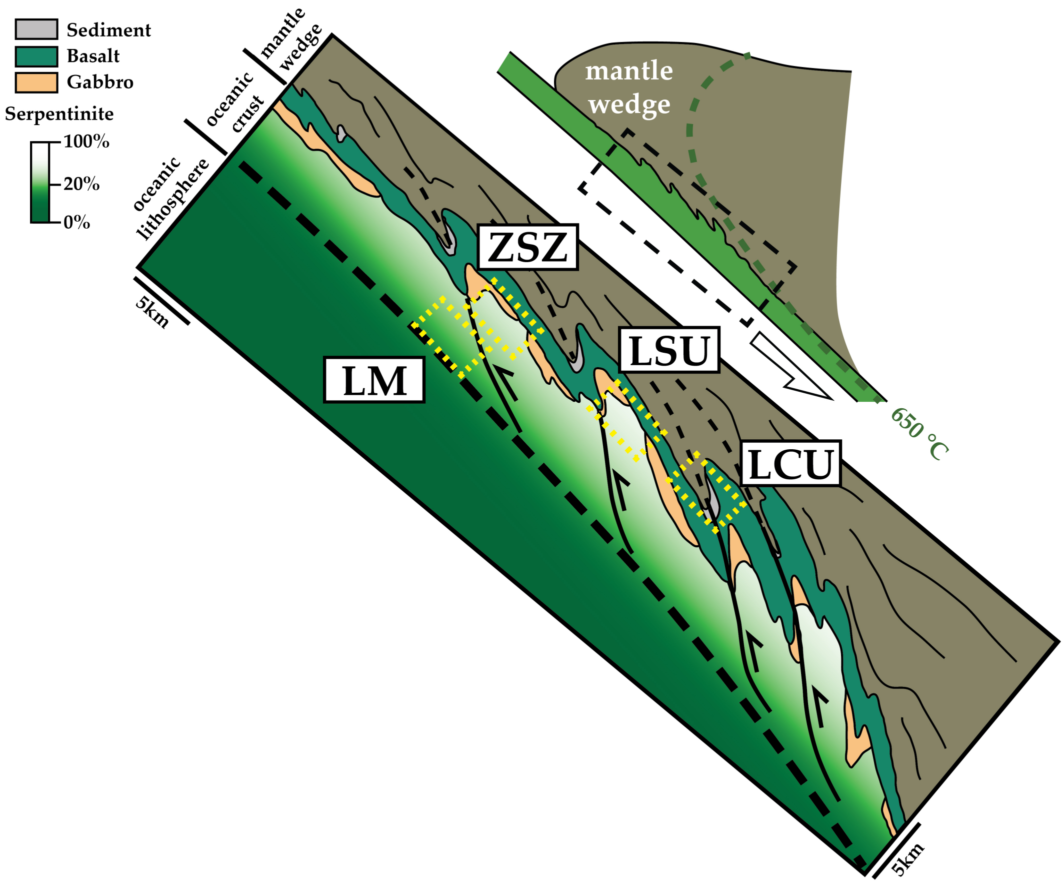

Fig. 4 - Schematic cartoon illustrating the possible architecture of the cold Alpine plate interface (adapted from Guillot *et al*., 2015). The different Alpine HP ophiolites (dashed yellow squares) accrete at different depths along the subduction plate interface. LM = Lanzo Massif; ZSZ = Zermatt-Saas Zone; LCU = Lago di Cignana Unit; LSU = Lago Superiore Unit. See text for discussion.

Records of deep subduction zone seismicity in the Lanzo Peridotite

The distribution of seismicity in subduction zones shows that intermediate-depth earthquakes occur within the top of the slab near the plate interface and in the mantle (Abers *et al.*, 2013; Bostock, 2013; Kita *et al.*, 2006), offering several implications for the relationship between earthquake triggering and structure (Bostock, 2013; Kita *et al.*, 2006). Abundant hydrous phases and pressurized fluids (Audet *et al.*, 2009) hamper seismic wave V_p/V_s velocities in plate interface domains, making them the preferential sites for dehydration embrittlement earthquakes (Abers *et al.*, 2013; Hacker *et al.*, 2003). Differently, Wadati-Benioff seismicity occurs within slabs, in the dry lower oceanic crust or in the subducting lithospheric mantle (Bostock, 2013). Here, hydration concentrates along discrete horizons, near major oceanic and/or bend-faults at outer rise settings (Peacock, 2001).

Alpine HP ophiolitic complexes are hydrated sections of oceanic slab, pervasively recrystallized into blueschist to eclogite facies during their burial and exhumation history (Angiboust & Agard, 2010; Guillot *et al.*, 2015). The Lanzo Massif and Moncuni, instead, fit an intra-slab lithosphere somehow accreted and exhumed along the plate interface. Pseudotachylytes are absent in surrounding serpentinite and in other hydrated eclogite-facies Alpine rocks. The only potential earthquake records in such rocks are eclogitic breccias in metagabbro

(Angiboust *et al.*, 2012a). The observations derived from this work agree with the available literature on eclogitic pseudotachylyte, documenting their development either inside, or at the contacts between metastable dry rocks (Andersen *et al.*, 2014; Lund & Austrheim, 2003). Stiff unaltered peridotite and gabbro cut by oceanic serpentinite layers, form large part of the seismogenic lithospheric slab mantle. Ultramafic bodies of dimensions comparable to the Lanzo Massif and Moncuni are below the resolution of seismic imaging and thus uneasy to detect. In such setting, Moncuni-like earthquakes may be either related to the breakup of subducting plate asperities during accretion at the plate interface, or to collision and/or indentation of rigid dry rock bodies. It is here suggested that such stiff and unaltered sections of lithospheric mantle work as resisters, accumulating and releasing stress into short-term cataclasite and pseudotachylyte structures during intermediate-depth earthquakes. Other earthquake-related structures described in Alpine HP ophiolites, as eclogite breccias (Angiboust *et al.*, 2012a), might form, instead of pseudotachylytes, when pore-fluid pressure and hydro-fracturing are involved as earthquake triggering mechanism.

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