

LIGHT ELEMENTS, STABLE AND RADIOGENIC ISOTOPES (B, O, SR, PB) IN ULTRAMAFIC/MAFIC ROCKS AS TRACERS OF MASS TRANSFER ALONG THE SLAB/MANTLE INTERFACE IN SUBDUCTION ZONES

ENRICO CANNAÒ

Dipartimento di Scienze della Terra, Ambiente e Vita, Università di Genova, C.so Europa 26, 16132 Genova

Subduction zones represent the main settings for the geodynamic activity of the Earth and are identified as the main sites of important geological processes involving mass transfer to depth, geochemical recycling of volatile and fluid-mobile elements and the genesis of seismic activity. These processes control the refertilization of the Earth's mantle and also determine and/or condition the arc and intraplate magmatism.

The evolution of convergent motions leads to orogenic belts formation, where tectonic slices of subducted materials are exposed. These materials record the main metamorphic processes of fluid/rock interaction occurred during prograde burial at great depth and represent a natural laboratory for field, petrological and geochemical studies.

The definition of the interaction processes and the recognition of the origin and of the evolution of the subduction materials represent an important objective within the international scientific debate. In this regard, the following work is focussed to the study and analyse of some of these tectonic and geochemical processes that characterize the subduction zones.

The presence of low viscosity channels in between the plates act as major sites for the exhumation of high- and ultrahigh pressure (HP-UHP) terranes. Many authors suggest that these environments can represent domains of intense tectonic and chemical mixing between different rock reservoirs. The matrix of these channels can be made of serpentine and/or (meta)sedimentary materials. Recently, petrological models individuate the slab-mantle interface mélange as main sources for arc magmatism. The chemical and tectonic mixing derive from the interaction between three major end-members: serpentinites and altered oceanic crust, metasediments and supra-subduction mantle.

In light of these features, geochemical studies of fluid-mobile elements (FME) joined with B, O, Sr and Pb isotopic analyses of high pressure mélanges terranes were performed with the aims of constrain the tectonic processes and mass transfer during accretion of slab and supra-subduction mantle in plate-interface domains. Here, we focus on *i*) metasediment-dominated matrix mélange from Cima di Gagnone (Adula-Cima Lunga Unit, Central Alps), enclosing lenses of eclogite-facies de-serpentinized garnet peridotites and chlorite harzburgite and *ii*) HP serpentinites from the Voltri Massif (Ligurian Western Alps).

Cima di Gagnone

The Cima di Gagnone area is situated in the Adula-Cima Lunga unit (Central Alps) and is characterized by gneiss and garnet micaschists enclosing lenses of garnet peridotites and chlorite harzburgite deriving from complete dehydration of ancient serpentinites and serpentinized peridotites subducted during the Alpine orogenesis. Olivine + ortho- and clino-pyroxene + Mg-amphibole + garnet form the peak assemblage in the garnet peridotite, with evidence of the chlorite stage assemblage, whereas in the chlorite harzburgite the eclogite metamorphism produces olivine + orthopyroxene + chlorite + F-Ti clinohumite. In turn, the chlorite harzburgite enclose boudins of mafic rocks, eclogite and HP metaroddingite. P-T estimation from the literature for ultramafic rocks individuates a maximum of about 800 °C and 3GPa for chlorite harzburgite. These values correspond to the minimum P-T condition for the stability of the HP assemblage in the garnet peridotites (Scambelluri *et al.*, 2014). Into eclogite and metaroddingite, garnet-pyroxene geothermometer yields to eclogite peak temperature of about 800 °C for pression between 2.0 and 2.5 GPa. Hydration during retrograde metamorphism linked to the Lepontine dome lead to formation of garnet-bearing amphibolite and amphibolite-bearing blackwall on eclogite and metaroddingite, respectively, and formation of chlorite on garnet in garnet peridotites and tremolitic

amphibole in the chlorite harzburgite. The evidence of the HP event in the metasediments is the presence of high Si phengite in micafish microstructure relicts. Geobarometer yield pressure of about 2.1 GPa in a temperature range of 700-800 °C. The lower pressure recorded by the country metasediments can be due to retrograde re-equilibration of phengite mica. However, the high pressure event producing dehydration of ancient serpentinites is also shared by the eclogite mafic bodies and by the host metasediments. This point out that the entire rock suite has experienced the same prograde history.

Metaperidotite from Cima di Gagnone show low [B], negative $\delta^{11}\text{B}$ (between -1 and -10‰) and high Sr and Pb isotopic ratios ($^{87}\text{Sr}/^{86}\text{Sr}$ up to 0.7124 and $^{206}\text{Pb}/^{204}\text{Pb}$ up to 18.894). Comparable values are displayed by HP mafic rocks, whereas the retrograde garnet peridotites and blackwall show Sr isotopic composition close to 0.71, high radiogenic enrichment for Pb isotopes ($^{206}\text{Pb}/^{204}\text{Pb}$ up to 18.940) and $\delta^{11}\text{B}$ close to -8‰. Host metasediments have negative B isotopic composition (close to -12‰) and high radiogenic Sr and Pb isotopic signature ($^{87}\text{Sr}/^{86}\text{Sr}$ up to 0.7286 and $^{206}\text{Pb}/^{204}\text{Pb}$ up to 18.978). The $\delta^{11}\text{B}$ of the ultramafic rocks suggests *i*) isotopic fractionation during metamorphic dehydration of serpentinitized mantle rocks precursor at HP ($\delta^{11}\text{B}$ from +10‰ to +40‰, typical values in abyssal serpentinites) coupled with *ii*) interaction between them and host-derived fluids during prograde to peak history (Fig. 1a).

The high radiogenic fingerprints of Sr and Pb in ultramafic rocks are higher than those of the depleted mantle and Jurassic seawater and provide evidence of interaction between the country rocks and ultramafic-mafic bodies. The compiled dataset from the PhD thesis shows that the isotopic composition and trace elements of ultramafic and mafic rocks were reset towards crustal values during exchange with the mélange matrix in the subduction setting. The exchange process brought into ultramafic rocks fluid-mobile elements such as B, Pb, Th, U, As and Sb. Compared to a pelitic protolith, the Gagnone metasediments are depleted in As and Sb (and in minor amount in B). This variable depletion is coupled with increase of the same elements in chlorite harzburgite, in the associated eclogite-metarodingite, and in garnet peridotites. These features indicate element exchange between the two systems, together with re-equilibration of metaperidotite and mafic rocks towards crustal values. The involvement of fluid-mobile elements like As and Sb, transported at relatively low-temperature (300 °C, Bebout *et al.*, 1999), suggests that tectonic accretion of ultramafic slices to the sedimentary veneer should have occurred since the early stages of subduction.

In the $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 1b) are visible the effects of superposed fluid rock interaction episodes recorded by the Gagnone rock suite and enables to distinguish the effects of retrograde fluid overprint on the geochemical signature acquired during peak metamorphism. The diagram shows the isotopic composition of the entire sample suite, characterized by a large range of $^{206}\text{Pb}/^{204}\text{Pb}$ (18.292-19) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.70729-0.72108). This heterogeneity can be explained by means of superposed fluid-rock interactions affecting the samples. The $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of one group of garnet peridotite, chlorite harzburgite and high-pressure mafic rocks plots between 18.29 and 18.66. These samples fall along three mixing lines between the Erro-Tobbio high-pressure serpentinitized peridotite (used here as protolith of the Gagnone ultramafic rocks) and the paragneiss with highest $^{87}\text{Sr}/^{86}\text{Sr}$ and low $^{206}\text{Pb}/^{204}\text{Pb}$, which preserves significant modal amounts of eclogite-facies minerals. The mixing lines display the possible changes in isotopic composition during interaction of the Erro-Tobbio protolith with a fluid sourced by the high-pressure metasediments. The three mixing lines intercept four garnet peridotites, two chlorite harzburgite, the preserved eclogite and metarodingite. The degrees of interaction individuated by the model suggest a maximum of 2% crustal component added to these rocks by the fluid. The $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of samples showing higher amounts of retrograde minerals shift towards values as high as 19.0 and about 0.71 of $^{87}\text{Sr}/^{86}\text{Sr}$ (and also $\delta^{11}\text{B} = -10‰$). We relate this shift to retrograde fluid infiltration enhancing partial re-equilibration of the Pb and Sr isotopic signatures acquired during prograde interaction between host metasediments and ultramafic-mafic bodies. I therefore interpret the isotopic compositions of samples plotting close to the dashed mixing lines as acquired during prograde to peak exchange in the subduction interface mélange of Gagnone.

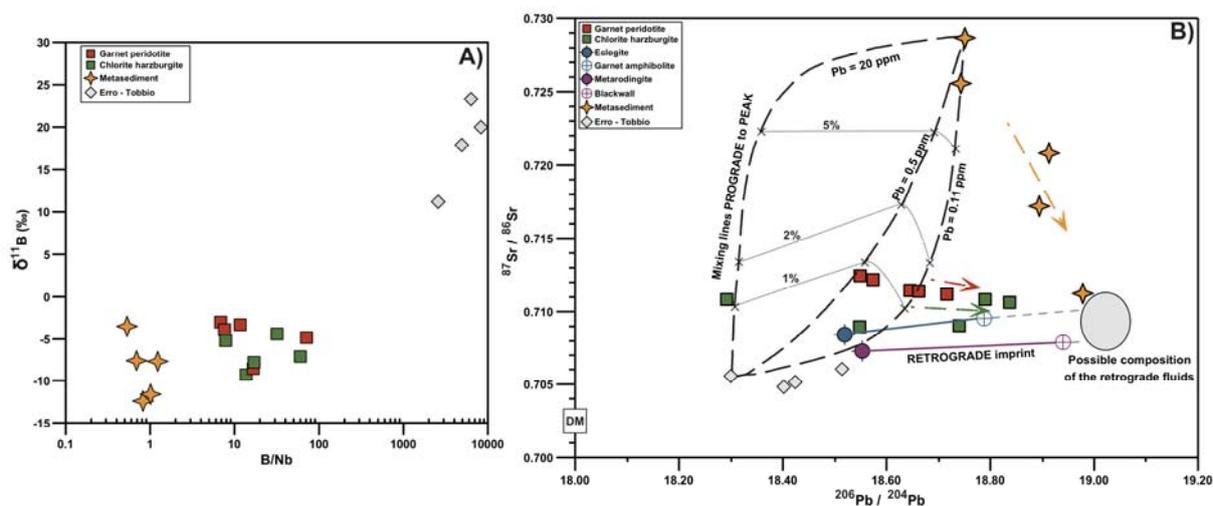


Fig. 1 - a) In a $\delta^{11}\text{B}$ vs. B/Nb ratio plot ultramafic rocks fall in between the high pressure serpentinized rocks and the metasediments of Gagnone. A possible interaction between these end-member reservoirs seems occurred during subduction processes. b) Mixing lines (with different Pb content in the protolith) in a $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plot show prograde to peak interaction between high pressure ultramafic rocks and crustal reservoirs. The degree of interaction is also reported along the three different mixing lines (1-2-5%). Ultramafic samples show 1-2% degree of interaction with crustal component. Retrograde imprint leading higher Pb isotope ratio is also visible in particular with the blackwall and garnet-bearing amphibolite mafic rocks. The retrograde field is individuated by the intersection of the retrograde trends shown by all lithologies. Note that the composition of the retrograde fluids is quite different from those of the prograde/peak one.

The Gagnone case study can serve as a guideline to understand peridotite and serpentinized peridotite contamination during interaction with sediment-derived fluids in subduction settings. I think this context is relevant, as it may disclose the exchange processes between two rock systems that largely control the water and fluid-mobile element budgets for subduction. This interaction is not only representative of mélangé settings; it can also play a role when considering hydration of forearc mantle by uprising slab fluids.

Fluid inclusions trapped into high pressure minerals of the garnet peridotites and chlorite harzburgite allow to calculate the $K_{d\text{fluid/mineral}}$ and to determine the composition of their hydrated precursors. Data obtained provide high enrichment in FME, such as Cs, Rb, Ba, As, Sb, Pb, and Sr in both garnet peridotite and chlorite harzburgite. These results highlight the interaction with sediment-derived fluids and the high potential of hydrated ultramafic rocks as major carrier to depth of incompatible elements. Moreover, garnet peridotites are most enriched in FME with respect the chlorite harzburgite, interpreted as of slab provenience, and in particular of abyssal and subducted serpentinites (Deschamps *et al.*, 2013). This suggests that the garnet peridotite could derive from supra-subduction setting flushed by hybrid fluids (serpentinite + sedimentary components). Oxygen isotopes performed in some samples of metaperidotite seem support this interpretation. Chlorite harzburgite show maximum values of +3‰ of $\delta^{18}\text{O}$, compatible with the oceanic stage at higher temperature coupled with O isotopic fractionation after dehydration at high temperature. Garnet peridotites, instead, display values close to those of the mantle ($\delta^{18}\text{O}$ range between +4.5 and +5.5‰). Mixing model in a $\delta^{18}\text{O}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ plot indicates that interaction between serpentinite and sedimentary fluids can provide the geochemical features observed into the garnet peridotite. No evidence of partial melting in the metasedimentary hosts point to dry conditions at high pressure conditions, but the dehydration of chlorite, instead, could supply free water into the systems. The formation of the garnet-bearing assemblages of the garnet peridotite is reached only if the dehydration of chlorite peridotites occurs at the top of the plate interface. Taking into account these field and geochemical constraints,

the garnet peridotite may derive from metasomatized supra-subduction mantle and embedded into *mélange* at peak conditions.

The peak pressure-temperature conditions achieved for Gagnone metaperidotite correspond to top-slab temperature at sub-arc depths reproduced in thermal models. Therefore, the eclogite-facies metamorphism and the deserpentinization process recorded by the Gagnone metaperidotites can be representative of sub-arc environments. The dehydration of such hydrated peridotites could supply huge amount of fluids enriched in FME into the source of arc magmas, with major geochemical implications. The direct link between subduction input and volcanic arc output established by numerous authors is reflected by distinctive LILE enrichment and by volatile-rich composition of arc magmas with respect to unaltered mantle values. In particular, the significant enrichment in arc lavas of LREE and LILE preferentially hosted in sediments has long suggested the direct involvement of sedimentary materials and altered oceanic crust in fluid and element loss from slabs at subarc depth. However, a number of recent works provided different views of the transfer process, suggesting that hydrated (serpentinized) mantle rocks from the slab or from the supra-subduction hanging wall mantle are relevant to fluid and element transfer to depth and delivery to arcs. The general transfer mechanism is not fully understood. Some authors suggest sub-arc slab dehydration through the interplay of serpentinite dehydration and fluid interaction with different slab layers to mobilize the elements. Others propose that the hanging wall mantle wedge fixes and transports to depth the fluids and elements uprising from the slab. A third class of models suggests the diapiric uprise of buoyant plate-interface serpentinite and/or *mélange* layers into the mantle wedge and their direct melting in hot subarc mantle regions. The correspondence of peak pressure-temperature estimates for the Gagnone *mélange* with subarc conditions suggested by thermal models and geophysical imaging of subduction zones encourages the use of these rocks to understand the role of deserpentinization of Gagnone-type peridotites in affecting the isotopic signature of arc lavas. Fig. 2a reports the $\delta^{11}\text{B}$ vs. Nb/B compositions of the Gagnone metaperidotite samples less affected by retrograde re-equilibration (Fig. 1b), together with reference mantle, high-pressure Erro-Tobbio serpentinite and metasediments.

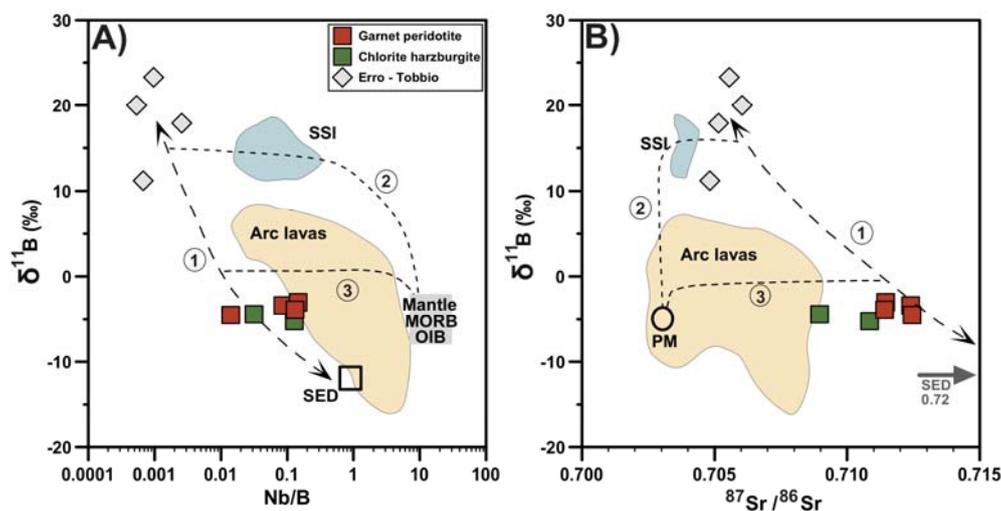


Fig. 2 - a) $\delta^{11}\text{B}$ vs. Nb/B ratio and b) $\delta^{11}\text{B}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ isotopes plot show the major geochemical implications of the interaction processes at the plate interface environment in arc magma genesis. Early elements exchange from sediment/crustal to ultramafic rocks allow ultramafic rocks to become reservoir enable them to acquire sedimentary geochemical fingerprint that moves along the dashed line number 1. Uprising fluids from dehydration of serpentine pure component provide geochemical anomalies in the above mantle as show by the South Sandwich Island lavas (SSI; mixing line number 2). Dehydration of ultramafic rocks after exchange (as metaperidotite from Gagnone, dashed line number 3) supply geochemical heterogeneities observed for all other arc lavas. Arc lavas fields from Scambelluri & Tonarini (2012 and references therein). SED: sediments.

The dashed line connecting Erro-Tobbio serpentinite and sedimentary end-members (line 1) represents hypothetical serpentinite-sediment mixed reservoir, whose compositions depend on the amount of end-members involved. For example, addition to the mantle source of a relatively pure serpentinite fluid, as may occur in sediment-poor ocean-ocean convergent margins, leads to production of magmas like the South Sandwich Island arc (SSI in Fig. 2a; mixing line 2). Addition of a fluid sourced by a metasomatized Gagnone-type component (*e.g.*, dashed line 3) can generate a number of arc lavas with low to negative $\delta^{11}\text{B}$, representative of convergent margins with larger amounts of sediment involved (*e.g.*, Andes, El Salvador, Kurile, Phlegrean volcanic district, Turkey, Aleutian, and Cascades). Comparable features are shown by the $\delta^{11}\text{B}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ diagram of Fig. 2b, suggesting that the addition of a serpentinite component to the mantle (dashed line 2) generates the SSI arc lavas. If a Gagnone-type component is mixed to the mantle along dashed line 3, the corresponding arc lavas have higher radiogenic Sr component. Note that to form the latter lavas, addition of a fluid component directly sourced by sediments at subarc settings (plotting in Fig. 2b at high $^{87}\text{Sr}/^{86}\text{Sr}$ and negative $\delta^{11}\text{B}$ values) is not necessary.

Voltri Serpentinites

The area of study is situated in the Voltri Massif at the eastern termination of the Ligurian Western Alps. It consists of metaophiolitic rocks associated with metasediments that were involved in the Alpine orogenic processes, recording a complex structural and metamorphic evolution, from oceanic alteration to subduction and exhumation events. Lherzolite, serpentinites, metagabbros and metabasalts from oceanic lithosphere, and metasediments (micaschists, calcschists, quartzites, and marbles) from the oceanic cover are the main lithologies forming the Voltri Massif. Many studies on this ophiolite were concentrated in the Erro-Tobbio area made of lherzolites more or less serpentinitized with associated eclogite and metaroddingite bodies. Here we focus our attention on serpentinites located in the core of the Voltri Massif. These rocks are made essentially of antigorite and magnetite, with minor amount of chlorite and relicts of mantle pyroxene. Subduction recrystallization at 450-500 °C and 1.3-2.0 GPa produce partial replacement of antigorite by formation of metamorphic olivine, representing the partial dewatering of previous assemblages at eclogite facies conditions.

Serpentinites texture allows to distinguish between undeformed and mylonitic serpentinite domains and field relationships highlight that the undeformed rocks are enclosed in the deformed ones, along with eclogite and HP metaroddingite body rocks. In the undeformed domains are still preserved the old site of pyroxene and olivine mantle minerals, replaced by serpentine minerals during exposure at the ocean floor and followed by recrystallization of antigorite under increasing conditions. Instead, in the deformed domains, serpentinites show typical mylonitic foliation formed by iso-orientation of fine grains of antigorite and magnetite. Remnants of mantle pyroxene, partially recrystallized, are sometimes recognizable, in particular along major layers which record ancient pyroxene-rich horizon inside the mantle peridotites. The presence of old pyroxene site with different crystal orientation of the antigorite crystals with respect those of the main foliation, provide information about a second event of serpentinitization syn- or post-deformation. Both of these domains are cross-cut by neoblastic formation of metamorphic olivine along the mesh texture and in HP veins, as occurred in the Erro-Tobbio area (*e.g.*, Hermann *et al.*, 2000). Coronitic and mylonitic eclogite and metaroddingite are present in both serpentinite domains. The HP assemblage in the eclogite (omphacite+garnet+rutile+quartz) is partially overgrown by retrograde blue- to greenschist paragenesis.

Undeformed serpentinites show low concentrations in LILE and fluid-mobile elements, like As and Sb (0.1 and 0.01 ppm, respectively). B content is comparable with those of the subducted serpentinites (B = 25.9 and 32.2 ppm) whereas $\delta^{11}\text{B}$ values are up to +30‰, higher than those of the abyssal and forearc serpentinites, the HP serpentinite from the Erro-Tobbio (Scambelluri & Tonarini, 2012) and close to the values of HT serpentinites from the OPD LEG209 1274A/1272A (up to +40‰). Oxygen isotopic values are 4.5‰ and Sr and Pb isotopic ratio show low enrichment in radiogenic isotopes, with the Sr isotopic composition typical of serpentinites altered by Jurassic seawater interaction ($^{87}\text{Sr}/^{86}\text{Sr}$ up to 0.70693) whereas Pb isotopes are close to the mantle values ($^{206}\text{Pb}/^{204}\text{Pb}$ up to 18.205, $^{207}\text{Pb}/^{204}\text{Pb}$ up to 15.621 and $^{208}\text{Pb}/^{204}\text{Pb}$ up to 38.179).

Mylonitic serpentinites from Vara area display higher concentrations in LILE and fluid-mobile elements with respect to undeformed rocks, like As and Sb (up to 1.3 and 0.39 ppm, respectively). The boron contents range from 12.8 to 41.5 ppm. With respect to the undeformed rocks, the mylonitic serpentinites are less enriched in heavy ^{11}B , with $\delta^{11}\text{B}$ ranging between 17.0 and 22.3‰. $\delta^{18}\text{O}$ values vary between 5.1 and 5.9‰. The enrichments in some key trace elements are associated to enrichment in radiogenic component for the Sr and Pb isotopes (Fig. 4): $^{87}\text{Sr}/^{86}\text{Sr}$ ratio ranges between 0.70800 and 0.71055, whereas Pb isotopic fingerprints go up to $^{206}\text{Pb}/^{204}\text{Pb} = 18.725$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.726$ and $^{208}\text{Pb}/^{204}\text{Pb} = 38.916$. The sample MS VAR 10-10V, which is indicative of serpentinite with HP olivine-bearing veins, shows the same trace element pattern and the same O and radiogenic enrichment as the mylonitic serpentinites. The only exception is due to a slight $\delta^{11}\text{B}$ enrichment, up to 26.6‰, and to its very low $^{206}\text{Pb}/^{204}\text{Pb}$ ratio (18.091). The data presented here show a great correspondence between the different texture of the serpentinites and their geochemical signature, both in terms of trace elements and stable and radiogenic isotopes.

HP mafic rocks show low [B], negative $\delta^{11}\text{B}$ (down to -6‰) and not radiogenic enrichment ($^{87}\text{Sr}/^{86}\text{Sr}$ up to 0.7045; $^{206}\text{Pb}/^{204}\text{Pb}$ up to 18.372). No evidences of enrichment in FME are visible.

The undeformed serpentinites presented here show evidence of pseudomorphic replacement textures on ancient mantle olivine and pyroxene. These textures can be related to initial oceanic peridotites serpentinization by seawater. This initial stage is followed by static antigorite growth and by formation of metamorphic olivine during subduction zone recrystallization at increasingly P-T conditions. The trace element compositions of these rocks show limited enrichment in fluid-mobile elements, such as As and Sb (and also Cs and Pb), with respect to primitive mantle: this is indicative that the initial seawater serpentinization at the ocean floor was no longer reset by further chemical exchanges during subduction processes. The high boron isotopic fingerprint, the relative low $\delta^{18}\text{O}$ values coupled with the low Sr and Pb isotopic ratios shown by these rocks support the addition of seawater-derived fluid during oceanic alteration at the Jurassic time. By contrast, mylonitic serpentinites show significant differences with respect to the undeformed ones and these differences are key information in the understanding of the subduction processes affecting the Voltri Massif. Foliation development in deformed serpentinites is associated with increase in the concentrations in As and Sb, coupled with slight B isotopes depletion and radiogenic component in Sr and Pb isotopes (Fig. 3).

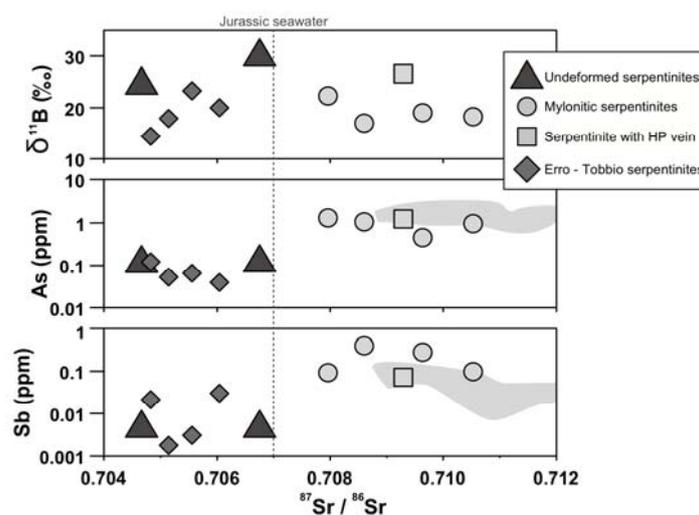


Fig. 3 - $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $\delta^{11}\text{B}$, As and Sb contents (ppm) of Voltri serpentinites. Undeformed serpentinites still record oceanic geochemical signature in terms of trace elements and isotopic signature. Mylonitic serpentinites show positive correlation between radiogenic Sr and As and Sb contents suggesting interaction with sediment-derived fluids. Slightly depletion in $\delta^{11}\text{B}$ could also reflect this interaction. For comparison fields for metaperidotite from Cima di Gagnone (grey colour) and data of the Erro-Tobbio rocks are reported. Vertical dashed line is the Sr isotopic ratio of seawater during Jurassic time.

Increasing of the As and Sb contents and, in particular, of radiogenic Sr and Pb isotope point to interaction with external fluids with sediment-like signature. Formation of metamorphic olivine at eclogite facies condition which shows the same enrichment in fluid-mobile elements and radiogenic isotopes, support and constrain the enrichment stage prior to eclogite-facies recrystallization.

If we compare the geochemical signature of the mylonitic serpentinites with those of the metaperidotite from Cima di Gagnone, showing clear evidence of interaction with sediment-derived fluids, the deformed rocks match quite well their $^{87}\text{Sr}/^{86}\text{Sr}$, As and Sb values. Analogously, the decrease in the ^{11}B isotope contents of the Voltri mylonites compared to the undeformed serpentinites can be attributed to the interaction with sediment-derived fluids, as reported for example in the Cima di Gagnone rock suite.

Pb isotopes highlight that the mylonitic serpentinites were affected by interaction with sediment-derived fluids coupled with a third reservoir. In particular this reservoir should show radiogenic Sr (close to 0.712) and ^{207}Pb (close to 15.80-15.85) but much lower ^{206}Pb and ^{208}Pb (close to 18.40-18.45 and 38.80-38.90, respectively). The most likely candidate for such a geochemical reservoir could be an older upper continental crust involved in subduction processes or their derived subcontinental sediments.

When we compare the trace elements budget of the mylonitic serpentinites from the Voltri Massif with the serpentinites bodies embedded in metasedimentary matrix from the Queyras Schistes lustrés complex from the Western Alps (Lafay *et al.*, 2013) some key informations can be observed. Positive anomalies and enrichments above the PM values are visible for Cs, B, Pb, As and Sb, once again, underlines the interaction between sediment-derived fluids and mylonitic rocks. While in the Queyras Schistes Lustrés complex and in the Cima di Gagnone mélange the ultramafic rocks are enclosed in metasedimentary matrix terranes and the provenance of the sediment-signature is now ascertained, in the Voltri area analyzed here, the sediments are far away. Geological relationships between the analyzed lithologies show that mylonitic serpentinites wrap around the undeformed ones and the eclogitic mafic rocks without evidence of nearby metasedimentary rocks. In this context, foliation development in the Voltri serpentinites acts as major site of fluid-flow and plays a key role in the partially resetting of the serpentinite geochemical signature (Fig. 4).

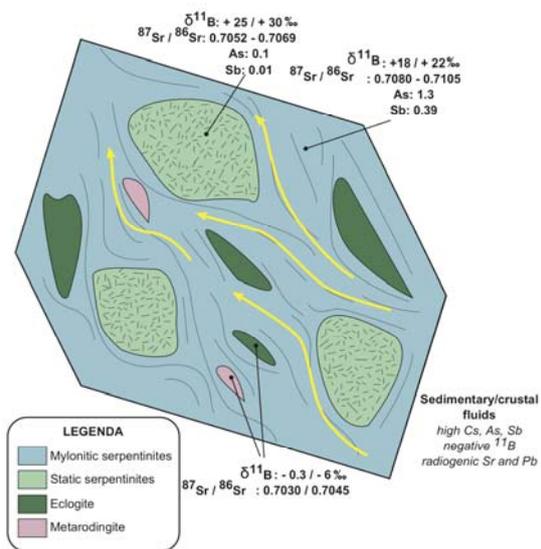


Fig. 4 - Sketch showing the main relationships between all lithologies exposed in the outcrop from Voltri area. With the yellow arrows are reported the fluid fluxes along the main foliation and the isotopic signature of the undeformed and mylonitic serpentinites. Note that mafic rocks do not show significantly enrichment in FME and radiogenic isotopes.

The preserved undeformed domains record the oceanic stage and represent the compositions of the starting materials, allowing an understanding of fluid and deformation-mediated trace element exchange during interaction processes. The ability of serpentinites to retain incompatible elements allow mylonitic serpentinites to increase their budget up to 150% of B, 1000% of As, 7600% of Sb and 1100% of Cs with respect to the undeformed rocks.

Formation of serpentinites and serpentinitized peridotites are linked to hydration environment, therefore exposure of oceanic lithospheric mantle at slow-ultraslow spreading ridges and along major transform faults are key environments for their formation. In these settings seawater is the main geochemical reservoir able to transfer its geochemical signature to the newly formed rocks. Ranero *et al.* (2003) proposed that the presence of along strike-normal faults near the trench can play a major role on the deep hydration of the mantle rocks. Such structures form in response to the bending of the subducting plate prior to its entrance in the subduction zones. These *bend-faults* can act as major site for fluid flux into the lithospheric mantle: infiltration of fluids with sedimentary signature can supply the geochemical anomalies observed in the Voltri mylonitic rocks. These structures can be reactivated during subduction processes leading to the formation of mylonitic foliation into serpentinites. Another key scenario for hydration of ultramafic rocks are the subduction channel domains, where slices of slab and wedge materials can be accreted to the slab-mantle interface and undergo hydration by uprising slab fluids. The geochemical fingerprints of such fluids are related to the material involved in subduction processes, which could derive from (meta)sediments, altered oceanic crust and/or hydrated minerals breakdown or phase transformation from ultramafic rocks. In light of these major sites of hydration, the Voltri serpentinites from static domains clearly show evidence of formation at the oceanic seafloor, because their B, O, Sr and Pb isotopic signature coupled with FME contents shows typical seawater values. The geochemical features of the deformed serpentinites are quite different, and can be related either to the bend-faults or to subduction channel environments.

The geochemical features of the Voltri serpentinites and of the Gagnone metaperidotite documented here underline the key role of hydrated mantle (*i.e.*, serpentinites) in fluid-mediated mass transfer into deep. Their capacity to retain fluid-mobile elements and to reset their pre-subduction geochemical imprint has important consequence in the recycling of elements via fluids during the antigorite-out reaction with major tectonic and geochemical implications. They are able to trace the interaction with external fluids, both from sediment and/or altered oceanic crust derivation, helping us to unravel the tectonic evolution of complex and mélange terranes.

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