

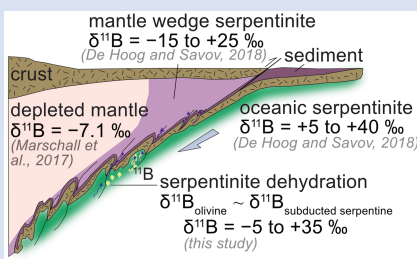
Serpentinite dehydration in the subducted lithosphere produces no B isotopic fractionation

M. Ulrich^{1*}, S. Chatterjee¹, J. De Hoog², D. Rubatto^{1,3}



<https://doi.org/10.7185/geochemlet.2507>

Abstract



The fate of boron (B) and its isotopes during serpentinite dehydration is a matter of debate. To contribute to a better understanding of the B isotopic fractionation upon serpentinite dehydration, we present *in situ* $\delta^{11}\text{B}$ analyses of antigorite and olivine from subducted high pressure serpentinites from the Western Alps (Zermatt-Saas and Erro-Tobbio). The different isotopic compositions of antigorite in different parts of the units ($\delta^{11}\text{B}$ of -5 to $+10$ ‰ and $+13$ to $+19$ ‰ for Zermatt-Saas, and $\delta^{11}\text{B}$ of up to $+26$ ‰ for Erro-Tobbio) are inherited from variable serpentinisation conditions on the sea floor. Serpentine dehydration via the brucite-out reaction during subduction produces metamorphic olivine in oxygen (O) isotopic equilibrium with antigorite. This olivine shows near zero B isotopic fractionation with coexisting antigorite

($\Delta^{11}\text{B}_{\text{Ol-Atg}}$ of -0.7 ± 3.4 ‰), which implies little B isotopic fractionation during serpentinite dehydration. In contrast, significant B isotopic disequilibrium ($\Delta^{11}\text{B}_{\text{Ol-Atg}}$ of $+25$ ‰) is found between antigorite and olivine formed in shear bands, shear zones and veins, indicating influx of channelled external fluids, including serpentinite-derived fluids from a protolith with a different isotopic composition.

Received 9 August 2024 | Accepted 6 January 2025 | Published 28 February 2025

Boron and Its Isotopes in Serpentinite

Serpentinites play a critical role in fluid transport and element recycling processes within subduction zones, impacting geological and geochemical dynamics on a global scale. Fluid transfer at mantle depths occurs mainly in subduction zones where serpentinites dehydrate and release aqueous fluid into the mantle wedge (Ulmer and Trommsdorff, 1995). Boron is a relatively fluid-mobile element, which is enriched in serpentinites, and its isotopes are a powerful tracer of fluid processes such as fluid production upon dehydration and subsequent fluid transfer. The B isotopic composition of ocean floor serpentinites varies depending on the serpentinisation conditions from $\delta^{11}\text{B} = +5$ to $+40$ ‰ (De Hoog and Savov, 2018 and references therein), which is higher compared to the upper mantle value of -7.1 ± 0.9 ‰ (Marschall et al., 2017). Subducted high pressure (HP) serpentinites (also referred to as slab serpentinites) generally maintain a high $\delta^{11}\text{B}$ ($>+10$ ‰), whereas mantle wedge serpentinites show an isotopically lighter range of compositions with $\delta^{11}\text{B} = -14$ to $+10$ ‰ (Martin et al., 2020). These relatively low $\delta^{11}\text{B}$ values ($\delta^{11}\text{B} < +10$ ‰) likely represent serpentinisation of the mantle wedge by crustal fluids derived from the subducting slab (e.g., Yamada et al., 2019; Martin et al., 2020; De Hoog et al., 2023). However, negative $\delta^{11}\text{B}$ values in serpentine from ophicarbonates of oceanic derivation (Cannaò et al., 2024) demonstrate how heterogeneous the input in subduction zones can be.

Previous work has shown that dehydration of former ocean floor serpentinites during subduction can be a complex process possibly involving external fluids, which can modify the B isotopic signature and lead to isotopic disequilibrium between serpentinite residue and newly formed minerals, such as metamorphic olivine (Clarke et al., 2020). Therefore, a micro-scale approach is necessary to decipher the extent to which B incorporation into metamorphic olivine fractionates B isotopes, and to evaluate whether an external fluid is involved (e.g., De Hoog et al., 2014; Clarke et al., 2020).

Metamorphic olivine, produced during the breakdown of brucite and the serpentine polytype antigorite, can incorporate high contents of B compared to primary mantle olivine (up to 100 $\mu\text{g/g}$ versus <0.11 $\mu\text{g/g}$; Clarke et al., 2020 and references therein). The extent to which B is retained or lost during dehydration at the lizardite to antigorite transition and at the olivine-in reaction, and how these reactions affect the fractionation of B isotopes, is still controversial (e.g., Scambelluri and Tonarini, 2012; De Hoog et al., 2014; Harvey et al., 2014; Cannaò, 2020).

Besides temperature, B isotopic fractionation is affected by factors such as potential B loss, fluid pH, and B coordination in the mineral. Boron in serpentine substitutes for Si^{4+} and Al^{3+} in predominantly tetrahedral coordination (Pabst et al., 2011), whereas B in olivine is thought to be present as B^{3+} in predominantly trigonal coordination, substituting for Si^{4+} coupled to an O vacancy (Ingrin et al., 2014). As the heavy B isotope (^{11}B) is preferentially incorporated in trigonal and the light B isotope

1. Institute of Geological Sciences, University of Bern, Bern CH-3012, Switzerland
2. Grant Institute, School of GeoSciences, University of Edinburgh, Edinburgh EH9 3FE, United Kingdom
3. Institut des Sciences de la Terre, University of Lausanne, Lausanne CH-1015, Switzerland
* Corresponding author (email: michelle.ulrich@unibe.ch)

(^{10}B) in tetrahedral coordination (Kowalski *et al.*, 2013), olivine is expected to have a heavier B isotopic composition than the coexisting serpentine. However, recent quantum mechanical modelling suggests that, in water-rich environments (such as dehydrating serpentinites), tetrahedral B-Si-H complexes may dominate in olivine (Muir *et al.*, 2022), although B in tetrahedral coordination in olivine has not yet been documented in natural samples. This might impact the estimates on B isotopic equilibrium fractionation, which are currently based on the assumption of B in olivine being trigonally and in serpentine being tetrahedrally coordinated (*e.g.*, Li *et al.*, 2022). Therefore, isotopic equilibrium fractionation between serpentine and metamorphic olivine remains poorly constrained.

In this study, we present *in situ* $\delta^{11}\text{B}$ data, measured by secondary ion mass spectrometry (SIMS), of antigorite and metamorphic olivine from HP serpentinites from the Western Alps (the Zermatt-Saas unit in Switzerland and the Erro-Tobbio unit in Italy; Fig. S-1). Whole rock strontium (Sr) isotope analyses were performed on eight Zermatt-Saas samples to evaluate if any sediment-derived slab fluids might have been involved, potentially affecting the B isotopic signature of the investigated samples. The $\delta^{11}\text{B}$ data obtained on antigorite and olivine are coupled with their O isotopic compositions and B contents (Ulrich *et al.*, 2024; Vesin and Ulrich *et al.*, 2025) to elucidate the fate of B and its isotopes during serpentinite dehydration. Based on our results, we suggest that serpentinite dehydration in the forearc produces no significant isotopic fractionation between antigorite and metamorphic olivine during the brucite-out reaction.

Zermatt-Saas and Erro-Tobbio HP-Serpentinites

Serpentinite samples were collected from the Zermatt-Saas HP ophiolite (Fig. S-1), which represents a relic of subducted oceanic lithosphere of the Jurassic Tethys Ocean (*e.g.*, Rubatto *et al.*, 1998). The former harzburgites were serpentinised at the ocean floor and reached peak metamorphic conditions of 550–600 °C and 2.2–2.5 GPa during the Eocene subduction (*e.g.*, Kempf *et al.*, 2020 and references therein). The field relations, petrology, major element, trace element and O isotopic compositions of the samples have been presented in Ulrich *et al.* (2024) and are summarised in Table S-1. The antigorite serpentinite samples are from two nearby sites, the Lower and the Upper Theodul Glacier (LTG and UTG, respectively). Antigorite from the two sites differ in arsenic (As), antimony (Sb) and B concentrations and the O isotopic composition (Ulrich *et al.*, 2024). The positive B-(As-Sb)- $\delta^{18}\text{O}$ correlation within each site has been interpreted as temperature dependent B uptake during oceanic serpentinisation (Ulrich *et al.*, 2024). Samples contain from approximately 25–40 vol. % metamorphic olivine produced *in situ* by the brucite-out reaction ($\text{Atg} + \text{Brc} = \text{Ol} + \text{fluid}$) to up to 90 vol. % metamorphic olivine produced during subsequent reactive fluid flow in shear bands, shear zones and veins. Where olivine is produced *in situ* by the brucite-out reaction, olivine and antigorite are in O isotopic equilibrium (Ulrich *et al.*, 2024). On the other hand, olivine in shear bands, shear zones and veins is in O isotopic equilibrium with antigorite in samples from the UTG outcrop, but in O isotopic disequilibrium with antigorite in samples from the LTG outcrop, indicating channeling of an external serpentinite-derived fluid with low $\delta^{18}\text{O}$ between +5 and +6 ‰ (Ulrich *et al.*, 2024).

The serpentinites from the Erro-Tobbio metaophiolite complex are also former harzburgites from the Jurassic Tethys oceanic lithosphere that reached peak metamorphic conditions

of 500–600 °C and 1.8–2.5 GPa (Scambelluri *et al.*, 1991). Here, we report *in situ* $\delta^{11}\text{B}$ of antigorite, whereas metamorphic olivine *in situ* $\delta^{11}\text{B}$ data are from Vesin and Ulrich *et al.* (2025). Metamorphic olivine was analysed from an HP-vein and an olivine shear band, both consisting of about 90 vol. % olivine and showing O isotopic equilibrium with coexisting antigorite (Vesin and Ulrich *et al.*, 2025). More details about field relations, petrology, *in situ* trace element concentrations, and *in situ* O isotopic compositions of the samples are in Vesin and Ulrich *et al.* (2025) and Table S-1. Analytical details regarding SIMS analyses are in Section 1 of the Supplementary Information. The $\delta^{11}\text{B}$ analyses of the matrix-matched reference materials are given in Tables S-2a and S-2b, and the $\delta^{11}\text{B}$ data and SIMS spots locations are given in Table S-3a and Figure S-2.

$\delta^{11}\text{B}$ of Subducted Serpentine Inherited from Ocean Floor Alteration

The two Zermatt-Saas HP ophiolite localities UTG and LTG, which are suggested to have experienced different serpentinisation conditions based on trace elements and O isotopes (Ulrich *et al.*, 2024), contain antigorite with two distinct $\delta^{11}\text{B}$ signatures (Fig. 1). Samples from the UTG outcrop have antigorite $\delta^{11}\text{B}$ average values of +13 to +19 ‰ (Table S-3b). These high $\delta^{11}\text{B}$ values overlap with literature data from oceanic, forearc, and other subducted serpentinites (Fig. 1). Antigorite from the LTG outcrop has significantly lower $\delta^{11}\text{B}$ values, mostly ranging between –5 and +10 ‰ (sample $\delta^{11}\text{B}$ averages range from –2 to +5 ‰ except for sample ZS-32). Such low values are comparable to mantle wedge serpentinites that have experienced interaction with slab-derived metamorphic fluids from altered ocean crust and/or sediments (Yamada *et al.*, 2019; Martin *et al.*, 2020; De Hoog *et al.*, 2023), even though the Zermatt-Saas serpentinites are clearly of oceanic origin (*e.g.*, Kempf *et al.*, 2020).

The whole rock $^{87}\text{Sr}/^{86}\text{Sr}$ of the Zermatt-Saas samples (Supplementary Information Section 1 for analytical details and Table S-4 and Fig. S-3 for data) from both sites are mostly close to the Sr isotopic composition of Jurassic sea water. Some samples (mainly UTG-samples ZS-02, ZS-10 and ZS-03 with the exception of LTG-sample EK-MF) are slightly more radiogenic while having a higher $\delta^{11}\text{B}$ antigorite. Sample ZS-02 with the highest $^{87}\text{Sr}/^{86}\text{Sr}$ values indicate a sediment contribution of maximum 2 ‰, which seems not to affect the B isotopic composition. The other samples show insignificant interaction between the subducted sediment end member and the HP serpentinites. Thus, we exclude that the low $\delta^{11}\text{B}$ in antigorite of the LTG-samples is due to input from sediment-derived fluids.

Low (<+10 ‰) to negative $\delta^{11}\text{B}$ values in subducted serpentinite may also be the result of B loss and associated depletion of heavy ^{11}B during the lizardite to antigorite transition (Cannaò, 2020; Cannaò and Debret, 2024). Our sample set does not provide evidence for B loss being responsible for the distinct $\delta^{11}\text{B}$ in antigorite among the two Zermatt-Saas localities, as the B content in antigorite from the two sites overlaps. However, the B concentration in antigorite from each site shows a positive correlation with the As and Sb content and the O isotopic composition (Ulrich *et al.*, 2024), but an inverse correlation with its B isotopic composition. The correlation between B content and B isotopes is also observed for the two Erro-Tobbio samples, where antigorite with the higher $\delta^{11}\text{B}$ ($\delta^{11}\text{B}$ of $+26 \pm 2$ ‰ versus $+14 \pm 2$ ‰) contains less B and has lower $\delta^{18}\text{O}$ ($\delta^{18}\text{O}$ of $+5.8 \pm 0.4$ ‰ versus $+6.4 \pm 0.6$ ‰; Vesin and Ulrich *et al.*, 2025). Such negative correlation between $\delta^{11}\text{B}$ and B content and furthermore O isotopes is also described by Vesin *et al.* (2024) in oceanic

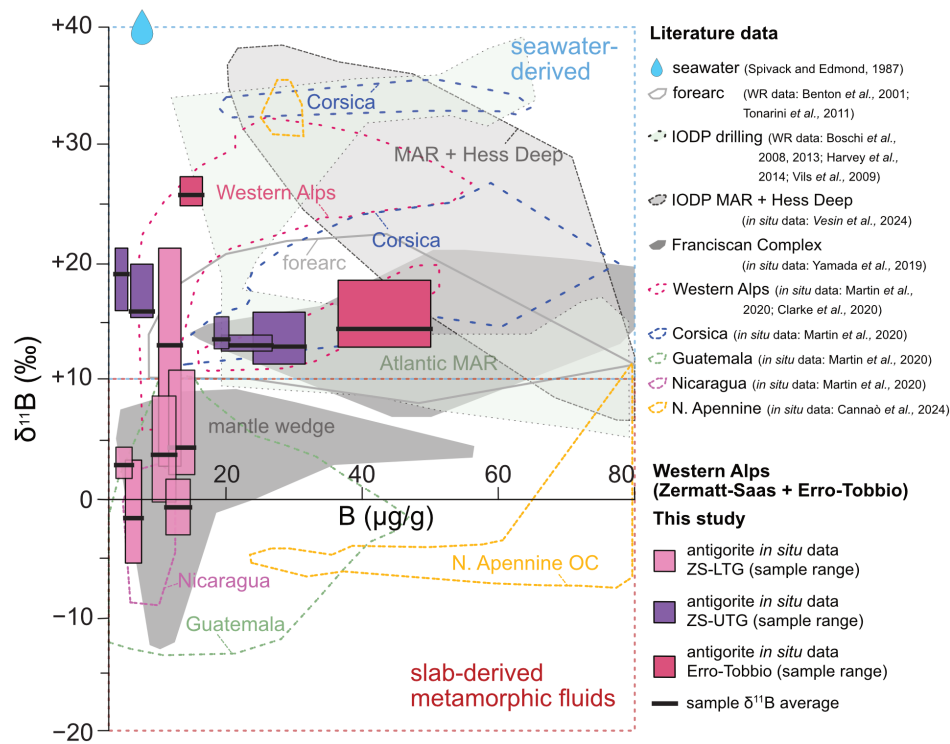


Figure 1 Boron concentration versus $\delta^{11}\text{B}$ of serpentinites from various settings (modified from Martin *et al.*, 2020). Boxes represent antigorite *in situ* $\delta^{11}\text{B}$ data from this study, with B concentrations of Zermatt-Saas and Erro-Tobbio samples taken from Ulrich *et al.* (2024) and from Vesin and Ulrich *et al.* (2025), respectively.

serpentine from IODP samples (Mid Atlantic Ridge and Hess Deep).

We therefore conclude that the different $\delta^{11}\text{B}$ compositions of antigorite from the Zermatt-Saas and Erro-Tobbio samples are most likely inherited from compositional differences obtained during ocean floor serpentinisation because (i) the HP serpentine shows the same element isotope correlation as its oceanic equivalents, and (ii) low to negative $\delta^{11}\text{B}$ values have been documented in oceanic serpentinites produced by oceanic hydrothermal vent fluids (Cannaò *et al.*, 2024). We acknowledge that pH and oxidation state also can have an effect on the B isotopic composition, which, however, cannot be assessed with our data.

$\delta^{11}\text{B}$ in Metamorphic Olivine and Implications for B Isotopic Fractionation

The metamorphic olivine in the Zermatt-Saas samples shows different isotopic composition according to locality (Fig. 2): (i) UTG samples have $\delta^{11}\text{B}$ olivine averages ranging from $+12 \pm 1 \text{‰}$ to $+18 \pm 2 \text{‰}$ (2 s.d.), coexisting with high $\delta^{11}\text{B}$ antigorite (sample averages of $+13 \pm 2 \text{‰}$ to $+19 \pm 4 \text{‰}$); (ii) LTG samples contain olivine with even higher $\delta^{11}\text{B}$ values (sample averages range from $+27$ to $+31 \text{‰}$), coexisting with generally lower $\delta^{11}\text{B}$ antigorite (-5 to $+10 \text{‰}$, with one sample ranging up to $+20 \text{‰}$). This results in different apparent mineral-mineral B fractionation ($\Delta^{11}\text{B}_{\text{Ol-Atg}} = \delta^{11}\text{B}_{\text{Ol}} - \delta^{11}\text{B}_{\text{Atg}}$) for the two localities. By comparing $\Delta^{11}\text{B}_{\text{Ol-Atg}}$ with $\Delta^{18}\text{O}_{\text{Atg-Ol}}$ from the same samples (Ulrich *et al.*, 2024), we find that samples exhibiting olivine-antigorite O isotopic equilibrium generally have $\Delta^{11}\text{B}_{\text{Ol-Atg}}$ near zero (-2.3 to $+0.4 \text{‰}$ for individual samples with an overall average of $-0.7 \pm 3.7 \text{‰}$; Fig. 3a, Table S-3b).

In the two Erro-Tobbio samples, metamorphic olivine is in O isotopic equilibrium with antigorite (Vesin and Ulrich *et al.*, 2025) and has high $\delta^{11}\text{B}$ of $+13 \pm 2 \text{‰}$ and $+24 \pm 1 \text{‰}$, respectively (Fig. 2). Antigorite in these samples also has high $\delta^{11}\text{B}$ of $+14 \pm 2 \text{‰}$ and $+26 \pm 2 \text{‰}$, and thus $\Delta^{11}\text{B}_{\text{Ol-Atg}}$ is near zero ($-0.9 \pm 2.8 \text{‰}$), as for the equilibrated Zermatt-Saas samples (Fig. 3a). This strengthens the conclusion that a near zero $\Delta^{11}\text{B}_{\text{Ol-Atg}}$ value represents equilibrium B isotopic fractionation during serpentinite dehydration. A near-zero $\Delta^{11}\text{B}_{\text{Ol-Atg}}$ ($-0.7 \pm 3.4 \text{‰}$, Zermatt-Saas and Erro-Tobbio samples combined) contrasts with studies that have inferred larger isotopic fractionation values between olivine and antigorite of $+10$ to $+15 \text{‰}$ by considering olivine with B only in trigonal coordination (Cannaò, 2020; Clarke *et al.*, 2020; Li *et al.*, 2022). Our results conflict with these speciation models, but are supported by *ab initio* calculations by Muir *et al.* (2022), which proposed that B in olivine is dominantly in tetrahedral coordination in water-saturated systems at subduction zone conditions, which, in turn, might lead to limited B isotope fractionation between olivine and serpentine. Our results are consistent with a tetrahedral coordination of B in olivine, although this still needs to be confirmed by crystallographic measurements.

A large positive $\Delta^{11}\text{B}_{\text{Ol-Atg}}$ of up to $+25 \text{‰}$ is found in the Zermatt-Saas LTG samples (Fig. 3a), where metamorphic olivine and antigorite are not in O isotopic equilibrium. In these samples, olivine formation is attributed to the migration of ^{11}B -enriched external fluids in shear bands, shear zones and veins that act as fluid channels (Ulrich *et al.*, 2024). External in this context means a fluid derived from serpentinites that has a different O and B isotopic composition.

Sample EK-FA is an exception to the general trend (Figs. 2 and 3a) as it shows a large $\Delta^{11}\text{B}_{\text{Ol-Atg}}$ even when olivine and antigorite are in O isotopic equilibrium, and it is mineralogically similar to the other studied samples. A possible explanation is that

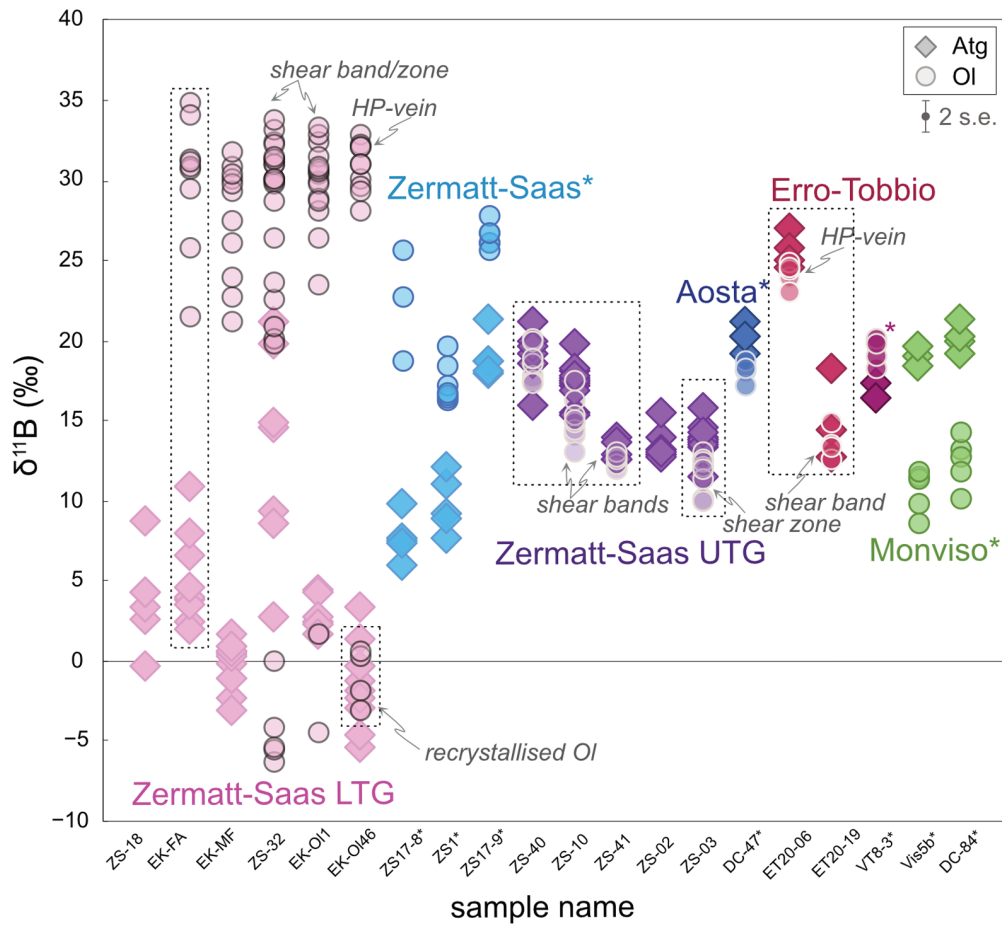


Figure 2 *In situ* $\delta^{11}\text{B}$ of antigorite and olivine from the studied samples compared to the dataset of other HP serpentinites from the Western Alps (Zermatt-Saas, Aosta, Erro-Tobbio and Monviso, marked by *) from Clarke *et al.* (2020). Boxes with dotted lines indicate samples from this study with olivine-antigorite O isotopic equilibrium (Ulrich *et al.*, 2024; Vesin and Ulrich *et al.*, 2025). Mineral abbreviations: Ol, olivine; Atg, antigorite.

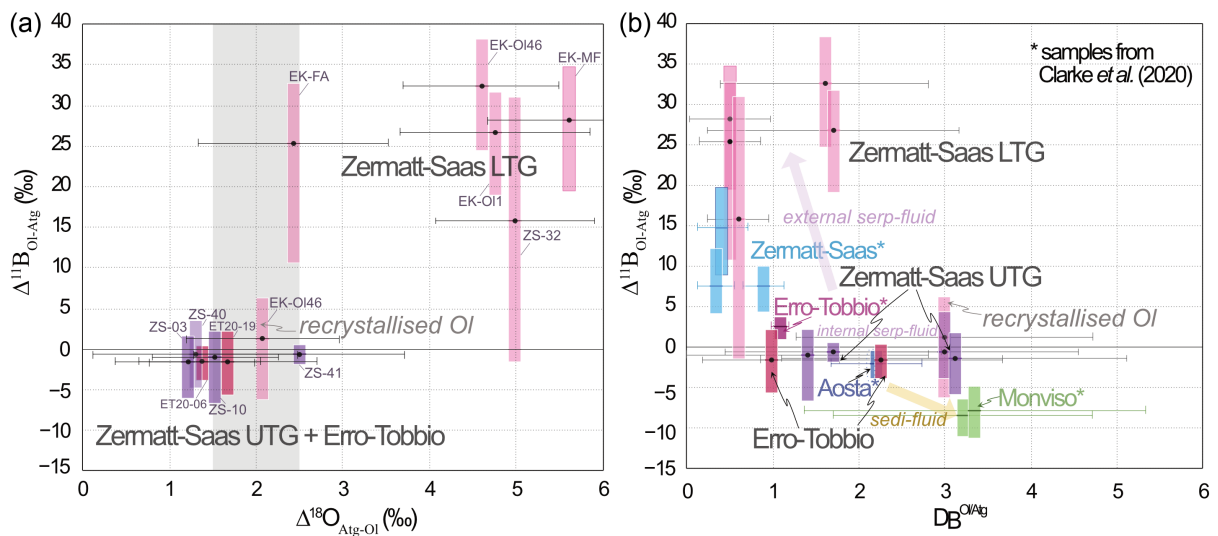


Figure 3 (a) $\Delta^{11}\text{B}_{\text{OI-Atg}}$ versus $\Delta^{18}\text{O}_{\text{Atg-OI}}$ and (b) $\Delta^{11}\text{B}_{\text{OI-Atg}}$ versus $D_B^{\text{OI/Atg}}$ ($\delta^{18}\text{O}$ data and $D_B^{\text{OI/Atg}}$ values from Ulrich *et al.*, 2024). Bars for $\Delta^{11}\text{B}_{\text{OI-Atg}}$ indicate the range from the smallest possible value ($\delta^{11}\text{B}_{\text{OI}}$ min – $\delta^{11}\text{B}_{\text{Atg}}$ max) to the largest possible value ($\delta^{11}\text{B}_{\text{OI}}$ max – $\delta^{11}\text{B}_{\text{Atg}}$ min), while the sample average is indicated by the black dots. For $\Delta^{18}\text{O}_{\text{Atg-OI}}$ and D_B values, the sample average \pm the propagated uncertainty (2 s.d.) are reported. The grey vertical band in (a) indicates the range of equilibrium $\Delta^{18}\text{O}_{\text{Atg-OI}}$ at 550–600 °C, described in Ulrich *et al.* (2024). $\delta^{11}\text{B}$ and D_B datasets marked with an asterisk (*) in (b) are from Clarke *et al.* (2020).

the B isotopic system is more sensitive than O and could record in this sample a minor influence of the external fluids that were not sufficient to modify the isotopic composition of a major element such as O. An alternative explanation is that B in olivine in this sample is in trigonal instead of tetrahedral coordination, resulting in a larger positive $\Delta^{11}\text{B}_{\text{Ol-Atg}}$. However, the variability in $\Delta^{11}\text{B}_{\text{Ol-Atg}}$ in sample EK-FA is quite large and rather suggests B isotopic disequilibrium. Furthermore, a different B coordination might be unlikely as *P-T* conditions, which have a main control on the B coordination, are similar to the other samples. Thus, we favour the first explanation.

In contrast, negative $\Delta^{11}\text{B}_{\text{Ol-Atg}}$ values are reported in another unit of the Western Alps, the Monviso serpentinites, and are attributed to the influx of slab-derived mafic or sedimentary fluids during the olivine-in reaction (Clarke *et al.*, 2020; Fig. 3b). The external fluids in the Monviso also explain the high B content in the metamorphic olivine, and, in turn, high olivine-antigorite B partitioning values ($D_{\text{B}}^{\text{Ol/Atg}}$), exceeding the estimated sample-internal equilibrium range between 0.6 and 0.9 (Clarke *et al.*, 2020). $D_{\text{B}}^{\text{Ol/Atg}}$ values in our samples range from 0.5 to 3.1, regardless of whether olivine and antigorite are in O and apparent B isotopic equilibrium (Ulrich *et al.*, 2024; Fig. 3b). The variable $D_{\text{B}}^{\text{Ol/Atg}}$ values may be due to fluids passing through serpentinite rocks having variable B contents, while the isotopic composition might, or might not, be relatively homogeneous (referred to as internal and external migration, respectively). The migration of these fluids in shear zones and veins (open system) leads to B enrichment in metamorphic olivine.

In summary, we propose that fluid production and internal fluid migration produces $\Delta^{11}\text{B}_{\text{Ol-Atg}}$ values close to zero, whereas non-zero $\Delta^{11}\text{B}_{\text{Ol-Atg}}$ values (LTG and Monviso) likely indicate fluid migration from other sections of the lithosphere, e.g., metasediments, altered ocean crust or serpentinite having a different isotopic composition.

We further conclude that, at the temperatures of the olivine-in reaction (500–600 °C; Scambelluri *et al.*, 1991; Kempf *et al.*, 2020), metamorphic olivine has a similar B isotopic composition as the subducted serpentine from which it forms, and that serpentinite dehydration will not result in significant changes in the B isotopic composition of the slab. Therefore, subducted serpentinites retain their (heterogeneous) $\delta^{11}\text{B}$ sea floor signatures and their dehydration in subduction zones contributes to the heterogeneity of arc lavas.

Acknowledgements

We thank Anne-Sophie Bouvier and Thomas Bovay for setting up the B isotope measurements of serpentine and olivine at the SwissSIMS facility. Enrico Cannào, Jörg Hermann, Martin Wille, Qasid Ahmad, Sebastian Flöter and Jesse Walters are warmly thanked for insightful scientific discussions. We acknowledge the financial support by the Swiss National Science Foundation (project Nr. 191959) to D. Rubatto. Enrico Cannào and an anonymous reviewer are thanked for their valuable comments. We further thank Horst Marschall for editorial handling.

Editor: Horst R. Marschall

Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2507>.



© 2025 The Authors. This work is distributed under the Creative Commons Attribution 4.0 License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited. Additional information is available at <http://www.geochemicalperspectivesletters.org/copyright-and-permissions>.

Cite this letter as: Ulrich, M., Chatterjee, S., De Hoog, J., Rubatto, D. (2025) Serpentine dehydration in the subducted lithosphere produces no B isotopic fractionation. *Geochem. Persp. Lett.* 34, 11–16. <https://doi.org/10.7185/geochemlet.2507>

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 and Planetary Science Letters* 187, 273–282. [https://doi.org/10.1016/S0012-821X\(01\)00286-2](https://doi.org/10.1016/S0012-821X(01)00286-2)
- BOSCHI, C., DINI, A., FRÜH-GREEN, G.L., KELLEY, D.S. (2008) Isotopic and element exchange during serpentinization and metasomatism at the Atlantis Massif (MAR 30°N): Insights from B and Sr isotope data. *Geochimica et Cosmochimica Acta* 72, 1801–1823. <https://doi.org/10.1016/j.gca.2008.01.013>
- BOSCHI, C., BONATTI, E., LIGI, M., BRUNELLI, D., CIPRIANI, A., DALLAI, L., D'ORAZIO, M., FRÜH-GREEN, G.L., TONARINI, S., BARNES, J.D., BEDINI, R.M. (2013) Serpentinization of mantle peridotites along an uplifted lithospheric section, Mid Atlantic Ridge at 11° N. *Lithos* 178, 3–23. <https://doi.org/10.1016/j.lithos.2013.06.003>
- CANNAÒ, E. (2020) Boron isotope fractionation in subducted serpentinites: A modelling attempt. *Lithos* 376–377, 105768. <https://doi.org/10.1016/j.lithos.2020.105768>
- CANNAÒ, E., DEBRET, B. (2024) Variable $\delta^{11}\text{B}$ signatures reflect dynamic evolution of the Mariana serpentinite forearc. *Geochemical Perspectives Letters* 30, 13–19. <https://doi.org/10.7185/geochemlet.2416>
- CANNAÒ, E., TIEPOLO, M., AGOSTINI, S., SCAMBELLURI, M. (2024) Fossil hydrothermal oceanic systems through *in-situ* B isotopes in ophicarbonates (N. Apennines, Italy). *Chemical Geology* 645, 121899. <https://doi.org/10.1016/j.chemgeo.2023.121899>
- CLARKE, E., DE HOOG, J.C.M., KIRSTEIN, L.A., HARVEY, J., DEBRET, B. (2020) Metamorphic olivine records external fluid infiltration during serpentinite dehydration. *Geochemical Perspectives Letters* 16, 25–29. <https://doi.org/10.7185/geochemlet.2039>
- DE HOOG, J.C.M., SAVOV, I.P. (2018) Boron Isotopes as a Tracer of Subduction Zone Processes. In: MARSCHALL, H., FOSTER, G. (Eds.) *Boron Isotopes: The Fifth Element*. Springer, Cham, 217–247. https://doi.org/10.1007/978-3-319-64666-4_9
- DE HOOG, J.C.M., HATTORI, 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. *Contributions to Mineralogy and Petrology* 167, 990. <https://doi.org/10.1007/s00410-014-0990-x>
- DE HOOG, J.C.M., CLARKE, E., HATTORI, K. (2023) Mantle wedge olivine modifies slab-derived fluids: Implications for fluid transport from slab to arc magma source. *Geology* 51, 663–667. <https://doi.org/10.1130/G51169.1>
- HARVEY, J., GARRIDO, C.J., SAVOV, I., AGOSTINI, S., PADRÓN-NAVARTA, J.A., MARCHESI, C., LÓPEZ SÁNCHEZ-VIZCAÍNO, V., GÓMEZ-PUGNAIRE, M.T. (2014) ^{11}B -rich fluids in subduction zones: The role of antigorite dehydration in subducting slabs and boron isotope heterogeneity in the mantle. *Chemical Geology* 376, 20–30. <https://doi.org/10.1016/j.chemgeo.2014.03.015>
- INGRIN, J., KOVÁCS, 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. *American Mineralogist* 99, 2138–2141. <https://doi.org/10.2138/am-2014-5049>
- KEMPF, E.D., HERMANN, J., REUSSER, E., BAUMGARTNER, L.P., LANARI, P. (2020) The role of the antigorite + brucite to olivine reaction in subducted serpentinites (Zermatt, Switzerland). *Swiss Journal of Geosciences* 113, 16. <https://doi.org/10.1186/s00015-020-00368-0>
- 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*. *Geochimica et Cosmochimica Acta* 101, 285–301. <https://doi.org/10.1016/j.gca.2012.10.007>

- LI, Y.-C., WEI, H.-Z., PALMER, M.R., MA, J., JIANG, S.-Y., CHEN, Y.-X., LU, J.-J., LIU, X. (2022) Equilibrium boron isotope fractionation during serpentinization and applications in understanding subduction zone processes. *Chemical Geology* 609, 121047. <https://doi.org/10.1016/j.chemgeo.2022.121047>
- MARSHALL, 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* 207, 102–138. <https://doi.org/10.1016/j.gca.2017.03.028>
- 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. *Chemical Geology* 545, 119637. <https://doi.org/10.1016/j.chemgeo.2020.119637>
- MUIR, J.M.R., CHEN, Y., LIU, X., ZHANG, F. (2022) Extremely Stable, Highly Conductive Boron-Hydrogen Complexes in Forsterite and Olivine. *Journal of Geophysical Research: Solid Earth* 127, e2022JB024299. <https://doi.org/10.1029/2022JB024299>
- PABST, S., ZACK, T., SAVOV, I.P., LUDWIG, T., ROST, D., VICENZI, E.P. (2011) Evidence for boron incorporation into the serpentine crystal structure. *American Mineralogist* 96, 1112–1119. <https://doi.org/10.2138/am.2011.3709>
- RUBATTO, D., GEBAUER, D., FANNING, M. (1998) Jurassic formation and Eocene subduction of the Zermatt–Saas-Fee ophiolites: implications for the geodynamic evolution of the Central and Western Alps. *Contributions to Mineralogy and Petrology* 132, 269–287. <https://doi.org/10.1007/s004100050421>
- SCAMBELLURI, M., TONARINI, S. (2012) Boron isotope evidence for shallow fluid transfer across subduction zones by serpentinized mantle. *Geology* 40, 907–910. <https://doi.org/10.1130/G33233.1>
- SCAMBELLURI, M., HOOGERDIJN STRATING, E.H., PICCARDO, G.B., VISSERS, R.L.M., RAMPONE, E. (1991) Alpine olivine- and titanite clinohumite-bearing assemblages in the Erro-Tobbio peridotite (Voltri Massif, NW Italy). *Journal of Metamorphic Geology* 9, 79–91. <https://doi.org/10.1111/j.1525-1314.1991.tb00505.x>
- SPIVACK, A.J., EDMOND, J.M. (1987) Boron isotope exchange between seawater and the oceanic crust. *Geochimica et Cosmochimica Acta* 51, 1033–1043. [https://doi.org/10.1016/0016-7037\(87\)90198-0](https://doi.org/10.1016/0016-7037(87)90198-0)
- TONARINI, S., LEEAN, 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 and Planetary Science Letters* 301, 275–284. <https://doi.org/10.1016/j.epsl.2010.11.008>
- ULMER, P., TROMMSDORFF, V. (1995) Serpentine Stability to Mantle Depths and Subduction-Related Magmatism. *Science* 268, 858–861. <https://doi.org/10.1126/science.268.5212.858>
- ULRICH, M., RUBATTO, D., HERMANN, J., MARKMANN, T.A., BOUVIER, A.-S., DELOULE, E. (2024) Olivine formation processes and fluid pathways in subducted serpentinites revealed by in-situ oxygen isotope analysis (Zermatt-Saas, Switzerland). *Chemical Geology* 649, 121978. <https://doi.org/10.1016/j.chemgeo.2024.121978>
- VESIN, C., RUBATTO, D., PETKE, T. (2024) The history of serpentinisation at mid-ocean ridges: Insights from in situ trace elements coupled with oxygen and boron isotopes. *Chemical Geology* 654, 122060. <https://doi.org/10.1016/j.chemgeo.2024.122060>
- VESIN, C., ULRICH, M., RUBATTO, D., HERMANN, J., SCAMBELLURI, M. (2025) Chemical and isotopic exchanges in serpentinites during hydration and dehydration events in the Erro-Tobbio Massif (Italy): from ocean to subduction. *Journal of Petrology* 66, egaf088. <https://doi.org/10.1093/petrology/egaf008>
- VILS, F., TONARINI, S., KALT, A., SEITZ, H.-M. (2009) Boron, lithium and strontium isotopes as tracers of seawater–serpentine interaction at Mid-Atlantic ridge, ODP Leg 209. *Earth and Planetary Science Letters* 286, 414–425. <https://doi.org/10.1016/j.epsl.2009.07.005>
- 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>