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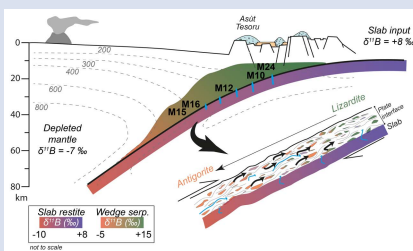
Variable $\delta^{11}\text{B}$ signatures reflect dynamic evolution of the Mariana serpentinite forearc

E. Cannao^{1*}, B. Debret²



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Abstract



This study aims to uncover the evolving dynamics of element mobility in serpentinised ultramafic clasts within the Asut Tesoru mud volcano in the Mariana forearc. By employing *in situ* analysis of trace elements and boron isotopes ($\delta^{11}\text{B}$), our findings document a progressive ^{11}B depletion from lizardite- to antigorite-bearing serpentinites, accompanied by a reduction in the incompatible element inventory in some samples. This pattern aligns with either a chemical evolution linked to phase transitions along the slab interface of shallow forearc serpentinites dragged down to depth, or interaction with shallow *vs.* deep slab fluids. Our results support a scenario of complex fluid and mechanical mixing along the plate interface in the Mariana subduction system, with major implications for the B recycling in convergent margins.

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Introduction

The serpentinisation of forearc mantle regions is a major outcome of slab devolatilisation during early subduction stages (e.g., Hyndman and Peacock, 2003), modulating global chemical recycling in convergent margins. A progressive and selective release of the trace element inventory from the slab with depth is documented (e.g., Bebout *et al.*, 1999), reflecting the mobility of elements based on their retention and redistribution in newly formed, rock forming and accessory minerals during mineral breakdown reactions to depths of up to 150–200 km (Spandler *et al.*, 2003). The study of forearc serpentinites may provide key insights into the mobility of elements at shallow depths. In this context, the Mariana forearc is an exceptional setting where partially to completely serpentinised clasts originating from the supra-subduction mantle can buoyantly rise toward the surface through forearc faults, generating mud volcanoes (Benton *et al.*, 2001; Savov *et al.*, 2007; Debret *et al.*, 2019). Serpentinite clasts preserve evidence of multiple serpentinisation stages reflecting various episodes of fluid infiltrations (Debret *et al.*, 2019); therefore, *in situ* analyses of fluid-mobile elements (FMEs) and redox-sensitive elements associated with the isotopic signature of stable isotope systematics can be used as tracers to disentangle the progressive changes in element mobility in the forearc region (e.g., Albers *et al.*, 2020; Geilert *et al.*, 2021). Among key FMEs, boron (B) is the best tracer of fluid sources and processes in subduction zones, and the large fractionation of its isotopes ($\delta^{11}\text{B}$) may provide pivotal information to unravel the active geochemical exchanges between upper mantle and slab-derived fluids at depths (e.g., De Hoog and Savov, 2018). It has been proposed that the B isotope signatures of serpentinites can be used to investigate fluid-mantle interactions discerning between seawater- and subduction-derived

fluids (Martin *et al.*, 2016). In the latter case, slab devolatilisation produces ^{11}B -rich fluids at shallow depths that progressively evolve to more ^{11}B -depleted compositions in response to Rayleigh fractionation associated with prograde metamorphic reactions (e.g., Marschall *et al.*, 2007). So far, the B geochemistry of Mariana's hydrated ultramafic clasts and mud matrix have been achieved by bulk analyses with the consequence that all geochemical information related to different generations of serpentine and subsequent metasomatic event(s) were homogenised and lost, together with potential intra- and inter-mineral variations. The benefits of the *in situ* approach also allow for maximising the information gathered from small aliquots of rock samples, such as those from IODP expeditions. Here, we focus on the serpentinised ultramafic clasts contained in the Asut Tesoru mud volcano in the Mariana forearc (IODP Exp 366) performing new *in situ* trace element and the first *in situ* boron isotope ($\delta^{11}\text{B}$) investigations to unravel transient fluid-mediated mass transfer in the shallow forearc mantle region.

Geological Background and Sample Description

The Mariana forearc is a non-accretionary subduction system where the Mesozoic Pacific plate is subducted west-northwestward beneath the Philippine Sea plate (Fig. 1). It hosts dozens of active mud volcanoes generated in response to the interaction of aqueous slab-derived fluids with forearc mantle wedge peridotites. These mud volcanoes consist of unconsolidated serpentinite mud and contain variably serpentinised ultramafic clasts, together with minor amounts of recycled metamorphosed slab materials (Tamblyn *et al.*, 2019; Fryer *et al.*, 2000). The Asut

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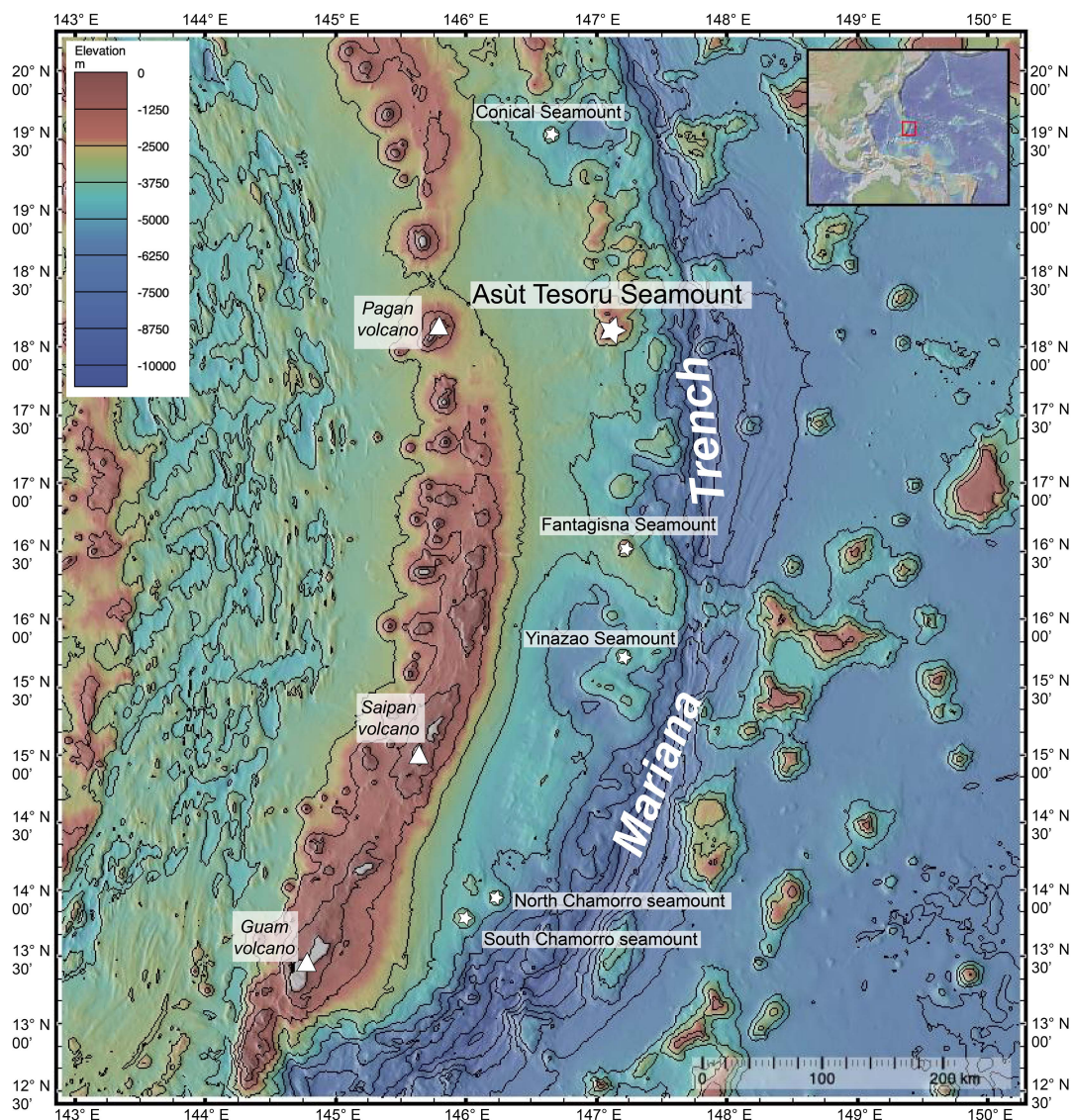


Figure 1 Location of the Asut Tesoru seamount imposed over the bathymetry map of the Mariana subduction system (generated with the GeoMapApp).

Tesoru serpentinite mud volcano ($18^{\circ} 06' N$ and $147^{\circ} 06' E$) is located at *ca.* 72 km from the trench and at about 18 km above the slab, where the temperature (T) at the slab-mantle interface is estimated at *ca.* $250^{\circ} C$ (Hulme *et al.*, 2010). The investigated samples (Table S-1) were drilled during the International Oceanic Discovery Program (IODP) Expedition 366 (Fryer *et al.*, 2018). Complete petrographic and whole rock geochemical characterisation of the samples can be found in Fryer *et al.* (2018) and Debret *et al.* (2019). Briefly, serpentinite clasts are subdivided in four main groups based on the type of serpentine variety (Fig. S-2): (i) lizardite (liz; sample M10), (ii) transitional (lizardite/antigorite-bearing; sample M12), (iii) antigorite-bearing (atg; samples M15 and M16), and (iv) shallow brucite and blue lizardite-bearing serpentinites (samples M20 and M24). The degree of serpentinisation increases from liz- to atg-bearing samples, together with the estimated T of serpentinisation that, based on O isotope data, range from 210 to $410^{\circ} C$ (Debret *et al.*, 2019). The progressive replacement of lizardite by antigorite at increasing T , as evidenced in sample M12, indicates that these samples record progressive burial and hydration of the forearc mantle region at depth. Samples of brucite (sample M20, mainly brucite \pm lizardite) and the blue lizardite-bearing serpentinite (sample M24; mainly brucite-lizardite)

represent the late low T ($<180^{\circ} C$) serpentinisation stage affecting ultramafic clasts during exhumation (Debret *et al.*, 2019).

Results

The *in situ* trace element data together with the B isotope compositions of serpentinite clasts (Table S-4) and the analytical methodology are provided in the Supplementary Information. Boron concentrations are higher for lizardite and antigorite in samples M10-M12-M16 (from 17 to 115 $\mu g/g$), respectively, whereas slightly lower contents are reported for the atg-bearing sample M15 (from 11 to 22 $\mu g/g$). Blue serpentinite and serpentinites in brucite samples show moderate B enrichment (22 ± 8 and 29 ± 16 $\mu g/g$, respectively). Brucite from sample M20 shows B content averaging at 11.5 ± 5.3 $\mu g/g$. Boron isotope compositions of serpentinites are strongly variable, ranging from -5 to $+21$ ‰. Higher $\delta^{11}B$ values pertain to lizardite and antigorite from sample M12 with mean values of $+12.0 \pm 2.3$ ‰ (2 s.d., $n = 2$) and $+17.4 \pm 6.4$ ‰ (2 s.d., $n = 3$), respectively. Lizardite from sample M10 has homogeneous $\delta^{11}B$ mean value of $+7.1 \pm 0.6$ ‰ (2 s.d., $n = 18$). Lizardite from brucite and blue

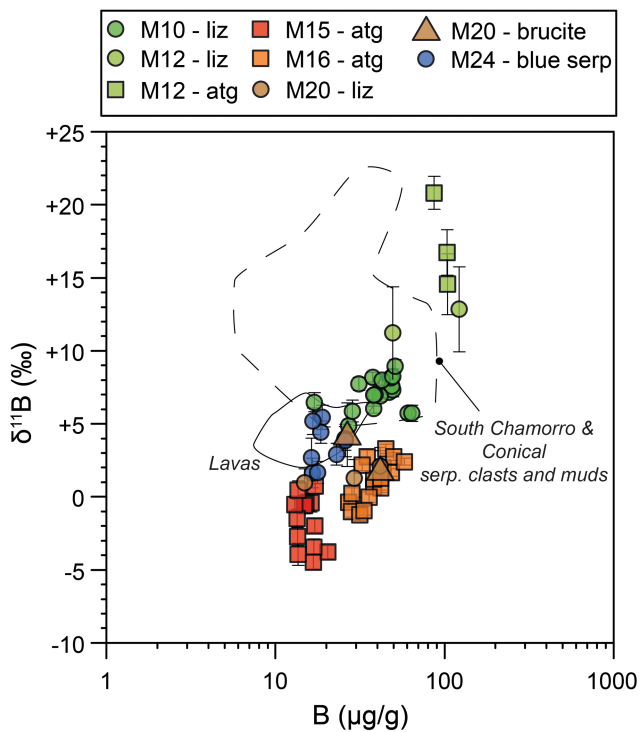


Figure 2 Relationship between $\delta^{11}\text{B}$ (‰) vs. B ($\mu\text{g/g}$). Data from South Chamorro (Wei *et al.*, 2005) and Conical (Benton *et al.*, 2001) seamounts, and the Mariana lavas (Ishikawa and Tera, 1999) are shown for comparison.

serpentine display overlapping $\delta^{11}\text{B}$ values, ranging between +1 and +6 ‰. Two $\delta^{11}\text{B}$ data from a serpentine-brucite mixture (sample M20) average $+2.5 \pm 1.6$ ‰ (2 s.d.), comparable with those of serpentine from the same sample (Fig. 2). Pure atg-bearing serpentines (M15 and M16) are characterised by $\delta^{11}\text{B}$ values ranging from -5 to $+4$ ‰, with the most negative values belonging to sample M15, which also has the lowest B contents. Overall, positive correlation between $\delta^{11}\text{B}$ vs. B contents is shown between samples (Fig. 2), with the atg-serpentinites from M15 falling at the lower end of these trends.

Discussion

The trace element variability and the $\delta^{11}\text{B}$ signatures of the serpentines from the Asùt Tesoru mud volcano point to a complex interaction with evolving fluid(s) released from the downgoing slab (*e.g.*, Albers *et al.*, 2020). The B isotope compositions of lizardite from all samples and antigorite from sample M12 mostly fall within the compositional whole rock $\delta^{11}\text{B}$ data available so far for both serpentine matrix (from +6 to +21 ‰) and serpentinised peridotite clasts (from +5 to +25 ‰) from the Conical (Benton *et al.*, 2001) and the South Chamorro (Wei *et al.*, 2005) Seamounts (Fig. 2). Such positive $\delta^{11}\text{B}$ values reflect the result of interaction between forearc mantle and ^{11}B -enriched aqueous fluids released from the subducting slab during its early devolatilisation (Benton *et al.*, 2001; Pabst *et al.*, 2012; Liu *et al.*, 2022). Pure antigorite-bearing samples M15 and M16 exhibit low B abundances and predominantly negative $\delta^{11}\text{B}$ values compared to liz-bearing samples (Fig. 2), indicating a significant difference in the chemistry of the interacting slab-derived fluids during subduction burial. This marks the first report of serpentines from the Mariana forearc with such light B isotope compositions (Benton *et al.*, 2001; Wei *et al.*, 2005), thus providing new insights into the chemical evolution of forearc serpentinites. Negative B isotope compositions (from +0.7

to -5.0 ‰) have been reported for several OIB-type metabasites collected from the summit of the Asùt Tesoru mud volcano during the same IODP expedition (Liu *et al.*, 2022). These negative B isotope imprints reflect the partial dehydration of the altered oceanic crust during shallow slab devolatilisation (*e.g.*, Pabst *et al.*, 2012), where ^{11}B -enriched aqueous fluids are extracted from the slab during prograde metamorphic reactions (*e.g.*, Marschall *et al.*, 2007). The recent working model for the Mariana subduction system proposed by Liu *et al.* (2022) suggests that progressive Rayleigh devolatilisation of altered oceanic crust with an initial $\delta^{11}\text{B}$ of +8 ‰ can reproduce the $\delta^{11}\text{B}$ characteristics of the metabasites from the Mariana forearc mud volcanoes, the serpentinite clasts and muds from the Conical Seamount and the Mariana arc lavas. However, this model fails to reproduce the $\delta^{11}\text{B}$ signatures of serpentines reported in this study (Fig. 3a). A recent computational study of Li *et al.* (2022), indicates that B isotope fractionation should occur between serpentine and fluids, even when B is four-fold coordinated in both phases (not implemented in the proposed model). This set the basis for a newly invoked scenario to explain the measured $\delta^{11}\text{B}$ signatures. Considering an initial $\delta^{11}\text{B}$ signature of the slab of *ca.* +8 ‰, and the B isotope fractionation between serpentine and fluids, lizardite (samples M10-M12) and antigorite (samples M15-M16) with variable $\delta^{11}\text{B}$ signatures (from +12 to -5 ‰) can be achieved by flushing the supra-subduction mantle region with slab-derived fluids at variable and increasing water/rock ratios from 5 to 90 (Fig. 3b; see Supplementary Information for details). The modelled increase in water/rock ratios from liz- to atg-bearing serpentinites is also consistent with the increase in the degree of serpentinisation (Fig. S-2) (Debret *et al.*, 2022). This scenario involves the direct hydration of shallow (for liz) and deeper (for atg) regions of the wedge mantle with fluids characterised by evolved $\delta^{11}\text{B}$ signatures (Fig. 4a). Higher $\delta^{11}\text{B}$ signatures approaching the values of the antigorite from sample M12 (*ca.* +20 ‰) can be attained assuming lower water/rock ratios during prograde phase transition (Fig. 3b). Such low water/rock ratios can also be invoked to explain the $\delta^{11}\text{B}$ signatures of the Conical and South Chamorro seamounts (up to +25 ‰). This model assumes a single $\delta^{11}\text{B}$ imprint as representative of the protolith slab input to explain the results for the entire dataset, which could be a limitation considering a certain degree of lateral variability in the composition of the input materials along the Mariana trench (1400 km in length). Furthermore, our approach does not consider the residence time of the serpentine clasts within the Mariana subduction system. Geochronological data indicate that the “plumbing system” of the Mariana mud volcanoes may sample clasts with a long history (*ca.* 46 Myr) of chemical and thermal evolution along the subduction interface (Tamblyn *et al.*, 2019). In this framework, the high $\delta^{11}\text{B}$ signatures and FME budget shown by antigorite from sample M12, as compared to lizardite from the same sample (Fig. S-4), suggest the involvement of ^{11}B - and FME-enriched slab fluids at depth that cannot be accounted for with a single stage model. A multi-stage model could also be considered to elucidate the relative enrichment in FMEs observed in antigorite from sample M16 (Fig. S-4), indicating that different fluids at different depths played roles in modifying the geochemistry of Mariana forearc serpentinites.

The low and negative $\delta^{11}\text{B}$ signatures observed in antigorite from samples M15 and M16 may also be interpreted as being related to B isotope fractionation during prograde phase transition. This idea follows the modelling attempt proposed by Cannò (2020), which suggests that the loss of B during the prograde serpentine phase transition could be associated with B isotope fractionation. Previous petrographic investigations and micro-chemical data indicate that antigorite in the Asùt Tesoru seamount primarily formed at the expense of lizardite with limited influx of external SiO_2 or other chemical components

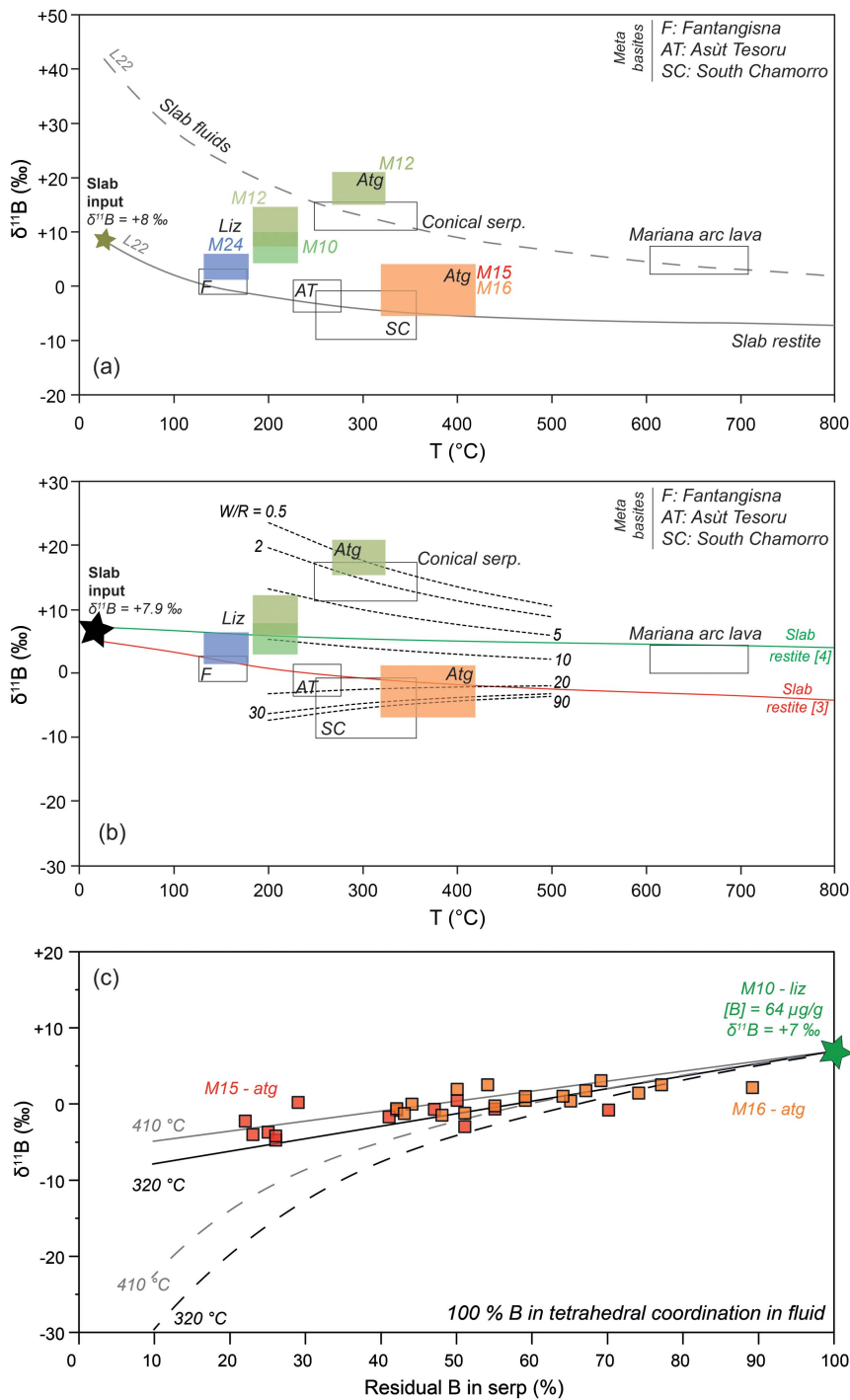


Figure 3 (a) Working Rayleigh dehydration modelling proposed by Liu *et al.* (2022; L22) to explain the B isotope variability in metabasites from the Fantangisña (F), Asüt Tesoru (AT) and South Chamorro (SC) seamounts (Pabst *et al.*, 2012; Liu *et al.*, 2022). Serpentinite clasts and muds from Conical (Conical serp.) are from Benton *et al.* (2001), Mariana lavas are from Ishikawa and Tera (1999); $\delta^{11}\text{B}$ data for the Asüt Tesoru serpentines presented herein are coloured boxes. (b) Modification of the working model proposed by Liu *et al.* (2022) considering B isotope fractionation between slab-derived fluids and serpentines (Li *et al.*, 2022). Green and red lines represent the $\delta^{11}\text{B}$ composition of slab restite at alkaline ([4]) and acid ([3]) conditions, respectively. Black dashed lines represent serpentine-fluid B isotope fractionation at different water/rock ratios (W/R; Table S-6 and Supplementary Information for details). (c) Variation of $\delta^{11}\text{B}$ and B content ([B]) according to serpentine phase transition (see Supplementary Information for details).

(Debret *et al.*, 2019). This scenario aligns with a progressive burial of the forearc mantle wedge during subduction. Considering an initial $\delta^{11}\text{B}$ signature for lizardite of +7 ‰ and 64 $\mu\text{g/g}$ of B (similar to sample M10), the antigorite from samples M15 and M16 loses 20 to 90 % of their initial B budget. According to calculation

(see Supplementary Information), either batch or Rayleigh devolatilisations under alkaline conditions can properly simulate most of the $\delta^{11}\text{B}$ signatures shown by antigorite (Figs. 3c, 4b). Given the high variability of the $\delta^{11}\text{B}$ signatures in serpentinite from the Conical Seamount (Benton *et al.*, 2001), if higher



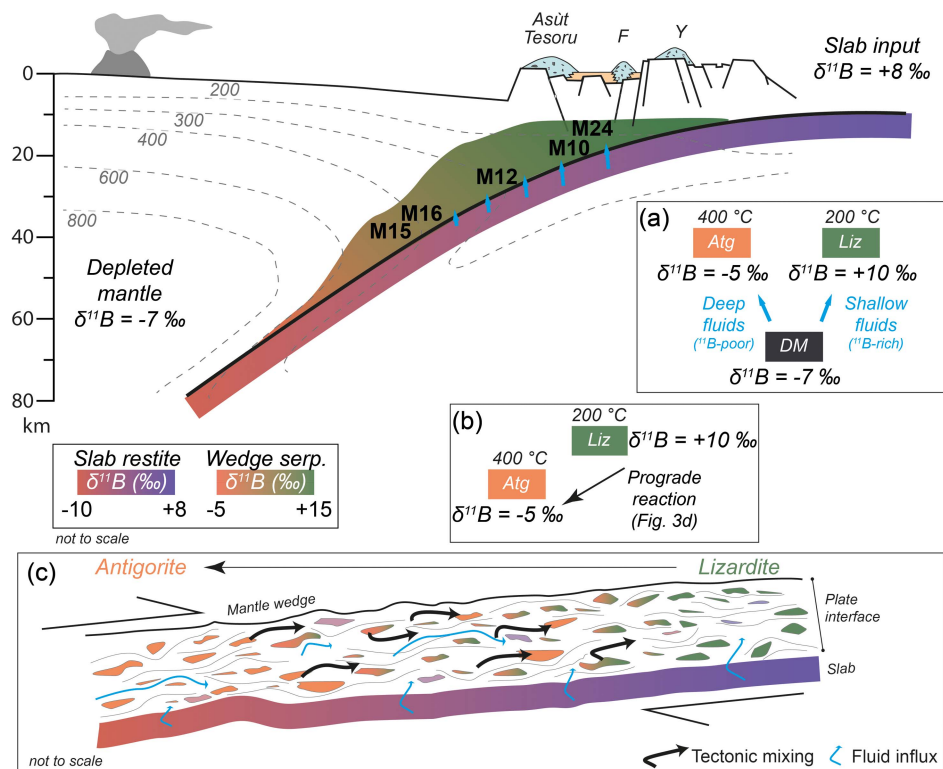


Figure 4 Cartoon illustrating the Mariana subduction setting showing the potential location of studied samples along the slab-mantle interface and the B isotope variation within the slab restite and in the wedge serpentinites. (a) Boron isotope composition of antigorite and lizardite flushed by deep and shallow slab fluids, respectively, according to model presented in Figure 3b. (b) Modification of the $\delta^{11}\text{B}$ imprint during lizardite to antigorite transition according to model presented in Figure 3c. (c) Schematic plate interface showing complex fluid and tectonic mixing where liz- and atg-bearing serpentinite clasts can be mixed together with portion of metamorphosed slab materials (see text for details). Modified after Debret *et al.* (2020) and references therein.

$\delta^{11}\text{B}$ for the precursor lizardite is assumed (e.g., $\delta^{11}\text{B} = +20$ ‰, $B = 81$ $\mu\text{g/g}$), most of the antigorite data from sample M16 cannot be reproduced, even considering 50 % of B speciation in fluids in trigonal coordination (Fig. S-8). If this is the case, the geochemistry of the antigorite may be overprinted by the interaction with deep slab fluids released from a different source and, potentially, at different time (Tamblyn *et al.*, 2019). The relative enrichment in As and Sb for sample M16 trend towards this hypothesis thus require a multi-stage evolution.

Both scenarios can appropriately explain the $\delta^{11}\text{B}$ variability from liz- to atg-bearing serpentinites, and reasonably operate simultaneously in subduction zones. Overall, our new trace element and B isotope results corroborate the scenario of complex transport mechanisms feeding the mud volcanoes in the Mariana forearc (Fig. 4c): shallow hydration of the forearc region progressively dragged down to depth before exhumation along the subduction channel(s), where pieces of metamorphosed slab materials can also be sampled (e.g., Pabst *et al.*, 2012; Tamblyn *et al.*, 2019; Liu *et al.*, 2022).

Implications for Subduction Dynamics and Deep Boron Recycling

The B isotope variability documented here provides new constraints to disentangle the dynamic evolution of forearc regions. Our data provide the first insights into the possibility of mixing within the subduction channel (Fig. 4), suggesting a scenario where the forearc serpentinites are truly dragged downward into the deeper wedge. The serpentine-dominated mélangé domains atop the subducting slab may trigger mechanical instabilities and

the formation of buoyant diapirs (Marschall and Schumacher, 2012). Such mélangé materials can penetrate within the hot corner of the mantle wedge feeding island arcs contributing to the heavy $\delta^{11}\text{B}$ imprints characterising the Mariana arc lavas (Ishikawa and Tera, 1999). Alternatively, the forearc serpentinites are prone to dehydration to form secondary peridotites (or metaperidotites) plus aqueous fluids coherent with the slab-top P - T conditions of the Mariana subduction system (Syracuse *et al.*, 2010). This transformation impacts the geochemistry of the arc magmatism and the metaperidotite that will be buried to depths (e.g., Cannàò *et al.*, 2020). Depending on the $\delta^{11}\text{B}$ of antigorite (e.g., -5 ‰ in M15 *vs.* $+21$ ‰ in M12), the progressive dehydration at deeper conditions of forearc serpentinites with $\delta^{11}\text{B}$ signatures comparable to the antigorite of the Asùt Tesoru will provide fluids with $\delta^{11}\text{B}$ from -1 to $+25$ ‰ (Table S-7). To match the B isotope signatures of Mariana lavas, a deep ^{11}B -rich reservoir is required, and the role of serpentinites is gaining ground based on $\delta^{11}\text{B}$ (Benton *et al.*, 2001) and also Fe and Mo isotope systematics (Freymuth *et al.*, 2015; Debret *et al.*, 2020; Li *et al.*, 2021; Chen *et al.*, 2023). The estimated B isotope signatures for serpentinite-derived fluids agree with those proposed to explain the B isotope signatures of the Mariana lavas (Ishikawa and Tera, 1999). Despite the B coordination in olivine still being debated (see Supplementary Information), the newly formed secondary peridotites should have a $\delta^{11}\text{B}$ imprints ranging from -2 to $+24$ ‰ (Table S-7). The existence of isotopically heavy B deep reservoir(s) is not required to match B mass balance calculations (Marschall *et al.*, 2017), however, our work points out that a significant amount of ^{11}B -rich secondary peridotites might be injected beyond the arc into the deep Earth's mantle, contributing to its geochemical heterogeneity.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2416>.



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Variable $\delta^{11}\text{B}$ signatures reflect dynamic evolution of the Mariana serpentinite forearc

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Supplementary Information

The Supplementary Information includes:

- Analytical Methods
- Background Geochemical Data
- Geochemical Modelling
- Tables S-1 to S-7
- Figures S-1 to S-9
- Supplementary Information References

Analytical Methods

In situ trace element determination

The *in situ* trace element compositions of rock-forming minerals (serpentine and brucite) and mineral relicts (olivine and orthopyroxene) were determined using a laser ablation microprobe system (Analyte Excite 193nm ArF excimer, Teledyne Photon Machines) coupled with a single-collector quadrupole inductively coupled plasma mass spectrometer (ICP-MS) iCAP-RQ (Thermo Fisher Scientific) hosted at the Geochemistry, Geochronology and Isotope Geology Laboratory at the Dipartimento di Scienze della Terra “A. Desio”, Università degli Studi di Milano (Italy). The laser ablation system is equipped with a double volume ablation cell (HelEx II) for fast wash out. Ablated particles were transported to the ICP-MS using He gas at a flow rate of 0.52 and 0.35 L/min into the sample chamber and in the HelEx II cup, respectively. Laser spot size range from 40 to 65 μm for unknown and was fixed to 40 μm for standard glasses. A laser fluence of 3.0 J/cm² and repetition rate of 10 Hz were used for both standards and mineral unknown. Each spot was analysed for a total of 110 s: (i) 40 s of background analyses (laser off), which include 10 s of laser warm up, (ii) 60 s of laser ablation measuring isotope peak intensity followed by (iii) 10 s of wash out time. The synthetic basaltic glass GSD-2g (Wilson, 2018) was used as external standard, whereas ²⁹Si (for serpentine, olivine, orthopyroxene) and ²⁵Mg (for brucite) were used as internal standards. Quality control was achieved analysing as unknown in each analytical run the andesitic glass ARM3 (Wu *et al.*, 2019) and the USGS reference basaltic glass BCR-2g (GeoReM database). Precision is often better than 10 % and accuracy is within 15 % of the preferred values for most of the elements.

In situ B isotope determination

The *in situ* B isotope compositions of serpentines have been measured using the same laser microprobe system used for the determination of trace element connected to a double focusing multi-collector (MC-)ICP-MS, Neptune XT (Thermo Fisher Scientific) installed at the Geochemistry, Geochronology and Isotope Geology Laboratory at the Dipartimento di Scienze della Terra “A. Desio”, Università degli Studi di Milano (Italy). The laser ablation system was operated in single spot mode with a laser fluence of 3.5 J/cm², repetition rate of 10 Hz and fixed spot size of 85 μm in diameter. These



laser parameters were kept constant for both standards and serpentine unknown to minimise potential isotope fractionation (Kimura *et al.*, 2016). Ablation was carried out under He flux at flow rate of 0.51 L/min and 0.24 L/min into the sample chamber and in the HelEx II arm, respectively. Nitrogen gas was used as additional gas at a flow rate of ca. 5 mL/min and added downstream of the ablation cell in order to improve the sensitivity. The Neptune XT was operated in low resolution mode, using Ni Jet-sample and X-skimmer cones to improve the sensitivity. The ^{11}B and ^{10}B ion beam were measured in H4 and L2, respectively, using Faraday cup detector system both equipped with $10^{13}\ \Omega$ resistors, thus ensuring an optimal signal/noise ratio. The tau correction was applied before data are exported. The radio frequency of the ICP torch was set to 1000 W. The system was tuned daily by ablating the NIST SRM612 synthetic glass (B content ca. 35 $\mu\text{g/g}$; Jochum *et al.*, 2011) with a spot size of 40 μm at a rate of 10 Hz and a laser fluence of 6.0 J/cm^2 , resulting in a mean sensitivity on ^{11}B of at least 1.0 $\text{mV}/\mu\text{g/g}$. The signal measured (tens to hundreds of mV) for ^{10}B and ^{11}B , used to calculate the $^{11}\text{B}/^{10}\text{B}$ ratio, are corrected from instrument background that were below 0.10 and 0.50 mV, respectively. Each analyses comprises 156 cycles of 0.524 s integration time and each measurement included 30 s of background acquisition (laser off; comprising 10 s of laser warm up), 40 s of data acquisition followed by 8 s of was out time. Data treatment was made off-line, using an *in-house* spreadsheet. Ratios exceeding the 2 standard deviation (2 s.d.) of the mean have been regarded as outliers and discharged. Note that no downhole isotope ratio fractionation was observed. The analytical precision is commonly dependent upon the intensity of B signal, which is related to the B content of the analysed material. However, the relatively high 2 standard error (s.e.) shown by some analyses with high B content (e.g., sample M12) is related to the small thickness of the available rock specimen in thin section.

The results are reported in the common delta(δ)-notation as permil (‰) and expressed relative to the isotopic ratio of the reference boric acid NIST SRM 951 ($^{11}\text{B}/^{10}\text{B} = 4.04362 \pm 0.00137$ 2 s.d.; Catanzaro *et al.*, 1970). Mass-bias fractionations were corrected using the standard-sample bracketing approach. A matrix-matching reference material, the Koh-ol olivine (Bouihol *et al.*, 2012; provided by C.J. De Hoog), was used as calibrating standard to avoid potential Ca-induced interference on the measured $^{11}\text{B}/^{10}\text{B}$ ratios (see Fietzke and Anagnostou, 2023, for details). This olivine has relatively homogeneous B isotope composition (-4.6 ± 0.8 ‰ 2 s.d.; Clarke *et al.*, 2020) but variable B content, ranging from 60 to 120 $\mu\text{g/g}$ (Bouihol *et al.*, 2012; Cannaò *et al.*, 2024). Hereafter, the uncertainty of $\delta^{11}\text{B}$ data is reported as 2 s.d. for mean values and as 2 s.e. for single spot analyses. Quoted uncertainties are quadratic additions of the within run precision of each analysis and the reproducibility of the Koh-ol olivine during each analytical run, which range from 0.20 to 0.41 ‰ (2 s.d., $n = 9\text{--}15$; Table S-2). Estimated B concentrations were obtained by comparing the intensities of the unknown with that of the NIST SRM612 synthetic glass analysed within each runs. An in-house antigorite with ca. 16 $\mu\text{g/g}$ of B and $\delta^{11}\text{B}$ of $+22.3 \pm 0.4$ ‰ (sample MS VAR 10-01 in Cannaò *et al.*, 2016) was used to assess accuracy. The measured $\delta^{11}\text{B}$ range between $+19.80 \pm 0.78$ and $+22.68 \pm 0.64$ ‰ (2 s.e.; see Table S-3, Fig. S-1), with a mean of $+21.41 \pm 1.74$ ‰ (2 s.d., $n = 10$) overlapping the $\delta^{11}\text{B}$ bulk value obtained with TIMS after chemical purification (Cannaò *et al.*, 2016). Our results indicate the lack of isotope fractionation due to matrix effects (e.g., different water content between olivine and antigorite), signal intensities or instrumental bias, thus proving the high quality of the $\delta^{11}\text{B}$ data reported in this contribution. Further information about the analytical protocol can be found in Cannaò *et al.* (2024).

Background Geochemical Data

Chondrite-normalised (C1) rare earth element (REE) compositions of the serpentines for all samples (Fig. S-3) are depleted (from 0.002 to 0.5 times the C1) with mean $\text{La}_\text{N}/\text{Yb}_\text{N}$ ratios ranging from 0.05 to 0.33, except for the blue-serpentine ($\text{La}_\text{N}/\text{Yb}_\text{N}$ ratio of 1.41). Lizardite from samples M10, M12 and M20 show negative seawater-like Ce anomaly, which is slightly detected in atg-bearing samples. The REE pattern of the brucite from sample M20 overlap those of the coexisting serpentines. Primitive mantle-normalised trace element plots (Fig. S-4) show positive anomalies in several fluid-mobile (B, As, Sb) and redox-sensitive elements (e.g., Mo). The low- T liz-bearing sample M10 and the antigorite in the transitional sample M12 also shown variable enrichments in Cs, W and Li, that are lacking in the atg-bearing samples (M15–M16). Brucite from sample M20 shows variable enrichments in Sr, Ba, Cs, Li, Mo, W and Pb. Antigorite from transitional sample M12 show the highest and variable As contents (from 0.360 to 19.0 $\mu\text{g/g}$) followed by the atg-bearing sample M16 (1.29 ± 1.16 $\mu\text{g/g}$). Strontium concentrations decrease from liz- to atg-bearing samples, in agreement with bulk data (Debret *et al.*, 2019). Of relevance are the correlations between W/Ba ratio and Ba and Sr contents of the serpentines, where lizardite have high Ba contents and low W/Ba ratios, in contrast to antigorite showing low Ba contents and high W/Ba ratios (Fig. S-5). The high Ba and Mo contents in lizardite from sample M10, result in low W/Ba and Mo/Ce ratios (Fig. 2c), supporting the higher mobility of Ba compared to W and the mobilisation of Mo



in aqueous fluids during the onset of slab devolatilisation (e.g., König *et al.*, 2008; H.-Y. Li *et al.*, 2021). Evidence of Mo mobilisation at the Asüt Tesoru seamount has also been documented in near-surface pore water and resulted from microbially mediated dissolution of Mn oxyhydroxides (Hulme *et al.*, 2010). In the transitional sample M12, lizardite are characterised by higher As/Pb ratios than antigorite that positively correlate with W contents and W/Ba ratios. Decreasing $\delta^{11}\text{B}$ signatures from liz- to atg-bearing samples is also associated with relatively enrichment in the W/Ba ratios (Fig. S-5).

In Table S-3 are also reported the trace element concentrations of primary mantle minerals, olivine and orthopyroxene. As expected, olivine is enriched in Ni and Co and depleted in Cr, V, Sc and Ti compared to orthopyroxene relicts. Some analyses show anomalous high enrichments in B (up to 6 $\mu\text{g/g}$) that are interpreted to be representative of minor amount of serpentine present within the primary phases, e.g., minute serpentinised exsolution lamellae in orthopyroxene. Therefore, these data are not representative of the primary B inventory of the mantle phases.

Geochemical Modelling

Stable isotope systematics are sensitive to changes in the chemical-physical condition of a system and, particularly, B isotopes are strongly sensitive to variations in T and pH conditions. In solids and fluids, B occurs either in tetrahedral ([4]) or trigonal ([3]) coordination with O: ^{10}B prefers [4] coordination and ^{11}B the [3] one (Kakahana *et al.*, 1977). A relationship exists with B coordination and pH conditions: at low pH B is dominantly in trigonal coordination, whereas the tetrahedral coordination become dominant towards more alkaline conditions (Palmer and Swihart, 1996). This B speciation dominate the B isotope fractionation between coexisting phases at equilibrium conditions (first-order criteria) even though second-order effects must be considered (e.g., Palmer *et al.*, 1992; Y.-C. Li *et al.*, 2021). For a detail and exhaustive review on B isotope fractionation, see Kowalski and Wunder (2018).

According to literature, B is [4]-coordinated in serpentine (Pabst *et al.*, 2011) and in clay minerals (Spivack and Edmond, 1987), whereas in olivine B is commonly incorporated in trigonal coordination (Ingrin *et al.*, 2014). More recently, Muir *et al.* (2022) suggested that B can be incorporated in olivine in tetrahedral coordination if B in olivine can be related to an H defect. If so, the B isotope fractionation in the hydrated ultramafic system is more complex than previously thought. For the purpose of this work, we assume that B is in [4]-coordinated in serpentine and mica and [3]-coordinated in olivine (no B isotope fractionation between olivine [4] and fluid [3]–[4] are reported yet). In the proposed models (see below), the coordination of B in the fluid phase ranges from pure acid condition (100–0 % [3]–[4]) to pure alkaline condition (0–100 % [3]–[4]). Mixed condition considering 50–50 % of $\text{B}_{[3]}\text{--}\text{B}_{[4]}$ is also reported.

Boron isotope composition of serpentines flushed by shallow and deep slab-derived fluids

Hereafter we calculated the possible effect of B isotope fractionation between serpentine and slab-derived fluids produced during the progressive dehydration of slab material using Rayleigh distillation equations following the approach proposed by Liu *et al.* (2022), which is based on the work of Rosner *et al.* (2003). This geochemical modelling provides a general understanding of the trend(s) in B isotope signatures of serpentines formed during interaction with slab-derived fluids. It should be noted that this approach is a simplification of a complex system and is not intended to provide a complete and exhaustive analysis of the entire system, for which further investigations are required.

We provided geochemical models using updated B isotope fractionation factors, testing different conditions in term of initial $\delta^{11}\text{B}$ of the slab material and pH condition of the system, with the latter strongly affecting the amplitude of the B isotope fractionation between solids and fluids. Being micas the main repository for B in altered oceanic crust (e.g., Marschall *et al.*, 2007) and sedimentary sequences (besides tourmalines), the contribution of other phases were not considered. We used the mica-fluid B isotope fractionation of Kowalski *et al.* (2013) considering B speciation in fluid in both trigonal and tetrahedral coordination, reflecting acid/neutral vs. alkali conditions, respectively. We assumed that 80 % of the initial B was lost at 800 °C, and its release is assumed to be linear function with T (Rosner *et al.*, 2003). We used the available lizardite-fluid B isotope fractionation derived from the computational study of Li *et al.* (2022, B-lizardite-III_j structure), assuming B speciation in fluid is in both trigonal and tetrahedral coordination, consistently with the mica-fluid B isotope fractionation modelled. Three scenarios were considered with initial slab B contents and $\delta^{11}\text{B}$ signatures of 5.2 $\mu\text{g/g}$ and +3.4 ‰ (Smith *et al.*, 1995), 3.6 $\mu\text{g/g}$ and +7.9 ‰ (Yamaoka *et al.*, 2012), and 17 $\mu\text{g/g}$ and +21.7 ‰ (McCaig *et al.*, 2018). The first two pairs of data are representative of the present-day/fossil altered oceanic crust (Smith *et al.*, 1995) and bulk oceanic crust now exposed in Oman (Yamaoka *et al.*, 2012), respectively. The last



pair of data is representative of lower gabbro section from the Hess Deep fast-spreading ocean (McCaig *et al.*, 2018). Data and results are reported in Table S-5 and Figure S-6.

As general trends, slab-derived fluids are always enriched in ^{11}B compared to initial slab compositions, and lizardite has always lower $\delta^{11}\text{B}$ signatures than the slab restite. This is mainly due to the higher fluid-solid B isotope fractionation of lizardite compared to mica (Li *et al.*, 2022), which is related to B/Si ordering in layered silicate minerals (Y.-C. Li *et al.*, 2021) and of second-order effects on B isotope fractionation (see Kowalski and Wunder, 2018, for details). Notably, at low T (<200 °C) the B isotope fractionation for lizardite is more pronounced than at middle T (200–500 °C), which become less T -dependent, particularly in acid/neutral system conditions. An interesting result from the modelling, and in contrast with common thoughts (*e.g.*, Benton *et al.*, 2001; Tonarini *et al.*, 2011), is that the $\delta^{11}\text{B}$ composition of lizardite increase with T – *i.e.* with prograde subduction – even if the B isotope fractionation between lizardite and fluid decreases.

Overall, the validity of the three proposed scenarios is supported by literature data on high- P mafic rocks – *i.e.* blueschists and eclogites as representative of the slab restite. In the first two cases (Fig. S-6a,b), negative $\delta^{11}\text{B}$ signatures of the slab restite evolve towards lower values during progressive dehydration, in agreement with the common negative $\delta^{11}\text{B}$ imprints of mafic high- P rocks experienced dehydration during progressive subduction (*e.g.*, Peacock and Hervig, 1999; Pabst *et al.*, 2012; Liu *et al.*, 2022). In the last case (Fig. S-6c) the $\delta^{11}\text{B}$ signatures of the slab restite is always enriched in the heavy B isotope (*i.e.* positive $\delta^{11}\text{B}$). The occurrence of high- P mafic rocks with positive $\delta^{11}\text{B}$ signatures have been recently documented in the Voltri Massif (up to +10 ‰ at *ca.* 550 °C and 2.4 GPa; see Cannà *et al.*, 2023, for details).

Building upon the model parameters of Liu *et al.* (2022), if an initial $\delta^{11}\text{B}$ signature of the slab of +7.9 ‰ is assumed (Yamaoka *et al.*, 2012; Fig. S-6b), we obtained a good match for the slab restite and $\delta^{11}\text{B}$ signatures of metabasalts collected in the Asùt Tesoru, Fatangisña and South Chamorro seamounts (Liu *et al.*, 2022; Pabst *et al.*, 2012). The formation of lizardite and antigorite with variable $\delta^{11}\text{B}$ signatures from +20 to –5 ‰ can be achieved considering variable water/rock ratios at different T . Following the approach of Simon *et al.* (2016), reporting a dimensionless mass balance equations for a dynamic single-pass open system evolution, we calculated water/rock ratios (by weight) ranging from 5 to 90 (model parameters in Table S-6). The obtained water/rock ratios are consistent with the high fluid flux environment characterising the supra-subduction mantle in forearc regions. The calculation assumes B coordination in fluid is 50 % trigonal and 50 % tetrahedral, reflecting different degree of pH conditions as serpentinisation progress (*e.g.*, Seyfried and Dibble, 1980). Boron partition coefficient between rock and fluid (D_{B}) was fixed to 6, calculated following the approach of Foustoukos *et al.* (2008), which provides a broad correlation between pH and D_{B} . Figure S-7 reports the relationship between W/R ratios and $\delta^{11}\text{B}$ -B ($\mu\text{g/g}$) of the reacted rock (*i.e.* serpentinites) at different D_{B} and considering 50–50 % of B in trigonal and tetrahedral coordination. The change in D_{B} from high (20) to low (3) values should be representative of the increasing T during serpentinisation progress (*e.g.*, Seyfried and Dibble, 1980) in subduction settings. The lowest the D_{B} , the lowest the B contents in the serpentines (Fig. S-7b). Calculations considering lower initial $\delta^{11}\text{B}$ signature of the slab (*e.g.*, +3.4 ‰; Smith *et al.*, 1995), variable B speciation in the fluid phase and B partition coefficient however do not significantly change the results of the model and the interpretation of the data (Fig. S-8).

Boron isotope composition of serpentines during phase transition

It has been proposed that if B is released during the prograde lizardite to antigorite phase transition in subduction settings, B isotope fractionation should occur (Cannà, 2020, and references therein). If so, the newly formed high- P antigorite should be depleted in ^{11}B , due to its preferential affinity in the fluid released during the phase transition. The effect of B isotope fractionation associated with serpentine phase transition was modelled using the lizardite-fluid B isotope fractionation derived from the computational study of Li *et al.* (2022; B-lizardite-III_j structure), assuming B speciation in fluid is 100 % in tetrahedral coordination according to the alkaline condition of the serpentinite system during prograde subduction (*e.g.*, Debret and Sverjensky, 2017). Both batch and Rayleigh B isotope fractionations were modelled representing close *vs.* open evolution of the system, respectively. Calculations were done at 320 and 410 °C, overlapping the main T range of lizardite to antigorite transition during prograde subduction (Schwartz *et al.*, 2013) and the estimated T with antigorite-magnetite O isotope geothermometer (Debret *et al.*, 2019). Two cases were modelled based on different initial B contents and $\delta^{11}\text{B}$ signatures of the lizardite precursor. Values of 63 $\mu\text{g/g}$ and +7 ‰ were adopted as representative of the M10 lizardite sample (highest and mean values, respectively; Fig. 3c in the main text),



whereas values of 81 $\mu\text{g/g}$ and +20 ‰ were adopted as representative of the Conical serpentinites (values from Benton *et al.*, 2001; Fig. S-9). The latter is also used to test (i) how the variability in the initial [B] inventory and $\delta^{11}\text{B}$ signature of the lizardite and (ii) how the changes in B speciation in fluid in tetrahedral coordination from 100 % to 50 % may affect the results of the model.

Supplementary Tables

Table S-1 Sample information (modified from Debret *et al.*, 2019) and estimated pH-B composition of pore fluids where samples were collected (from Fryer *et al.*, 2018). TS: shipboard sample with thin section description available in Fryer *et al.* (2018).

Sample	Label identifier	Rock type	Nature of the embedding mud	Depth (m)	pH estimate	B in pore fluids (μM)
M10	366-U1493B-9X-CC-W 14/16	Liz-serpentinite (\pm Atg-Bru veins)	Large clast (>10 cm long) with no embedding mud	30.67	8.5	120
M12	366-U1495B-3G-CC-W 5/7	Transitional serpentinite (Liz + Atg)	Large clast (>10 cm long) with no embedding mud	4.84	9.2	450
M15	366-U1495B-6F-CC-W 10/12	Atg-serpentinite (+Bru)	Small clast (~2–5 cm long) with no embedding mud	10.71	11	500
M16 (TS63)	366-U1495A-3G-CC-W 13/15-TSB-TS_63	Atg-serpentinite (+Bru)	Small clast (~2–5 cm long) with no embedding mud	5.93	9.5	450
M20	366-U1496A-2F-4-W 12/14	Brucitite (\pm Serp)	Green serpentinite pebbly mud	6.2	12.5	1100
M24	366-U1496B-5F-1-W 77/82	Blue-serpentinite	Green serpentinite pebbly mud	16.77	12.5	1100



Table S-2 Boron isotope data of the Koh-OL olivine used as primary calibrating standard in two different analytical sessions. Reference $\delta^{11}\text{B}$ value of -4.6 ± 0.8 ‰ from Clarke *et al.* (2020). Boron content is estimated comparing the ^{11}B signal intensity between olivine and NIST 612 glass (see Analytical Methods).

# Analysis	B ($\mu\text{g/g}$)	$^{11}\text{B}/^{10}\text{B}$ measured	$^{11}\text{B}/^{10}\text{B}$ corrected	2 s.e.	$\delta^{11}\text{B}$ (‰)	2 s.e. (‰)
#1	72.2	4.5814	4.0241	0.0011	-4.82	0.26
#2	69.0	4.5824	4.0250	0.0011	-4.60	0.26
#3	64.7	4.5801	4.0230	0.0013	-5.10	0.31
#4	80.5	4.5837	4.0261	0.0011	-4.32	0.27
#5	79.4	4.5838	4.0263	0.0011	-4.29	0.27
#6	73.8	4.5828	4.0254	0.0011	-4.50	0.28
#7	90.5	4.5837	4.0252	0.0010	-4.56	0.24
#8	93.6	4.5844	4.0258	0.0010	-4.40	0.26
#9	82.5	4.5827	4.0243	0.0011	-4.77	0.28
#10	95.7	4.5832	4.0248	0.0012	-4.67	0.30
#11	95.7	4.5836	4.0253	0.0012	-4.53	0.31
#12	87.9	4.5832	4.0252	0.0012	-4.56	0.29
#13	73.4	4.5803	4.0254	0.0012	-4.50	0.30
#14	69.0	4.5791	4.0246	0.0011	-4.71	0.28
#15	65.5	4.5786	4.0244	0.0014	-4.75	0.34
#16	113.3	4.5849	4.0250	0.0008	-4.61	0.21
#17	112.0	4.5857	4.0258	0.0010	-4.41	0.25
#18	100.7	4.5846	4.0249	0.0010	-4.64	0.25
#19	110.9	4.5822	4.0247	0.0012	-4.68	0.30
#20	110.8	4.5824	4.0250	0.0011	-4.61	0.26
#21	104.7	4.5831	4.0258	0.0010	-4.41	0.26
#22	88.1	4.5802	4.0261	0.0012	-4.33	0.30
#23	79.0	4.5795	4.0256	0.0010	-4.45	0.25
#24	75.1	4.5787	4.0250	0.0012	-4.59	0.29
Mean	87.0	4.5823	4.0251		-4.58	
2 s.d.	31.4	0.0041	0.0015		0.36	

Table S-3 Boron isotope data of the MS VAR 10-01 antigorite used as quality control. Reference $\delta^{11}\text{B}$ value of $+22.3 \pm 0.4$ ‰ from Cannò *et al.* (2016).

# Analysis	B ($\mu\text{g/g}$)	$\delta^{11}\text{B}$ (‰)	2 s.e. (‰)
#1	15.4	+22.68	0.64
#2	17.4	+20.59	0.66
#3	13.3	+21.43	0.85
#4	14.8	+21.74	0.74
#5	15.0	+22.12	0.89
#6	16.7	+22.32	0.68
#7	18.6	+21.59	0.60
#8	14.6	+20.90	0.73
#9	14.5	+19.80	0.78
#10	16.3	+20.94	0.89
Mean	15.7	+21.41	
2 s.d.	3.2	1.74	

Table S-4 *In situ* trace element ($\mu\text{g/g}$) and $\delta^{11}\text{B}$ (‰) composition of serpentines from the Asùt Tesoru seamount. Trace elements were determined with LA-ICP-MS. Boron isotopes were measured with LA-MC-ICP-MS.

Table S-5 Boron isotope compositions of slab restite and slab-derived fluids together with lizardite in equilibrium with slab fluids at both alkaline and acid/neutral pH conditions of the system.

Table S-6 Geochemical parameters used to calculate the water/rock ratios. Concentrations are reported in ppm.

Table S-7 Rayleigh B isotope fractionation ($\Delta^{11}\text{B}$) between lizardite-fluids and olivine-lizardite (from Li *et al.*, 2022).

Tables S-4 to S-7 are available for download (.xlsx) from the online version of this article at <http://doi.org/10.7185/geochemlet.2416>.



Supplementary Figures

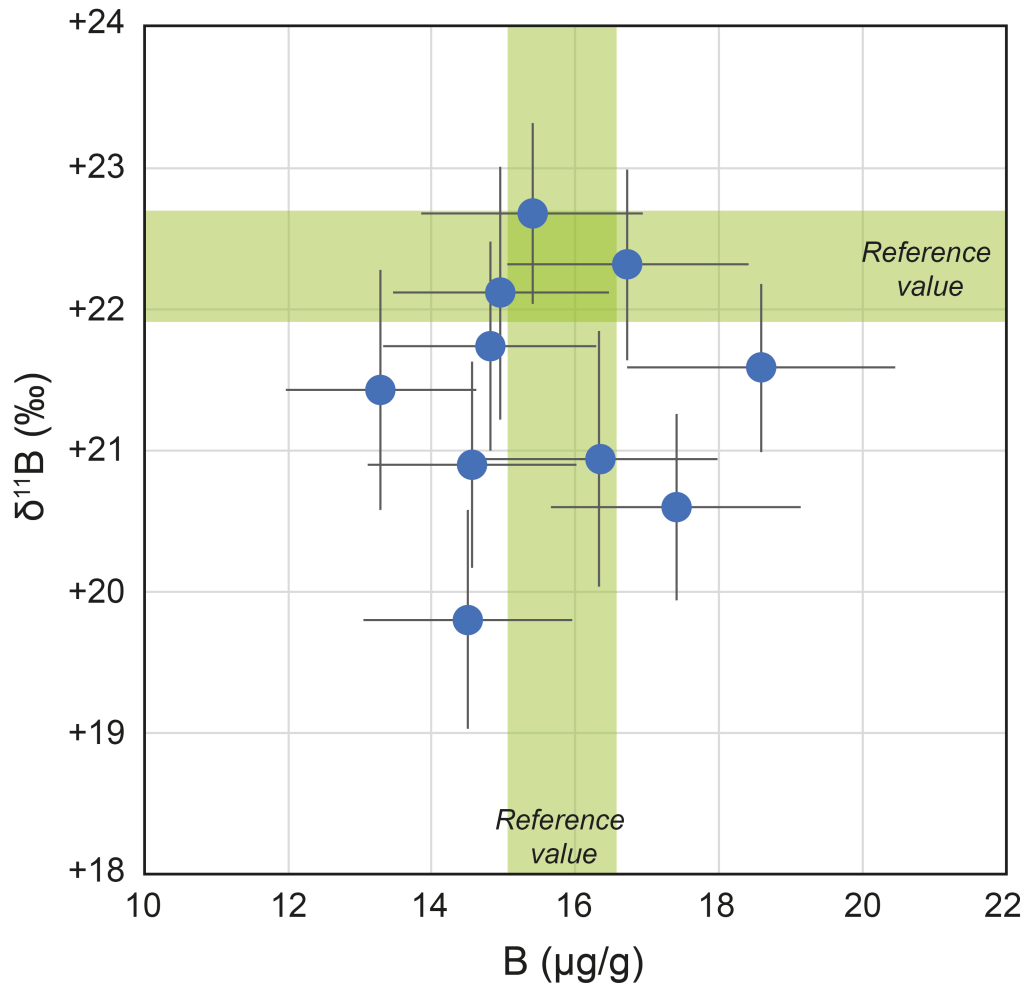


Figure S-1 B ($\mu\text{g/g}$) vs. $\delta^{11}\text{B}$ (‰) diagram of the MS VAR 10-01 antigorite measured as quality control. Error bars are 2 s.e. for $\delta^{11}\text{B}$ and estimated to be 15 % for B content (2 s.d.; see Cannaò *et al.*, 2024). Reference values are from Cannaò *et al.* (2016). Note that the $\delta^{11}\text{B}$ variability measured here for the MS VAR 10-01 antigorite is comparable with that of other reference antigorite used to correct for matrix effect at the Secondary Ion Mass Spectrometry (*e.g.*, Clarke *et al.*, 2020).

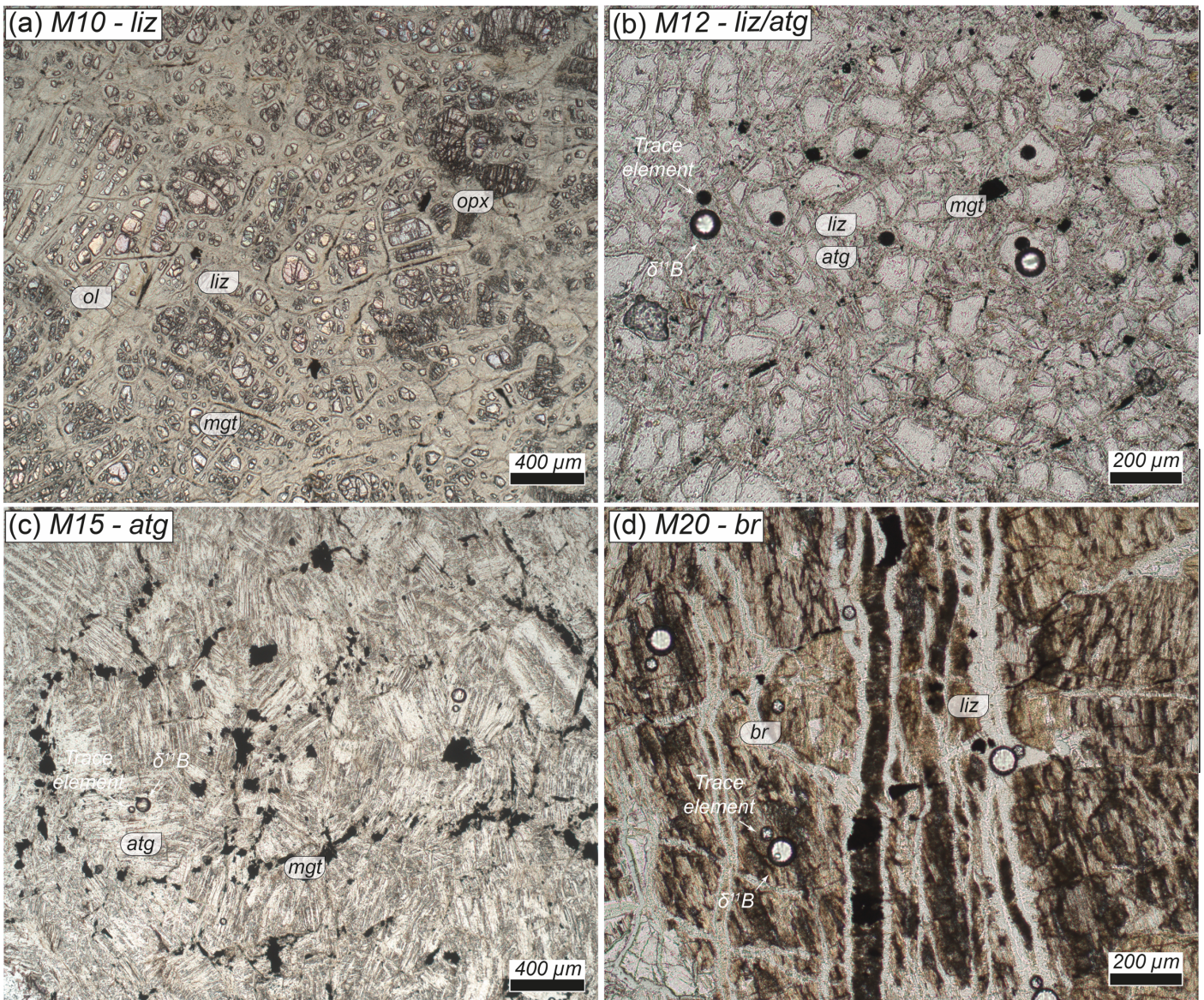


Figure S-2 Microphotographs of key samples from the Asùt-Tesoru seamount analysed in this study. **(a)** Lizardite-bearing sample (M10) showing lizardite (liz) replacing both olivine (ol) and orthopyroxene (opx) in mesh textures. Small isolated spinels and thin trails of magnetite (mgt) are visible. **(b)** Sample M12 showing lizardite replaced by antigorite (atg) along mesh texture. **(c)** Antigorite from sample M15 showing complex texture with abundant magnetite (see **(a)** for comparison). **(d)** Brucite sample M20 made of brucite (br) partially overprinted by lizardite along major veinlets. Opaque phases in this sample are Fe-bearing hydroxides or sulfides (Debret *et al.*, 2019, 2022). Laser ablation spots from the trace element and B isotope sessions are also visible.

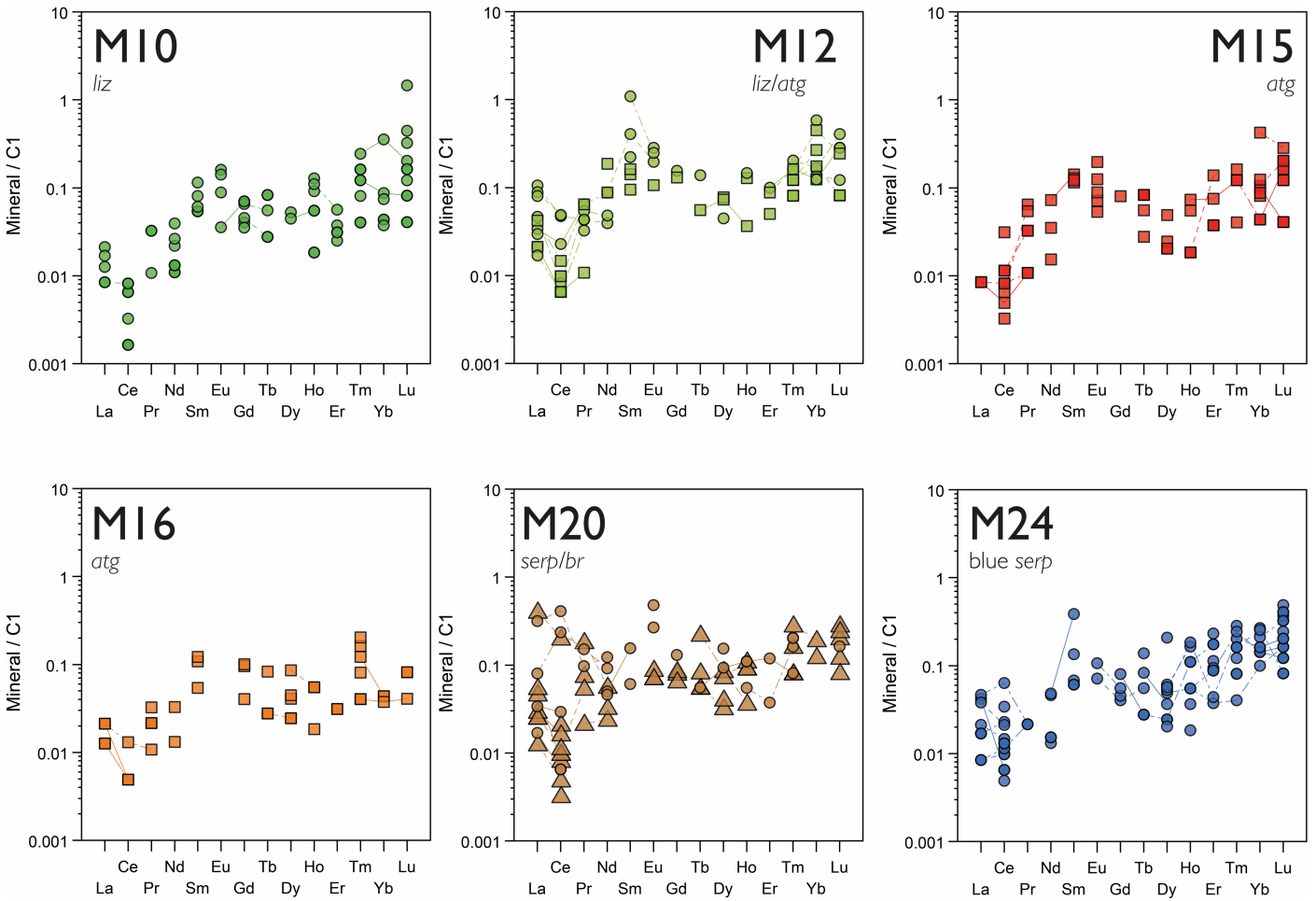


Figure S-3 Rare earth element patterns normalised to Chondrite (C1; McDonough and Sun, 1995) for the different Asùt Tesoru serpentinite samples. Circles, lizardite; squares, antigorite; triangles, brucite.

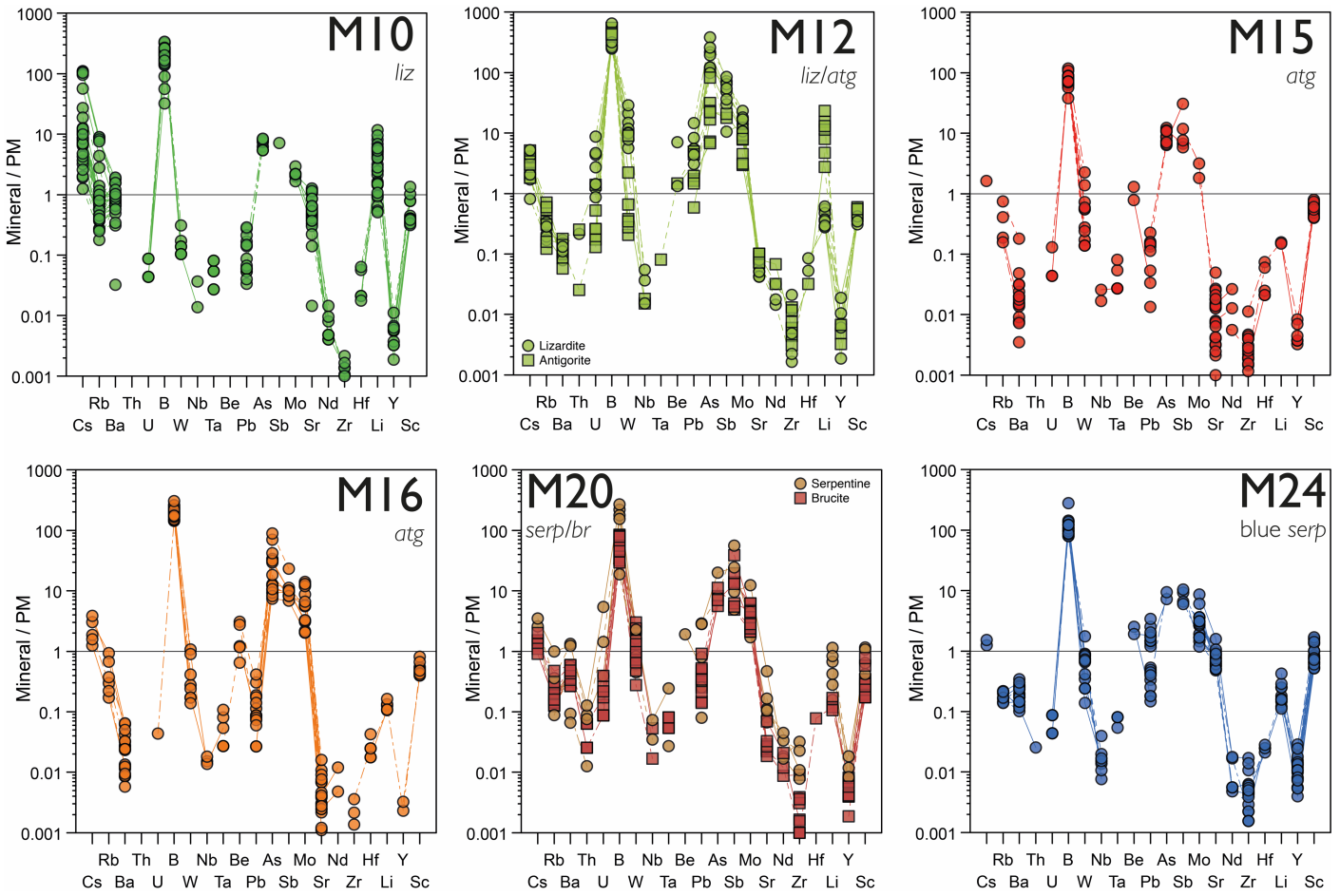


Figure S-4 Incompatible trace element spider diagrams normalised to the primitive mantle (PM; McDonough and Sun, 1995) for the different Asùt Tesoru serpentinite samples.

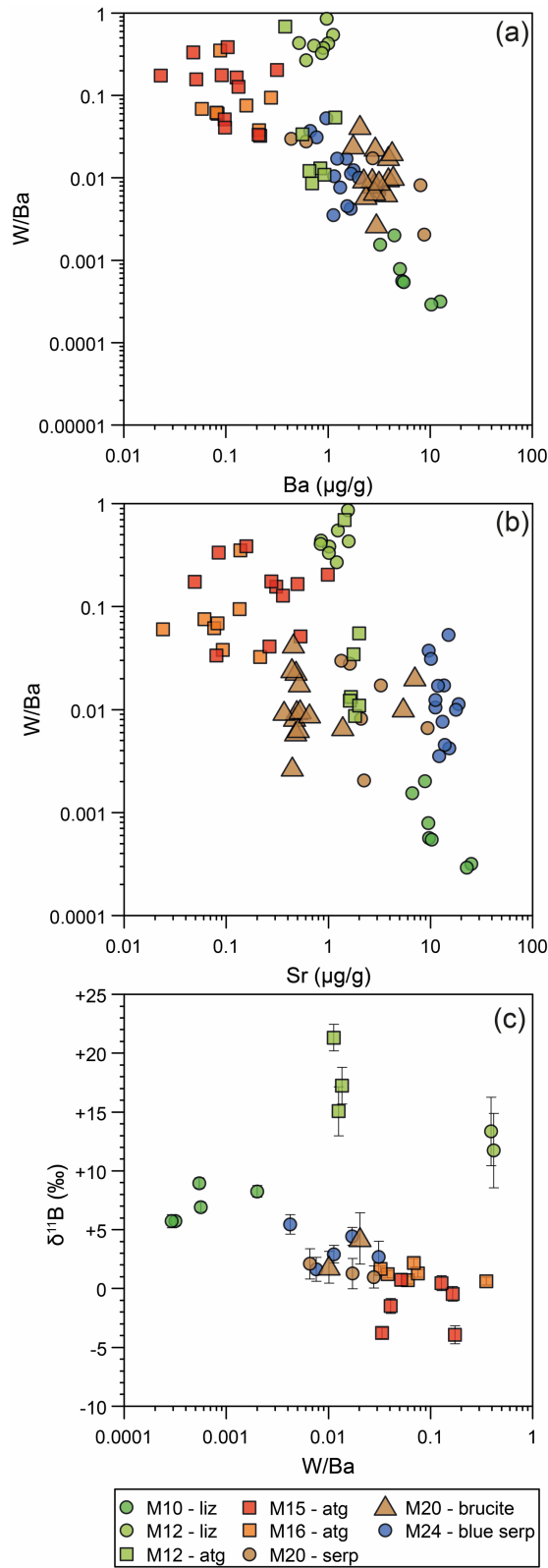


Figure S-5 Plots of trace element contents in serpentines for (a) Ba ($\mu\text{g/g}$) vs. W/Ba ratio and (b) Sr ($\mu\text{g/g}$) vs. W/Ba ratio. (c) Relationship between $\delta^{11}\text{B}$ (‰) and W/Ba ratio.

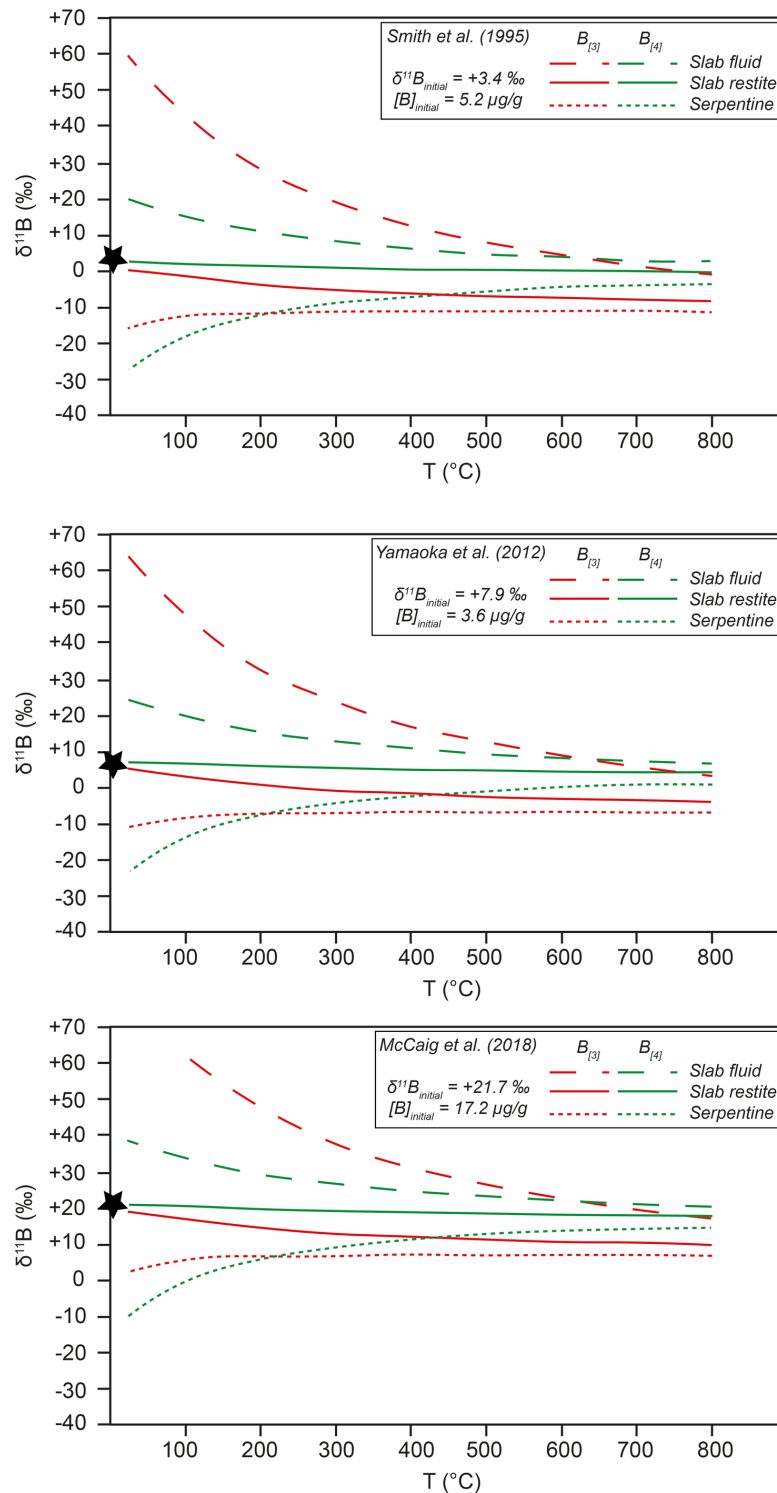


Figure S-6 Modelled B-isotope fractionation between slab-restite (solid lines), slab-fluid (coarse dashed lines) and serpentine (fine dashed lines) at acid/neutral (in red, [3]) and alkaline (in green, [4]) pH conditions of the system. The calculation assumes different starting composition of the slab input (black stars) as indicated in the boxes. Evolution of the serpentine B isotope signatures related to W/R ratios are reported in Figure S-7.

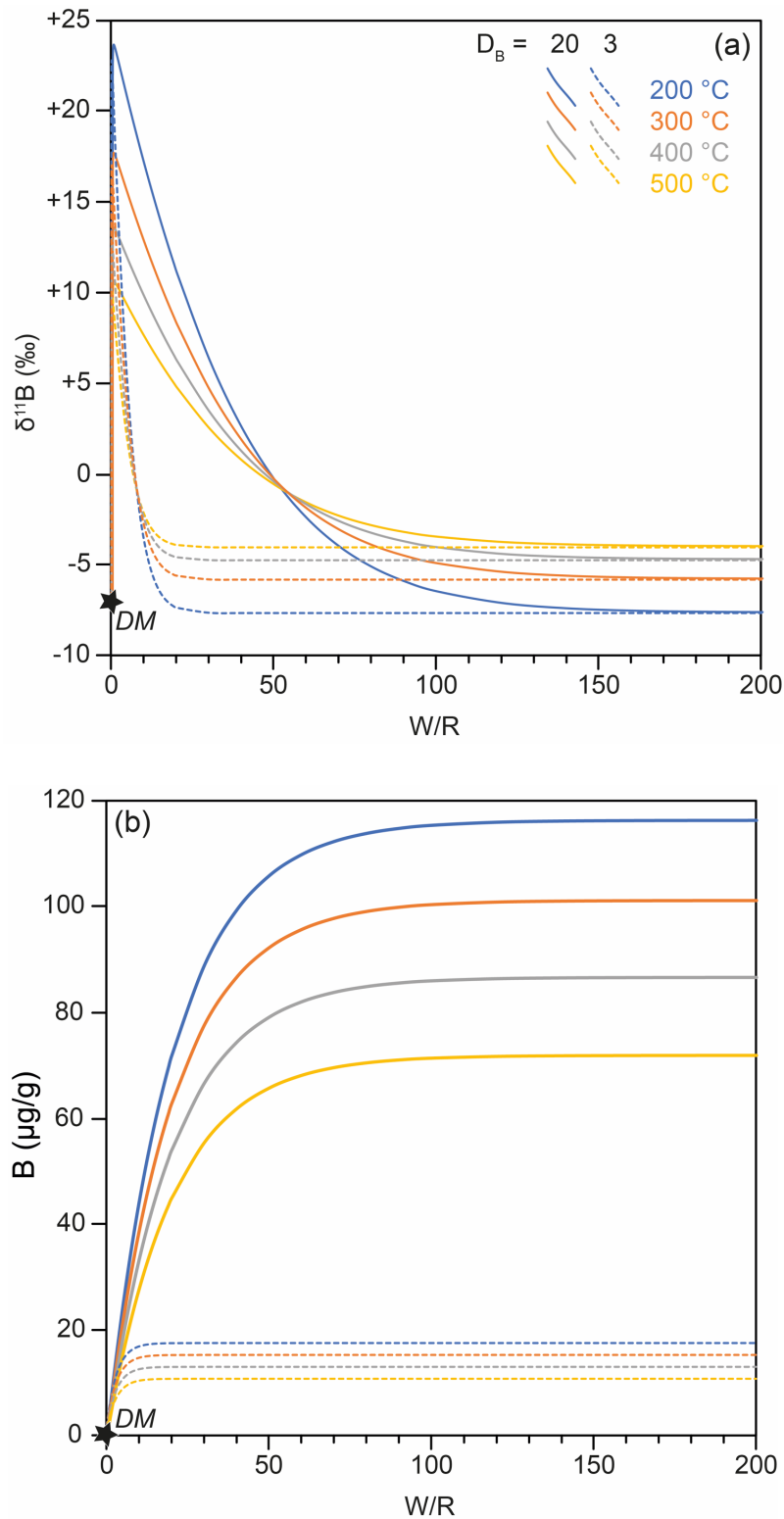


Figure S-7 Relations between W/R ratios and (a) $\delta^{11}\text{B}$ signatures and (b) B contents of the reacted rock (*i.e.* serpentinite) at different T (°C) and B partition coefficient (D_B). The calculation assumes mixed ([3–4]) B coordination in the system. Depleted mantle value (DM) from Marschall *et al.* (2017).

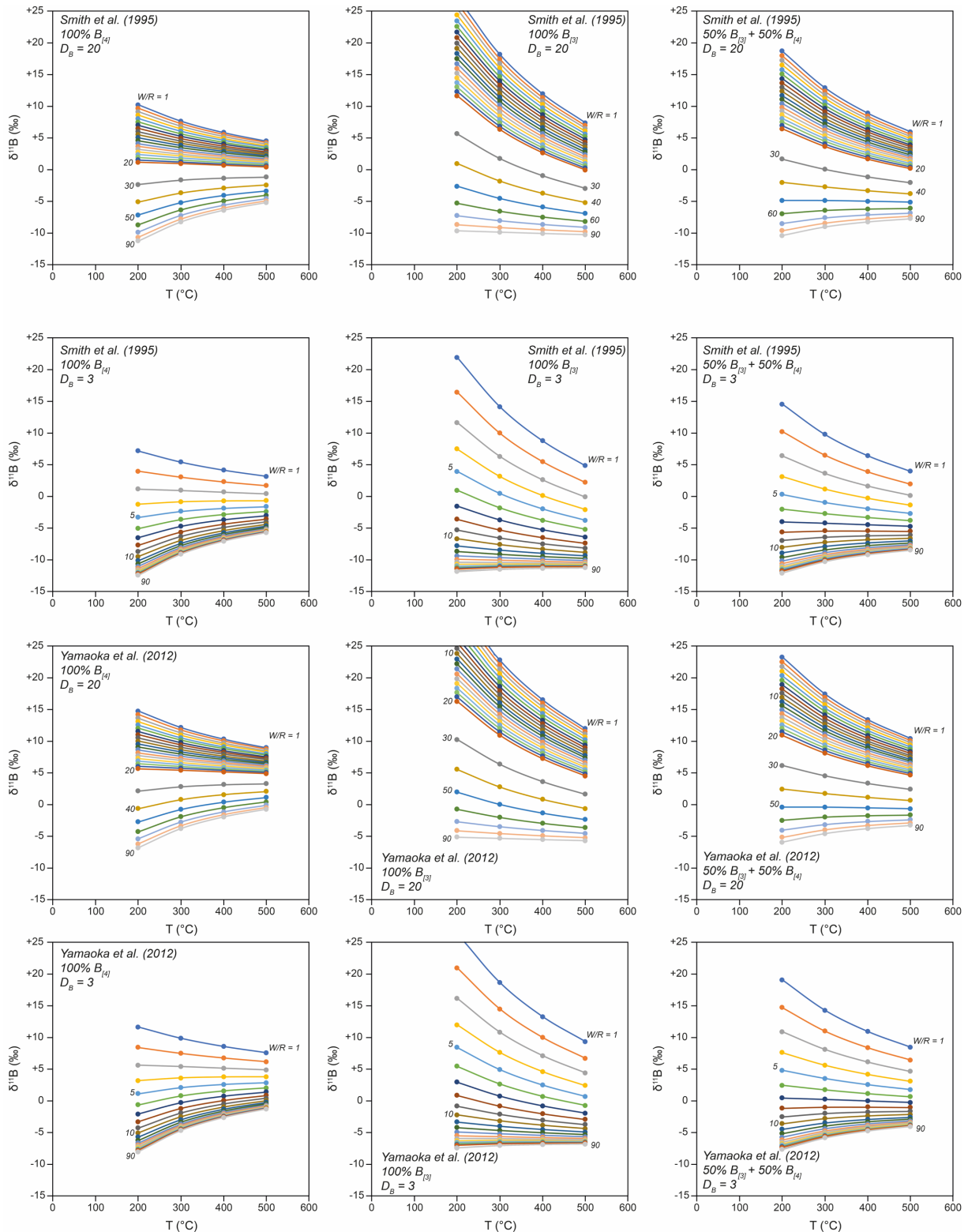


Figure S-8 Relations between $\delta^{11}\text{B}$ of serpentine and T (°C) for different water/rock ratios (W/R). The calculation assumes B in fluids in tetrahedral ([4]), trigonal ([3]) or mixed ([3–4]) coordination for B partition coefficient between serpentine and fluid (D_B) of 20 and 3 (see inset in each panel). The calculations are based on initial values of Smith *et al.* (1995) or Yamaoka *et al.* (2012). Positive $\delta^{11}\text{B}$ in serpentine can be achieved at low W/R ratios (ca. 1–5) at acidic or mixed conditions. If the pure alkaline endmember is considered, W/R ratios below 1 are required to form serpentine with $\delta^{11}\text{B}$ higher than ca. +10 ‰.



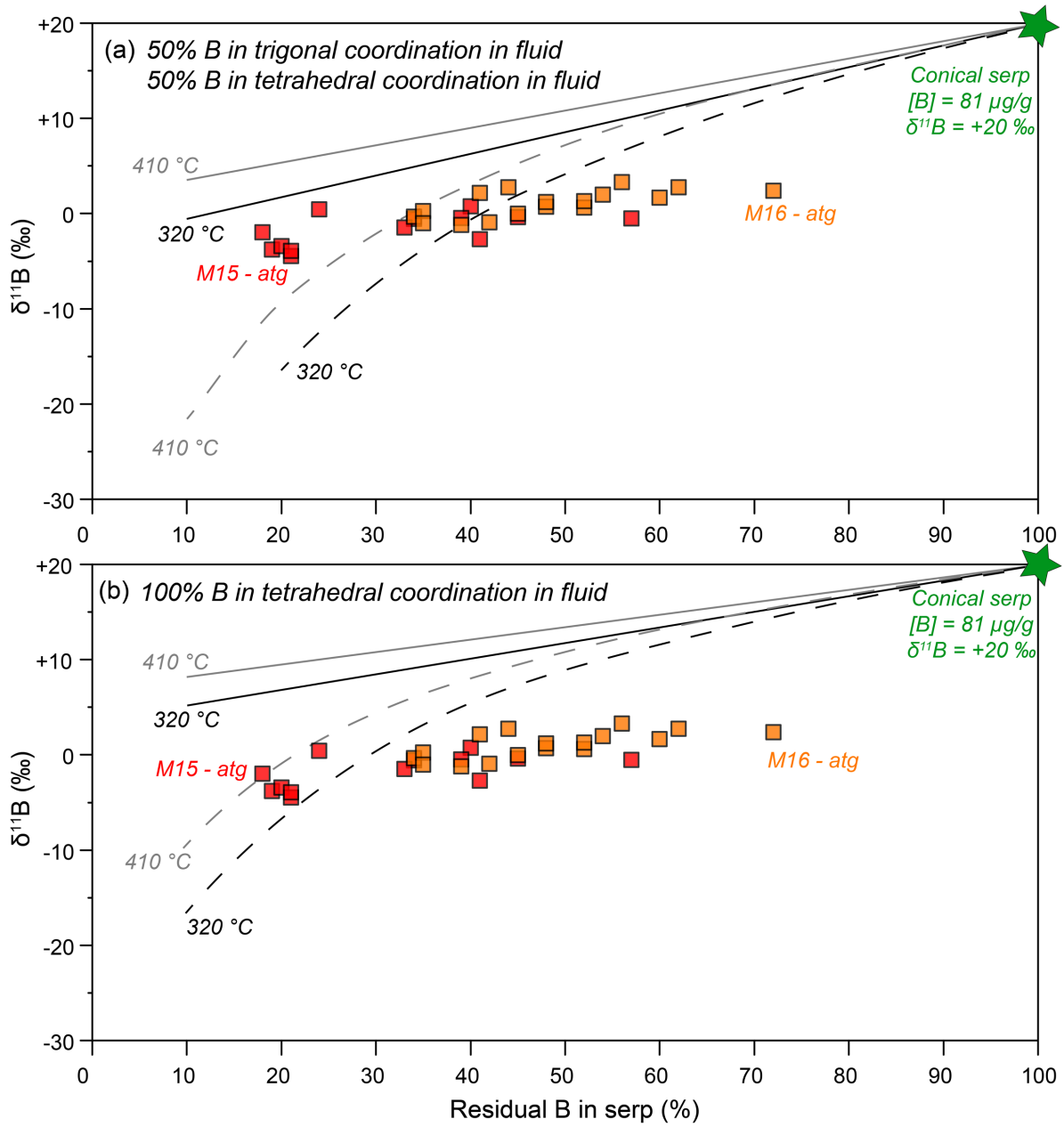


Figure S-9 Variations of [B] and δ¹¹B according to batch (solid lines) and Rayleigh (dashed lines) devolatilisation at 320 and 410 °C (black and grey, respectively) considering (a) 50 % to (b) 100 % alkaline condition of the system.

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