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E. Cannaò
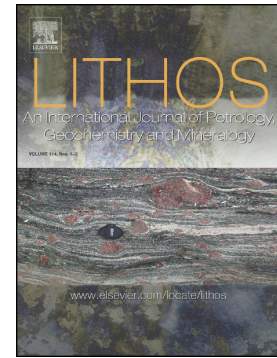
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Boron isotope fractionation in subducted serpentinites: a modelling attempt

Cannaò E.

Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano, Via S. Botticelli 23, 20133, Milano, Italy

Corresponding author: enrico.cannao@unimi.it

Abstract

Boron (B) and its isotopes are powerful geochemical tracers of subduction processes, enabling to understand the role played by fluids in large-scale mass-transfer at convergent margins. In such settings, oceanic and forearc serpentinites are the most important reservoirs for B and heavy B isotopes contributing to the genesis of arc lavas. Literature data support the release of significant amount of B during the chrysotile/lizardite to antigorite (atg) phase transition and during the partial to complete antigorite dehydration to form secondary peridotites. However, the information concerning the B-isotope fractionation associated to these reactions is limited. In this Letter, I attempt to model the B-isotope fractionation affecting subducted serpentinites through the *ab initio* B-isotope fractionation calculations provided for trigonal- and tetrahedral-coordinated B in both minerals and fluids. The obtained results mainly confirm serpentinites as the main vector of positive $\delta^{11}B$ to depth as shown by natural high-pressure serpentinites analysed so far. However, a lack of information on pH conditions hampers the proper estimate of the fractionation of B in serpentinites during their prograde evolution in subduction zones. This may represent a limit in the approach proposed here, since poor-alkaline (close to neutral) pH conditions can result in low (potentially negative) $\delta^{11}B_{atg}$ signatures. Finally, I try to address new research trends and major topics worth investigating to better unravel the B cycle in serpentinites and their dehydration products.

1. Introduction

Serpentinites are important components in the subducted oceanic lithosphere, playing a key role in the global cycles of volatiles, halogens and incompatible elements in subduction zones (e.g., Scambelluri et al., 2019 and references therein). Peridotite serpentinization by seawater and hydrothermal fluids induces relevant chemical and physical modifications of mantle rocks near the seafloor. Similarly, hydration of the forearc mantle by uprising slab fluids can stabilize hydrous

minerals like serpentine, talc and chlorite, modifying its geochemical and geophysical properties. The incorporation of structurally bound water within serpentine decreases the density of the lithospheric mantle and increases the rocks' volume up to 40%. Due to its large pressure-temperature (P-T) stability field (**Fig. 1**), the presence of significant volumes of serpentinites in subduction zones affects tectonic processes enabling the exhumation of dense eclogitic mafic material (Hermann et al., 2000) and may control the development of mélanges within the slab-mantle interface domains (Guillot et al., 2015).

From a geochemical point of view, serpentinites are important reservoirs for volatiles (H_2O and also CO_2 in ophicarbonates), halogens, noble gases and fluid mobile and incompatible elements (e.g., Scambelluri et al., 2019 and references therein). In particular, subduction zones serpentinites are primary vectors of boron (B) (e.g., Konrad-Schmolke and Halama, 2014; Scambelluri and Tonarini, 2012; Tenthorey and Hermann, 2004; Tonarini et al., 2011), a key element for the understanding of geological processes involving devolatilization reactions in subduction zone setting (De Hoog and Savov, 2018; Palmer, 2017). Boron is a light element with incompatible behaviour and has two naturally stable isotopes ^{11}B and ^{10}B in a ratio close to 4:1. These geochemical features and the relatively large mass difference between B isotopes lead to a significant variation in the isotopic signature of the Earth's major reservoirs, resulting in a total variance of about 10%. Detailed *in-situ* and high-resolution geochemical analyses showed that B is structurally incorporated within the low-T serpentine polymorphs (Pabst et al., 2011). Boron release may occur either during the phase transition from chrysotile/lizardite to antigorite during prograde subduction or during antigorite destabilization at high-P. The serpentine phase transition can release from 50 to 80% of the initial B budget ([B]) acquired during oceanic hydration (Debret et al., 2013; Deschamps et al., 2011; Kodolányi and Pettke, 2011; Scambelluri et al., 2004). Despite the fluid-mobile nature of B, its partition coefficient between fluid and metamorphic olivine ranges between 3 and 5 (Scambelluri et al., 2015; Tenthorey and Hermann, 2004), suggesting that it can be partially stored in the newly formed secondary peridotites and be transferred to deeper mantle. Recently, the

finding of blue B-bearing diamonds from the transition zone and lower mantle has been proposed as evidence for the recycling of former serpentinized oceanic lithosphere into the deep mantle (Cannaò et al., 2020b; Smith et al., 2018).

Particular attention has been devoted to understand the role of serpentinites as the main carrier of positive δ^{11}B in subduction zone fluids. In fact, it is widely documented that B isotopic signature in oceanic serpentinites is enriched in ^{11}B compared with altered oceanic crust, sedimentary lithologies and unaltered mantle values (e.g., De Hoog and Savov, 2018; Marschall et al., 2017). This positive δ^{11}B signature is shared also by shallow forearc serpentinites (Benton et al., 2001), thus reflecting the ^{11}B-rich nature of the fluids extracted from the subducting slab by early devolatilization reactions. For this reason, δ^{11}B is commonly used as a geochemical tracer to unravel chemical exchange between slab lithologies and mantle as well as to estimate the serpentinite contribution to the genesis of arc magmatism characterized by high δ^{11}B signatures (e.g., De Hoog and Savov, 2018; Halama et al., 2020; Prigent et al., 2018; Tonarini et al., 2011). Such powerful tracer behaviour of B and its isotopes for tracing fluid/rock interactions needs to be supported by information about the (re)distribution of ^{10}B and ^{11}B in minerals and fluids during serpentinite evolution along P-T paths compatible with those of subduction settings (Konrad-Schmolke et al., 2016; Tomanikova et al., 2019). However, although serpentine minerals are important for B transfer to depth, no data about B-isotope fractionation between serpentine and fluids are reported in literature neither between antigorite and metamorphic olivine (Kowalski and Wunder, 2017). To date, evidence of B-isotope fractionation due to B loss during phase transition among serpentine polymorphs and during olivine-in reaction at high-P are not yet documented in the natural rock records (De Hoog et al., 2014; Martin et al., 2020; Scambelluri and Tonarini, 2012). This suggests that secondary peridotites deriving from complete dehydration of oceanic serpentinites should inherit the positive δ^{11}B signatures of their protoliths. In fact, δ^{11}B-depleted isotopic composition of high-P de-serpentinized rocks (Cerro del Almirez, SE Spain and Cima di Gagnone, Central Alps) have been related to interaction with sedimentary-derived fluids during

subduction rather than being the result of the B isotopic fractionation during prograde dehydration process (Cannaò et al., 2015; Harvey et al., 2014). Therefore, the potential of serpentinites to record interactions with external reservoirs either in oceanic and forearc settings as well as during prograde subduction at high-P conditions (Deschamps et al., 2011) may obscures and overlaps the result of the B-isotope fractionation process. Consequently, we still need to investigate what is the extent of the B-isotope fractionation in serpentinites – i.e., negligible, limited, or strong.

This Letter try to provide the first model estimates of the B-isotope fractionation related to the key petrologic reactions taking place during serpentinites subduction (**Fig. 1**): chrysotile/lizardite to antigorite transition, olivine-in and antigorite-out reactions. The key parameters considered in the model(s) are the T at which these reactions occur and the tetrahedral ([4]) *vs.* trigonal ([3]) coordination of B in both minerals and fluids, which is, in the latter, linked to the pH conditions of the system significantly affecting the B isotope fractionation (Palmer et al., 1987). This modelling approach explores the potential of serpentinites to change their B isotopic composition through progressive reactions providing new perspectives to understand subduction zone processes via B isotopes.

2. Modelling the B-isotope fractionation during serpentinite subduction

A detailed and comprehensive review about the current knowledge of B-isotope fractionation between vapor-liquids-solids-melts (Kowalski and Wunder, 2017) shows its $T(-P)$ and pH dependence in various B-bearing geomaterials. To date, specific data on the B-isotope fractionation for serpentine-fluid and serpentine-olivine are not yet available. Because of the high charge and the small ionic radius, B should prefers the crystallographic site of $^{[4]}Si^{4+}$ or $^{[4]}Al^{3+}$ and be incorporated in [4]-coordination within the serpentine crystal structure (Pabst et al., 2011). On the contrary, B in olivine is hosted in [3]-coordination (Ingrin et al., 2014) according to the coupled substitution of B (and H) for Si as $B(OH)Si_{-1}O_{-1}$. The coordination of B within the fluids is complex and mainly pH-dependent: at alkaline condition ($\approx +3$ with respect to neutrality) the tetrahedral

$B(OH)_4^-$ species is dominant, whereas at pH condition closer and below the neutrality the dominant B species is the trigonal one – $B(OH)_3$; the heavy ^{11}B is preferentially partitioned in [3]-coordination, while the light ^{10}B in the tetrahedral one (Kakihana et al., 1977). Hereafter, I present to most suitable B-isotope fractionation factors that may better describe the behaviour of B-isotope redistribution during the serpentine phase transition and dehydration reactions affecting serpentinites during subduction (**Fig. 1**).

The core of the model applied here is based on the *ab initio* prediction of equilibrium of the B-isotope fractionation between minerals and aqueous fluids by Kowalski et al. (2013), where several B-isotope fractionations were investigated: [4]boromuscovite-[4]strongly basic (i.e., alkaline) fluid, [4]boromuscovite-[3]neutral fluid and [4]boromuscovite-[3]tourmaline. Kowalski and co-authors extensively discussed their approaches to calculate these B-isotope fractionations compared to those published in previous studies (e.g., Sanchez-Valle et al., 2005; Wunder et al., 2005). Since B is [4]-coordinated in mica, as in serpentine, and [3]-coordinated in tourmaline, as in olivine, I extrapolate their B-isotope fractionations (expressed as $\Delta^{11}B_{a-b} = \delta^{11}B_a - \delta^{11}B_b$) to model those of serpentine and olivine and the released fluids at both alkaline and neutral conditions. The resulting equations are the following:

$$\Delta^{11}B_{[4]serp-[4]fluid} = -5.99302 * (1000/K) + 3.13088$$

$$\Delta^{11}B_{[4]serp-[3]fluid} = -20.4158 * (1000/K) + 11.51$$

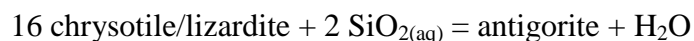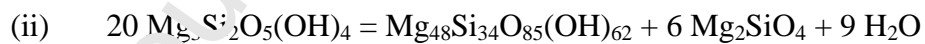$$\Delta^{11}B_{[3]ol-[4]serp} = 20.2821 * (1000/K) - 11.5019$$

where K is the *T* in Kelvin. As reported in Kowalski et al. (2013), the error of the calculations increases with the decrease of the *T* and is estimated to be within ±2‰ at low-*T*.

It is important to note that the critical limit of these extrapolations is that B behaves similarly in olivine and tourmaline: even if B is [3]-coordinated in both phases, these minerals have different crystal structures and, more importantly, B is a trace element in olivine and a major

element in tourmaline. An attempt to evaluate the effect of this extrapolation can be achieved by considering the isotopic fractionation between olivine and tourmaline for other elements, such as oxygen. By using the internally-consistent database for O-isotope fractionation between minerals produced by Vho et al. (2020), the $\Delta^{18}O_{olivine\text{-}tourmaline}$ is expected to range between +4.1 and +2.9‰ at 450 and 650 °C, respectively. These calculations suggest that the heavy isotope prefers olivine over tourmaline, therefore, the extrapolation of the B-isotope fractionation for [4]antigorite-[3]olivine modelled here might be underestimated and should be considered as minimum values.

2.1. The chrysotile/lizardite to antigorite transition

Formation of antigorite at the expense of chrysotile/lizardite can be described by a sequence of *T*-dependent reactions (**Fig. 1**) that can involve water retention (i), water release (ii-iii) or interaction with SiO_2-rich aqueous fluids (iv):

(i) $17\ Mg_3Si_2O_5(OH)_4 = Mg_{48}Si_{34}O_{85}(OH)_{62} + 3\ Mg(OH)_2$

            17 chrysotile/lizardite = antigorite + 3 brucite

(ii) $20\ Mg_3Si_2O_5(OH)_4 = Mg_{48}Si_{34}O_{85}(OH)_{62} + 6\ Mg_2SiO_4 + 9\ H_2O$

            20 chrysotile/lizardite = antigorite + 6 forsterite + 9 H_2O

(iii) $17\ Mg_3Si_2O_5(OH)_4 = Mg_{48}Si_{34}O_{85}(OH)_{62} + 3\ MgO_{(aq)} + 3\ H_2O$

            17 chrysotile/lizardite = antigorite + 3 $MgO_{(aq)}$ + 3 H_2O

(iv) $16\ Mg_3Si_2O_5(OH)_4 + 2\ SiO_{2(aq)} = Mg_{48}Si_{34}O_{85}(OH)_{62} + H_2O$

            16 chrysotile/lizardite + 2 $SiO_{2(aq)}$ = antigorite + H_2O
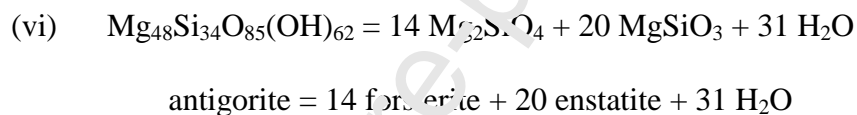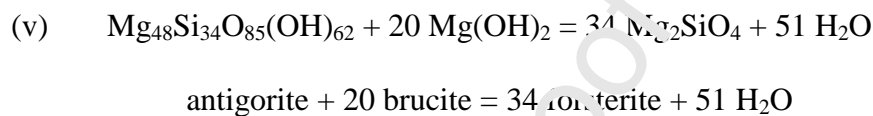
All the above reactions occur at about 300 °C and the coexistence of antigorite and lizardite may occur up to 380 °C and 0.9 GPa (Schwartz et al., 2013). Recently, Martin et al. (2020) provide *in-situ* B isotope analyses of subduction-zone serpentinites from Alpine Corsica characterized by both chrysotile/lizardite mixture and antigorite showing neither B loss, nor evidence of B-isotope fractionation during serpentine phase transition. However, other studies suggest that during the above phase transition [B] decreases from 50 to 80% of the initial concentration (Debret et al., 2013; Deschamps et al., 2011; Savov et al., 2007; Scambelluri et al., 2004) although no information about their δ^{11}B signatures is provided. In principle, this B loss should be accompanied by isotopic fractionation, at least for reactions (ii-iii). Reaction (iv) cannot be modelled because requires open system condition implying potential addition of unknown amounts of B from externally derived B and modification of the original δ^{11}B composition of serpentine. Considering that brucite is a B-poor mineral (Kodolányi et al., 2012), antigorite formed during reaction (i) is expected to preserves the primary [B] and δ^{11}B signatures.

The results of the modelled B-isotope fractionation during chrysotile/lizardite to antigorite transition (Δ^{11}B$_{atg-chr/liz}$) are shown in **Figs. 2A-D** for T of 300 and 380 °C by considering both alkaline and neutral pH fluids, that can represent end-member conditions (**Table 1**). At 300 °C and alkaline conditions ($\alpha = 0.9927$), the obtained Δ^{11}B$_{atg-chr/liz}$ range between -3.7 to -5.9‰ and between -5.2 and -11.9‰ based on batch and Rayleigh devolatilizations, respectively (**Figs. 2A, B**). Because during this reaction antigorite grows synchronously with chrysotile/lizardite breaking down, the batch devolatilization should better describe the B-isotope fractionation. Overall, the newly formed antigorite should have lower δ^{11}B compared to low-T polymorphs precursor. Although the pH composition of the fluid during the chrysotile/lizardite to antigorite transition is still unknown, more than 50% of the initial halogens (Cl and F) contents are removed from the serpentinite system (Debret et al., 2014; Scambelluri et al., 2004). Their release may shift the pH to lower values thus affecting B speciation and isotopic fractionation (i.e., B is [3]-coordinated in the fluid). At neutral conditions, the Δ^{11}B$_{atg-chr/liz}$ at 300 °C ($\alpha = 0.9762$) may result in -12.1 to -19.3‰

after 50 to 80% of B loss, respectively, and can be extremely higher considering a Rayleigh devolatilization (between -17.0 and -39.0‰; **Figs. 2C, D**).

2.2. Olivine-in and antigorite-out reactions

The production of metamorphic olivine related to prograde subduction mainly follows the reactions:

(v) $Mg_{48}Si_{34}O_{85}(OH)_{62} + 20\ Mg(OH)_2 = 34\ Mg_2SiO_4 + 51\ H_2O$

antigorite + 20 brucite = 34 forsterite + 51 H_2O

(vi) $Mg_{48}Si_{34}O_{85}(OH)_{62} = 14\ Mg_2SiO_4 + 20\ MgSiO_3 + 31\ H_2O$

antigorite = 14 forsterite + 20 enstatite + 31 H_2O

Reaction (v) occurs at about 450 °C (**Fig. 1**) and is often associated with development of olivine + chlorite + diopside + Ti-clinohumite veins and represent the major drain-network of the fluids released at high-P by serpentinites (Plümper et al., 2017). The complete breakdown of antigorite occurring via reaction (vi) releases about 12 wt.% of fluids; this reaction is mainly T-dependent occurring in a T range between 600 and 700 °C (**Fig. 1**) according to the Al content of antigorite (Padrón-Navarta et al., 2013).

Boron release to the fluid phase during these reactions is linked to the fluid/mineral partition coefficient, as established by experimental investigation and natural works to be ranging between 3 and 5 for olivine (Scambelluri et al., 2015, 2004; Tenthorey and Hermann, 2004). Mass balance dictates that up to 70% of B can be retained in the olivine (Scambelluri et al., 2019). This B loss should be associated with B-isotope fractionation due to the change in the B coordination from [4]antigorite to [3]olivine and, furthermore, since that [11]B prefers trigonal coordination, the metamorphic olivine will shows higher B isotope composition than the antigorite precursor. The

contribution of B incorporation in orthopyroxene is considered to be negligible due to its very low [B] (e.g., Scambelluri et al., 2004).

Considering a Rayleigh devolatilization, the modelled $\Delta^{11}B_{ol-atg}$ are +5.8 and +3.7‰ at 450 (reaction v) and 650°C (reaction vi), respectively (**Figs. 2E, F**). At neutral pH conditions, the isotopic composition of $_{[3]}$fluid released during brucite/antigorite consumption is strongly enriched in ^{11}B, showing a $\Delta^{11}B_{ol-fluid}$ of +16.9 and +10.6‰ at 450 and 650 °C, respectively. The isotopic composition of the fluid released at alkaline conditions ($_{[4]}$fluid) is slight enriched in ^{11}B, showing a $\Delta^{11}B_{ol-fluid}$ of +5.1‰ at 450 °C and +3.4‰ at 650 °C (**Figs. 2E, F**). According to the thermodynamic calculation of Galvez et al. (2016), the pH condition of the high-P fluid released from serpentinites decreases from about +2 to +0.5 with respect the pH-neutrality at 450 °C (olivine-in reaction) and at 650 °C (antigorite-out reaction), respectively. This suggests that the coordination of the B in fluids will evolve during progressive dehydration and the dominant B species in fluids will be the trigonal one (Kakihana et al., 1977), especially during the complete breakdown of antigorite. In order to maintain the isotopic equilibrium between reactants (antigorite/brucite) and products (olivine and fluids) during reactions (v) and (vi), the B isotopic composition of the antigorite-bearing serpentinite should be progressively depleted in $\delta^{11}B$ since both olivine and fluids are enriched in ^{11}B compared to the antigorite precursor (**Figs. 3E, F**). However, oxygen isotopes disequilibrium conditions have been recently documented in serpentinites affected by contact metamorphism producing olivine + talc + fluids (Lafay et al., 2019), suggesting that further studies are necessary to document the extent of isotopic disequilibrium during serpentinite dehydration, especially in subduction zone settings.

Remarkably, the modelled $\Delta^{11}B_{ol-atg}$ falls in the range of the olivine-antigorite B-isotope fractionation determined for natural samples in the preliminary study of Clarke et al. (2019), and in one olivine-vein/antigorite-host pair from the Alpine Voltri Massif (Cannaò et al., 2016) that shows a compatible $\Delta^{11}B_{ol-atg}$ of +7.6‰ associated with about 40% of [B] loss.

3. Implications for B-isotope fractionation of subducted serpentinites

Assuming a δ^{11}B value for the chrysotile/lizardite-bearing serpentinites of +13.1‰ (black symbol and field in **Figs. 3A, B**), corresponding to the average value of serpentinites from the Atlantis Massif (Boschi et al., 2008), the transition to antigorite-bearing serpentinites at 300°C releasing 80% of B at closed system condition can decrease the δ^{11}B of the rocks to value as low as +7.2‰, for alkaline fluid conditions, and to -6.2‰ at neutral pH. Applying the calculated Δ^{11}B$_{ol-atg}$ to the high-P antigorite-bearing serpentinites with a δ^{11}B$_{atg}$ of +7.2‰ (**Fig. 3A**), the δ^{11}B of metamorphic olivine produced during partial to complete dehydration of the antigorite can evolve from +13.1 to +10.9‰. The δ^{11}B$_{fluid}$ composition of the equilibrium fluid at neutral condition should ranges, on average, from 18.3 to 14.4‰ at alkaline pH conditions to higher value ranging from +30.2 to +21.7‰ at neutral pH conditions (**Fig. 3A**). These results are compatible with the positive δ^{11}B in natural antigorite-bearing serpentinites and metamorphic olivine from high-P veins (e.g., Scambelluri and Tonarini, 2012; De Hoog et al., 2014) and well match with the scenario requiring a serpentinite-derived component in the arc magma region to explain arcs with positive δ^{11}B (e.g., Tonarini et al., 2011) and with the δ^{11}B signature of serpentinite-derived fluids percolating within the slab at high P (e.g., Halama et al., 2020). However, considering the δ^{11}B$_{atg}$ of -6.2‰ obtained during serpentine phase transition at neutral pH conditions (**Fig. 3B**), the δ^{11}B$_{ol}$ and δ^{11}B$_{fluid}$ at 450 °C will be 0.4‰ and +16.5‰, respectively, and even lower at 650 °C (δ^{11}B$_{ol}$ = -2.9‰; δ^{11}B$_{fluid}$ = +8.1‰). At alkaline pH condition, the δ^{11}B composition of the fluids can be even lower ranging from +5.1 to +3.4‰ (not shown in **Fig. 3**). These results are considerably lower than expected, suggesting that the pH conditions of the system during the serpentine phase transition via reactions (ii) and (iii) drove the fractionation of B isotopes, thus playing a major control for the δ^{11}B of the subducted serpentinites.

It should be emphasized that the B isotopic composition of oceanic serpentinites is highly variable (see black fields in **Fig. 3**), therefore, the application of the model to oceanic serpentinites characterized by exceptionally high δ^{11}B (up to +40‰; Vils et al., 2009; **Fig. 3C**) should lead to the

formation of antigorite with still positive $\delta^{11}B$ signatures, even applying the B-isotope fractionation obtained at neutral pH condition that shows the larger B-isotope fractionation (**Figs. 2B, C**). Similarly, the premature stabilization of antigorite on the ocean floor (e.g., Ribeiro Da Costa et al., 2008) will directly transfer their positive $\delta^{11}B$ fingerprint at high-*P*.

Based on the above results of the model and taking into account the heterogeneity of the oceanic serpentinite compositions, the secondary peridotites produced after the complete dehydration of serpentinites uncontaminated by subduction processes should be significantly enriched in ^{11}B compared to Earth's mantle value ($\approx$ -7‰), from 0‰ to up to +45‰ (**Fig. 3**). The deep subduction of such materials represents an important mechanism to transfer ^{11}B in the deep mantle helping to unravel recycling of crustal components, at least from the onset of plate tectonic (e.g., Hulett et al., 2016).

4. Summary and perspectives

The modelling provided in this Letter, is the first attempt to assess the B-isotope fractionation potentially affecting serpentinites during subduction burial. Particular attention has been given to the serpentine phase transition and to the olivine-in reactions both occurring during prograde subduction, as well as to the antigorite-out major dehydration event at high-*P* conditions (**Fig. 1**). The obtained results confirm serpentinites as the primary reservoir providing ^{11}B in subduction setting. However, information on the pH condition of the system is crucially lacking, thus limiting a proper estimate of the B-isotope fractionation. Depending on the phase transition reaction (i.e., reaction (1) *vs.* reactions (2-3)), this may represent a major issue since pH conditions close to neutrality can result in low (even negative) $\delta^{11}B_{atg}$, a geochemical feature reported in several antigorite-bearing serpentinites from mélange terranes where a subduction-related interaction with slab-derived fluids is invoked (e.g., Martin et al., 2016; Yamada et al., 2019). The relationships between the B released during each key petrologic reaction progressively affecting subducted serpentinites and the associated B-isotope fractionation need to be investigated through

in-situ measurements in both natural rocks and/or experiments that will help to confirm or discharge the results of the model proposed here.

Finally, we have limited insights into the B isotope behaviour in chlorite (often associated with antigorite), Ti-bearing humite-groups minerals (reaction vi, vii and viii in **Fig. 1**) and dense high magnesium silicates (DHMSs, **Fig. 1**). The Ti-bearing humite-groups minerals are known to host significant amounts of B (e.g., Scambelluri et al., 2004; De Hoog et al., 2014) but no information about their isotopic signatures is yet available in literature. Concerning the DHMSs, which may form in the colder part of down-going slabs (**Fig. 1**), we still do not know if they are effectively able to incorporate and transport B to great depth. In more complex carbonate-bearing ultramafic system (i.e., ophicarbonates), the understanding of the B isotopes redistribution between silicates and carbonates might be a useful geochemical tool to unravel carbonation/de-carbonation and dissolution processes, which are matter of debate in the study of the deep carbon cycle (e.g., Cannaò et al., 2020a). Remarkably, the presence of stable carbonates at high-*P* will shift the pH of the system to more alkaline conditions (Manning et al., 2013), potentially affecting B-isotope fractionation during dehydration reaction i.e., B is predominantly [4]-coordinated in the fluid.

Projects focusing on these major research topics could expand our knowledge on B isotope behaviour in serpentinites helping us to better unravel global B cycle.

Figure captions

Figure 1. Temperature – pressure (*T-P*) diagram reporting key petrologic reactions in serpentinites. The roman numbers on each curve refer to the mineral reactions listed in the text. (vii: chlorite + clinopyroxene = olivine + garnet + H_2O; viii: Ti-clinohumite = olivine + ilmenite + H_2O; ix: Ti-chondrodite + antigorite = Ti-clinohumite + ilmenite/rutile + H_2O below 3 GPa; Ti-chondrodite + orthopyroxene = olivine + rutile + H_2O above 3 GPa). Modified from Cannaò and Malaspina (2018) and references therein; Ti-clinohumite and Ti-chondrodite curves from Shen et al. (2014). Dotted grey lines represent the range of the global array of top-slab geotherms of the D80 model of Syracuse et al. (2010).

Figure 2. Relative $\Delta^{11}B$ for chrysotile/lizardite to antigorite transition modelled with batch and Rayleigh devolatilization at 300 **(A-C)** and 380 °C **(B-D)**, in both alkaline (**A-B**) and neutral pH system conditions (**C-D**). Rayleigh devolatilization modelling the antigorite-olivine B-isotope fractionation ($\Delta^{11}B_{ol-atg}$) at 450 **(E)** and 650 °C **(F)** and the olivine-fluid B-isotope fractionation in both alkaline and neutral pH system conditions. See **Table 1** for the fractionation factor values (α).

Figure 3. B (ppm) vs. $\delta^{11}B$ (‰) of the oceanic serpentinites (in black) from the Atlantis Massif (Boschi et al., 2008) in (**A, B**) and the ODP Leg 209 (Vils et al., 2009) in (**C**), both situated along the Mid-Atlantic Ridge (MAR). The fields identified with different dashed contour refer to the calculated B contents and $\delta^{11}B$ signatures of antigorite-bearing serpentinites (80% B loss), metamorphic olivine (30% B loss), and released [3]fluids at 450-650 °C (assuming $D_{fluid/olivine} = 5$; Scambelluri et al., 2015) considering both alkaline (in green; **A**) and neutral (in red; **B, C**) pH conditions during the serpentine phase transition at 300 °C. The $\delta^{11}B$ range are calculated based on the results of the model proposed here and considering closed and open system conditions during the serpentine phase transition and the olivine in/antigorite-out reactions, respectively (see text for details). Symbols represent the average data for each field at the indicated *T*. In (**C**) are reported the calculations considering neutral pH conditions that represents the extreme condition shifting the

$\delta^{11}B_{atg}$ to lower values. Remarkably, the modelled antigorite-bearing serpentinites deriving from oceanic (chrysotile/lizardite) serpentinites characterized by exceptionally high $\delta^{11}B$ values (up to +40‰; Vils et al., 2009) still retain their positive $\delta^{11}B$ signatures even after the B-isotope fractionation at 300 °C and considering the loss of 80% of the initial B contents.

References

Benton, L.D., Ryan, J.G., Tera, F., 2001. Boron isotope systematics of slab fluids as inferred from a serpentine seamount, Mariana forearc. Earth Planet. Sci. Lett. 187, 273–282.

Cannaò, E., Agostini, S., Scambelluri, M., Tonarini, S., Godard, M., 2015. B, Sr and Pb isotope geochemistry of high-pressure Alpine metaperidotites monitors fluid-mediated element recycling during serpentinite dehydration in subduction mélange (Cima di Gagnone, Swiss Central Alps). Geochim. Cosmochim. Acta 163, 80–100. https://doi.org/10.1016/j.gca.2015.04.024

Cannaò, E., Scambelluri, M., Agostini, S., Tonarini, S., Godard, M., 2016. Linking serpentinite geochemistry with tectonic evolution at the subduction plate-interface: The Voltri Massif case study (Ligurian Western Alps, Italy). Geochim. Cosmochim. Acta 190, 115–133. https://doi.org/10.1016/j.gca.2016.06.034

Cannaò, E., Scambelluri, M., Bebout, G.E., Agostini, S., Pettke, T., Godard, M., Crispini, L., 2020a. Ophicarbonate evolution from seafloor to subduction and implications for deep-Earth C cycling. Chem. Geol. 546, 119626. https://doi.org/10.1016/j.chemgeo.2020.119626

Cannaò, E., Tiepolo, M., Bebout, G.E., Scambelluri, M., 2020b. Into the deep and beyond: Carbon and nitrogen subduction recycling in secondary peridotites. Earth Planet. Sci. Lett. 543, 116328. https://doi.org/10.1016/j.epsl.2020.116328

Clarke, E., De Hoog, J.C.M., Kirstein, L.A., Harvey, J., Debret, B., 2019. Boron isotopes in metamorphic olivine record external fluid infiltration during serpentinite dehydration in subduction zones, in: Goldschmidt 2019 Abstract. p. 1.

De Hoog, J.C.M., Hattori, K.K., Jung, H., 2014. Titanium- and water-rich metamorphic olivine in high-pressure serpentinites from the Voltri Massif (Ligurian Alps, Italy): Evidence for deep subduction of high-field strength and fluid-mobile elements. Contrib. to Mineral. Petrol. 167, 1–15. https://doi.org/10.1007/s00410-014-0990-x

De Hoog, J.C.M., Savov, I.P., 2018. Boron Isotopes as a Tracer of Subduction Zone Processes, in: Boron Isotopes. pp. 217–247. https://doi.org/10.1007/978-3-319-64666-4_9

Debret, B., Andreani, M., Godard, M., Nicollet, C., Schwartz, S.S., Lafay, R., 2013. Trace element behavior during serpentinization/de-serpentinization of an eclogitized oceanic lithosphere: A LA-ICPMS study of the Lanzo ultramafic massif (Western Alps). Chem. Geol. 357, 117–133. https://doi.org/10.1016/j.chemgeo.2013.08.025

Debret, B., Koga, K.T., Nicollet, C., Andreani, M., Schwartz, S., 2014. F, Cl and S input via serpentinite in subduction zones: Implications for the nature of the fluid released at depth. Terra Nov. 26, 96–101. https://doi.org/10.1111/ter.12074

Deschamps, F., Guillot, S., Godard, M., Andreani, M., Hattori, K., 2011. Serpentinites act as sponges for fluid-mobile elements in abyssal and subduction zone environments. Terra Nov. 23, 171–178.

Galvez, M.E., Connolly, J.A.D., Manning, C.E., 2016. Implications for metal and volatile cycles from the pH of subduction zone fluids. Nat. Publ. Gr. 539, 420–424. https://doi.org/10.1038/nature20103

Guillot, S., Schwartz, S., Reynard, B., Agard, P., Prigent, C., 2015. Tectonic significance of serpentinites. Tectonophysics 646, 1–19. https://doi.org/10.1016/j.tecto.2015.01.020

Halama, R., Konrad-Schmolke, M., De Hoog, J.C.M., 2020. Boron isotope record of peak metamorphic ultrahigh-pressure and retrograde fluid–rock interaction in white mica (Lago di Cignana, Western Alps). Contrib. to Mineral. Petrol. 175, 1–19. https://doi.org/10.1007/s00410-020-1661-8

Harvey, J., Garrido, C.J., Savov, I.P., Agostini, S., Padrón-Navarta, J.A., Marchesi, C., López

Sánchez-Vizcaíno, V., Gómez-Pugnaire, M.T., 2014. 11B-rich fluids in subduction zones: The role of antigorite dehydration in subducting slabs and boron isotope heterogeneity in the mantle. Chem. Geol. 376, 20–30. https://doi.org/10.1016/j.chemgeo.2014.03.015

Hermann, J., Müntener, O., Scambelluri, M., Mu, O., 2000. The importance of serpentinite mylonites for subduction and exhumation of oceanic crust. Tectonophysics 327, 225–238. https://doi.org/10.1016/S0040-1951(00)00171-2

Hulett, S.R.W., Simonetti, A., Rasbury, E.T., Hemming, N.G., 2016. Recycling of subducted crustal components into carbonatite melts revealed by boron isotopes. Nat. Geosci. 9, 904–908. https://doi.org/10.1038/ngeo2831

Ingrin, J., Kovacs, I., Deloule, E., Balan, E., Blanchard, M., Kohn, S.C., Hermann, J., 2014. Identification of hydrogen defects linked to boron substitution in synthetic forsterite and natural olivine. Am. Mineral. 99, 2138–2141. https://doi.org/10.2138/am-2014-5049

Kakihana, H., Kotaka, M., Satoh, S., Nomura, M., Okamoto, M., 1977. Fundamental Studies on the Ion-Exchange Separation of Boron Isotopes. Bull. Chem. Soc. Jpn. 50, 158–163.

Kodolányi, J., Pettke, T., 2011. Loss of trace elements from serpentinites during fluid-assisted transformation of chrysotile to antigorite — An example from Guatemala. Chem. Geol. 284, 351–362. https://doi.org/10.1016/j.chemgeo.2011.03.016

Kodolányi, J., Pettke, T., Spandler, C., Kamber, B.S., Ling, K.G., Gme, K., 2012. Geochemistry of ocean floor and fore-arc serpentinites: Constraints on the ultramafic input to subduction zones. J. Petrol. 53, 235–270. https://doi.org/10.1093/petrology/egr058

Konrad-Schmolke, M., Halama, R., 2014. Combined thermodynamic–geochemical modeling in metamorphic geology: Boron as tracer of fluid–rock interaction. Lithos 208–209, 393–414. https://doi.org/10.1016/j.lithos.2014.09.021

Konrad-Schmolke, M., Halama, R., Manea, V.C., 2016. Slab mantle dehydrates beneath Kamchatka-Yet recycles water into the deep mantle. Geochemistry Geophys. Geosystems 17, 1312–1338. https://doi.org/10.1002/2015GC006205.Received

Kowalski, P.M., Wunder, B., 2017. Boron Isotope Fractionation Among Vapor–Liquids–Solids–Melts: Experiments and Atomistic Modeling. https://doi.org/10.1007/978-3-319-64666-4_3

Kowalski, P.M., Wunder, B., Jahn, S., 2013. Ab initio prediction of equilibrium boron isotope fractionation between minerals and aqueous fluids at high P and T. Geochim. Cosmochim. Acta 101, 285–301. https://doi.org/10.1016/j.gca.2012.10.007

Lafay, R., Baumgartner, L.P., Putlitz, B., Siron, G., 2019. Oxygen isotope disequilibrium during serpentinite dehydration. Terra Nov. 1–8. https://doi.org/10.1111/ter.12373

Manning, C.E., Shock, E.L., Sverjensky, D.A., 2013. The Chemistry of Carbon in Aqueous Fluids at Crustal and Upper-Mantle Conditions: Experimental and Theoretical Constraints. Rev. Mineral. Geochemistry 75, 109–148. https://doi.org/10.2138/rmg.2013.75.5

Marschall, H.R., Wanless, V.D., Shimizu, N., Pogge von Strandmann, P.A.E., Elliott, T., Monteleone, B.D., 2017. The boron and lithium isotopic composition of mid-ocean ridge basalts and the mantle, Geochimica et Cosmochimica Acta. Elsevier Ltd. https://doi.org/10.1016/j.gca.2017.05.028

Martin, C., Flores, K.E., Harlow, G.E., 2016. Boron isotopic discrimination for subduction-related serpentinites. Geology 44, 899–902. https://doi.org/10.1130/G38102.1

Martin, C., Flores, K.E., Vitale-Brovarone, A., Angiboust, S., Harlow, G.E., 2020. Deep mantle serpentinization in subduction zones: Insight from in situ B isotopes in slab and mantle wedge serpentinites. Chem. Geol. 545, 119637. https://doi.org/10.1016/j.chemgeo.2020.119637

Pabst, S., Zack, T., Savov, I.P., Ludwig, T., Rost, D., Vicenzi, E.P., 2011. Evidence for boron incorporation into the serpentine crystal structure. Am. Mineral. 96, 1112–1119. https://doi.org/10.2138/am.2011.3709

Padrón-Navarta, J.A., Sánchez-Vizcaíno, V.L., Hermann, J.J., Connolly, J. a. D.D., Garrido, C.J., Gómez-Pugnaire, M.T., Marchesi, C., 2013. Tschermak's substitution in antigorite and consequences for phase relations and water liberation in high-grade serpentinites. Lithos 178, 186–196. https://doi.org/10.1016/j.lithos.2013.02.001

Palmer, M.R., 2017. Boron cycling in subduction zones. Elements 13, 237–242.
https://doi.org/10.2138/gselements.13.4.237

Palmer, M.R., Spivack, A.J., Sciences, P., 1987. Temperature and pH controls over isotopic
fractionation during adsorption of boron on marine clay 5.

Plümper, O., John, T., Podladchikov, Y.Y., Vrijmoed, J.C., Scambelluri, M., 2017. Fluid escape
from subduction zones controlled by channel-forming reactive porosity. Nat. Geosci. 10, 150–
156. https://doi.org/10.1038/ngeo2865

Prigent, C., Guillot, S., Agard, P., Lemarchand, D., Soret, M., Ulrich, M., 2018. Transfer of
subduction fluids into the deforming mantle wedge during nascent subduction: Evidence from
trace elements and boron isotopes (Semail ophiolite, Oman). Earth Planet. Sci. Lett. 484, 213–
228. https://doi.org/10.1016/j.epsl.2017.12.008

Ribeiro Da Costa, I., Barriga, F.J.A.S.V., Mellini, M., Wicks, F.J., 2008. Antigorite in deformed
serpentinites from the Mid-Atlantic Ridge. Eur. J. Mineral. 20, 563–572.
https://doi.org/10.1127/0935-1221/2008/0020-1808

Sanchez-Valle, C., Reynard, B., Daniel, I., Lecuyer, C., Martinez, I., Chervin, J.-C., 2005. Boron
isotopic fractionation between minerals and fluids: New insights from in situ high pressure-
high temperature vibrational spectroscopic data. Geochim. Cosmochim. Acta 69, 4301–4313.
https://doi.org/10.1016/j.gca.2005.03.054

Savov, I.P., Ryan, J.G., D'Antonio, M., Fryer, P., 2007. Shallow slab fluid release across and along
the Mariana arc-basin system: Insights from geochemistry of serpentinized peridotites from the
Mariana fore arc. J. Geophys. Res. Solid Earth 112, B09205.
https://doi.org/10.1029/2006JB004749

Scambelluri, M., Cannaò, E., Gilio, M., 2019. The water and fluid-mobile element cycles during
serpentinite subduction. A review. Eur. J. Mineral. 1–24.
https://doi.org/10.1127/ejm/2019/0031-2842

Scambelluri, M., Müntener, O., Ottolini, L., Pettke, T.T., Vannucci, R., 2004. The fate of B, Cl and

Li in the subducted oceanic mantle and in the antigorite breakdown fluids. Earth Planet. Sci. Lett. 222, 217–234.

Scambelluri, M., Pettke, T., Cannaò, E., 2015. Fluid-related inclusions in Alpine high-pressure peridotite reveal trace element recycling during subduction-zone dehydration of serpentinized mantle (Cima di Gagnone, Swiss Alps). Earth Planet. Sci. Lett. 429, 45–59. https://doi.org/10.1016/j.epsl.2015.07.060

Scambelluri, M., Tonarini, S., 2012. Boron isotope evidence for shallow fluid transfer across subduction zones by serpentinized mantle. Geology 40, 907–910.

Schwartz, S., Guillot, S., Reynard, B., Lafay, R., Debret, B., Nicollet, C., Lanari, P., Auzende, A.L., 2013. Pressure temperature estimates of the lizardite/antigorite transition in high pressure serpentinites. Lithos 178, 197–210.

Shen, T., Hermann, J., Zhang, L., Lü, Z., Padrón-Navarta, J.A., Xia, B., Bader, T., 2014. UHP metamorphism documented in Ti-chondrodite- and Ti-clinohumite-bearing serpentinized ultramafic rocks from Chinese southwestern Tianshan. J. Petrol. 56, 1425–1458. https://doi.org/10.1093/petrology/egu042

Smith, E.M., Shirey, S.B., Richardson, S.H., Nestola, F., Bullock, E.S., Wang, J., Wang, W., 2018. Blue boron-bearing diamonds from Earth's lower mantle. Nature 560, 84–87. https://doi.org/10.1038/s41586-018-0334-5

Syracuse, E.M., van Keken, P.E., Abers, G. a., 2010. The global range of subduction zone thermal models. Phys. Earth Planet. Inter. 183, 73–90.

Tenthorey, E., Hermann, J., 2004. Composition of fluids during serpentinite breakdown in subduction zones: Evidence for limited boron mobility. Geology 32, 865.

Tomanikova, L., Savov, I.P., Harvey, J., Hoog, J.C.M. De, Churikova, T.G., Gordeychik, B., Yogodzinski, G.M., 2019. A limited role for metasomatized subarc mantle in the generation of boron isotope signatures of arc volcanic rocks 47, 1–5. https://doi.org/10.1130/G46092.1/4678004/g46092.pdf

Tonarini, S., Leeman, W.P., Leat, P.T., 2011. Subduction erosion of forearc mantle wedge implicated in the genesis of the South Sandwich Island (SSI) arc: Evidence from boron isotope systematics. Earth Planet. Sci. Lett. 301, 275–284. https://doi.org/10.1016/j.epsl.2010.11.008

Vho, A., Lanari, P., Rubatto, D., 2020. An Internally-Consistent Database for Oxygen Isotope Fractionation Between Minerals. J. Petrol. 1–29. https://doi.org/10.1093/petrology/egaa001

Wunder, B., Meixner, A., Romer, R.L., Wirth, R., Heinrich, W., 2005. The geochemical cycle of boron: constraints from boron isotope partitioning experiments between mica and fluid. Lithos 84, 206–216.

Yamada, C., Tsujimori, T., Chang, Q., Kimura, J.-I., 2019. Boron isotope variations of Franciscan serpentinites, northern California. Lithos 334–335, 180–189. https://doi.org/10.1016/j.lithos.2019.02.004

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Table 1. Calculated B-isotope fractionation factors (α) used in Figure 2.

T (C°)	$\alpha_{[4]serp-[4]fluid}$	$\alpha_{[4]serp-[3]fluid}$	$\alpha_{[3]fluid-[4]serp}$
300	0.9927	0.9762	-
380	0.9940	0.9804	-
450	0.9949	0.9834	1.0167
650	0.9966	0.9894	1.0105

[3], [4]: trigonal *vs.* tetrahedral coordination of B in minerals and fluid

$\Delta^{11}B \approx 1000*\ln(\alpha)$

Highlights

- The B-isotope fractionation during serpentine subduction is modelled

- The B-isotope fractionation during phase transition is driven by the pH condition

- Secondary olivine and HP fluid show higher $\delta^{11}B$ signatures than antigorite

- Slab antigorite-bearing serpentinites could provide low $\delta^{11}B$ to depth
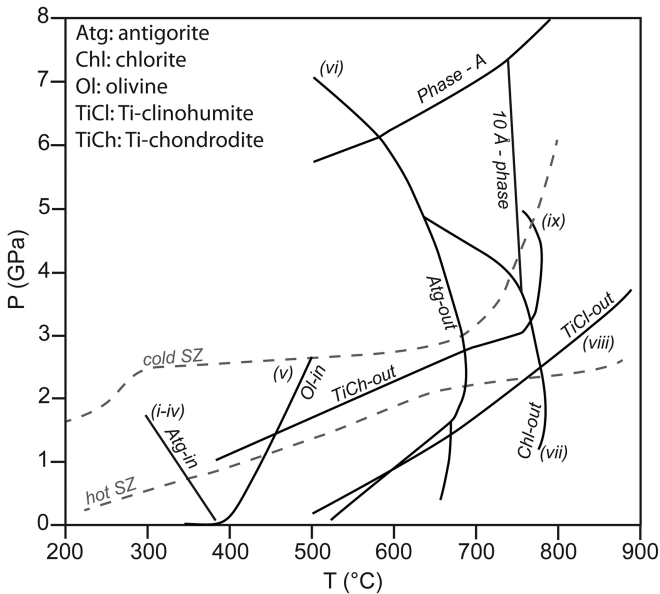
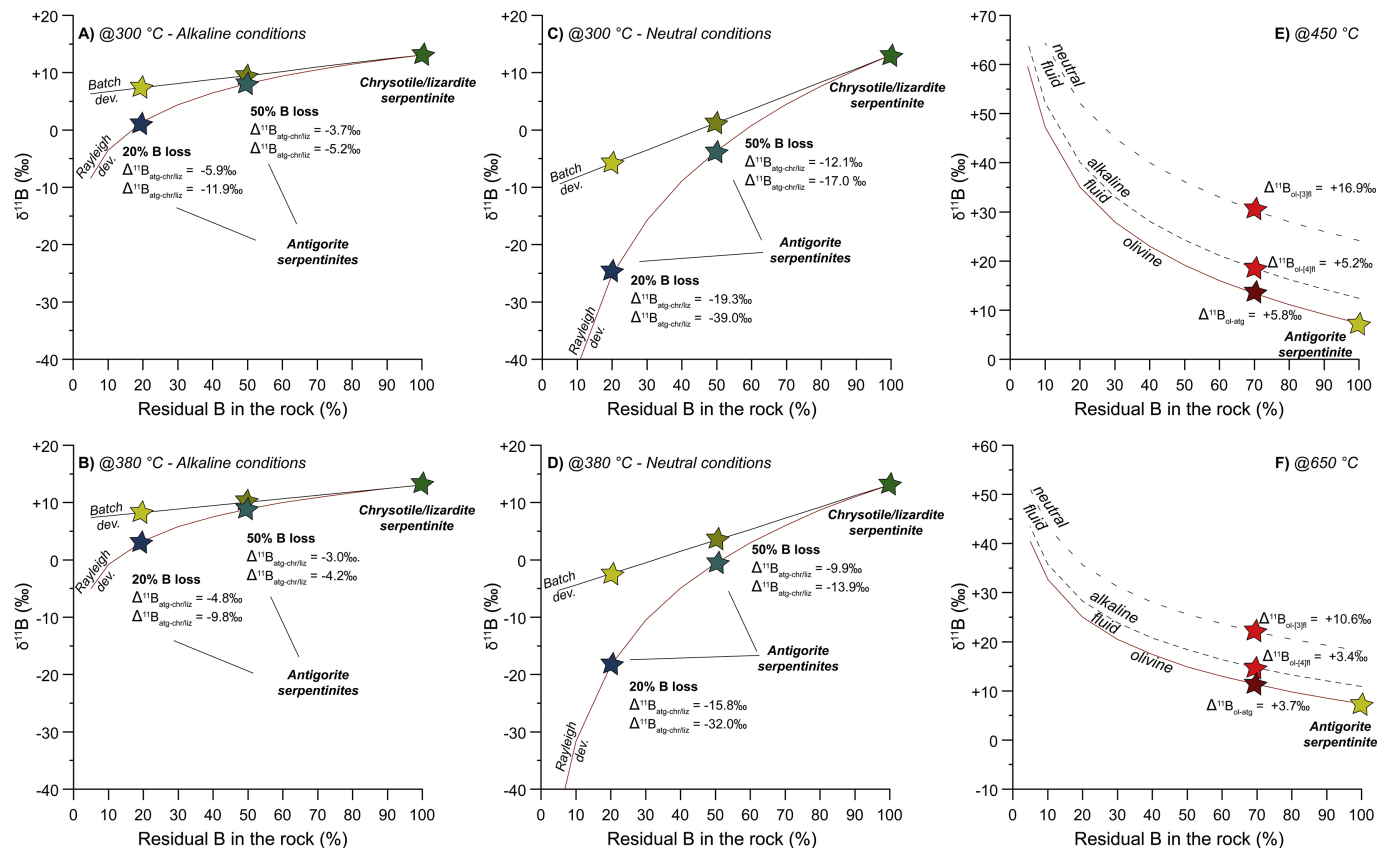- Further works are required to unravel the B-isotope fractionation of serpentinites
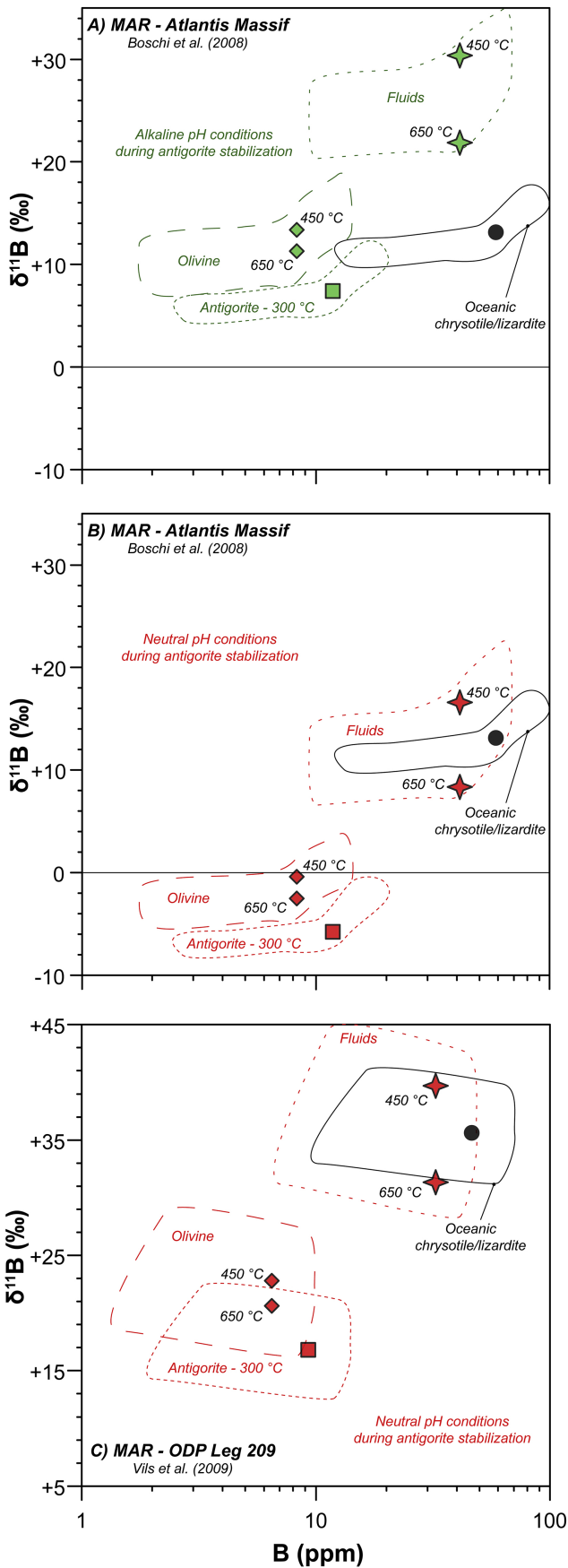
Figure 1

Figure 2

Figure 3