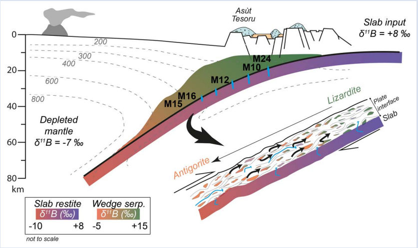
Geochemical Perspectives Letters

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

E. Cannaò[1*], B. Debret[2]

https://doi.org/10.7185/geochemlet.2416

Abstract



This study aims to uncover the evolving dynamics of element mobility in serpentinised ultramafic clasts within the Asùt Tesoru mud volcano in the Mariana forearc. By employing *in situ* analysis of trace elements and boron isotopes ($\delta^{11}B$), 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.

Received 14 December 2023 | Accepted 26 March 2024 | Published 3 May 2024

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 ($\delta^{11}B$) 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 Asùt Tesoru mud volcano in the Mariana forearc (IODP Exp 366) performing new *in situ* trace element and the first *in situ* boron isotope ($\delta^{11}B$) 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 Asùt

---

1. Dipartimento di Scienze della Terra “A. Desio”, Università degli Studi di Milano, Via Botticelli 23, 20133, Milano, Italy
2. Institute de physique du globe de Paris, Université de Paris, CNRS UMR 7154, 1 rue Jussieu, 75005 Paris, France
* Corresponding author (email: enrico.cannao@unimi.it)

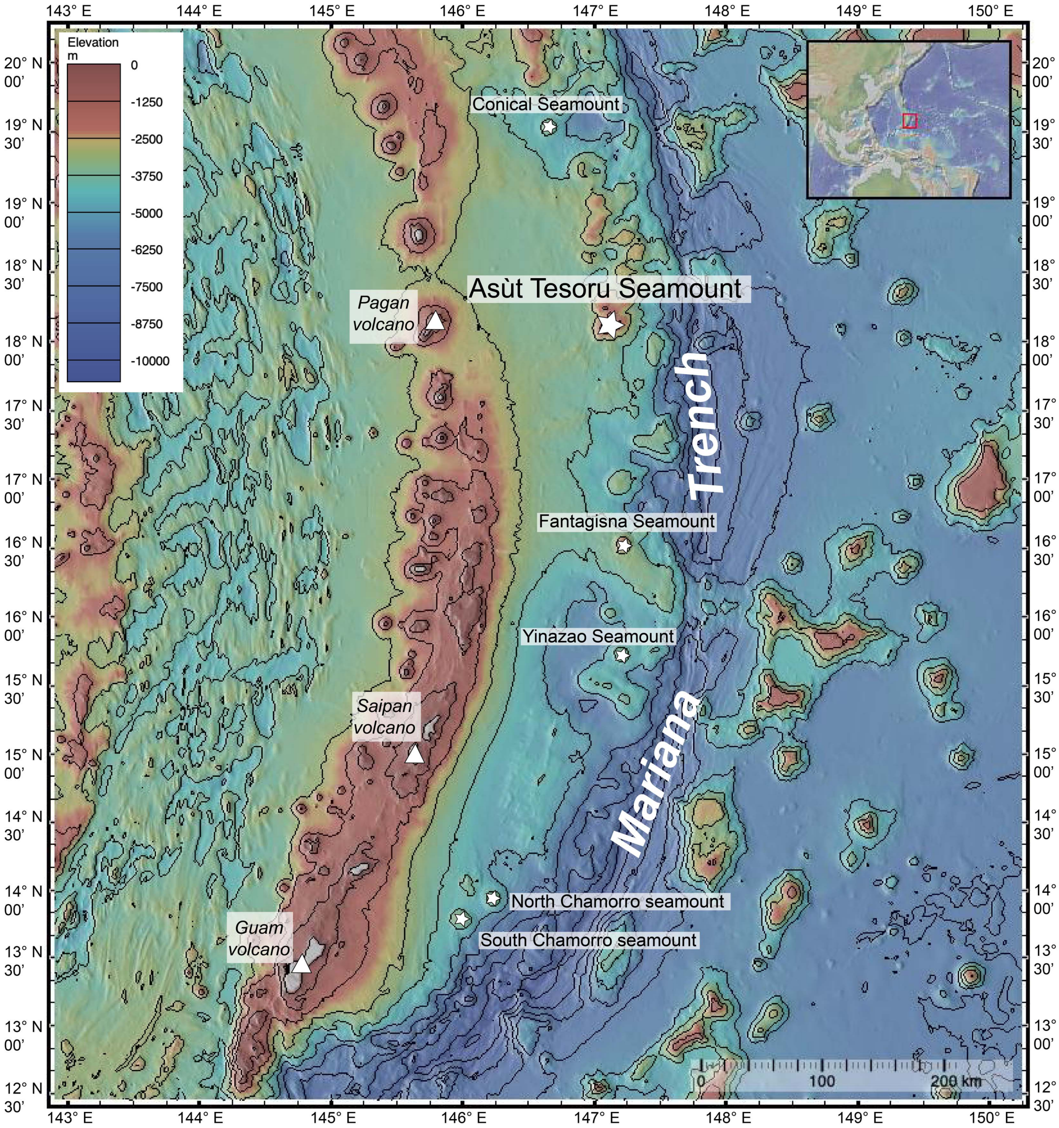


Figure 1 Location of the Asùt Tesoru seamount imposed over the bathymetry map of the Mariana subduction system (generated with the GeoMapApp).

Tesoru serpentinite mud volcano (18° 06′ N and 147° 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 °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 brucitite 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 °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 brucitite (sample M20, mainly brucite ± lizardite) and the blue lizardite-bearing serpentinite (sample M24; mainly brucite-lizardite) represent the late low T (<180 °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 serpentine 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 µg/g), respectively, whereas slightly lower contents are reported for the atg-bearing sample M15 (from 11 to 22 µg/g). Blue serpentine and serpentines in brucitite samples show moderate B enrichment (22 ± 8 and 29 ± 16 µg/g, respectively). Brucite from sample M20 shows B content averaging at 11.5 ± 5.3 µg/g. Boron isotope compositions of serpentines are strongly variable, ranging from −5 to +21 ‰. Higher δ^{11}B values pertain to lizardite and antigorite from sample M12 with mean values of +12.0 ± 2.3 ‰ (2 s.d., $n = 2$) and +17.4 ± 6.4 ‰ (2 s.d., $n = 3$), respectively. Lizardite from sample M10 has homogeneous δ^{11}B mean value of +7.1 ± 0.6 ‰ (2 s.d., $n = 18$). Lizardite from brucitite and blue

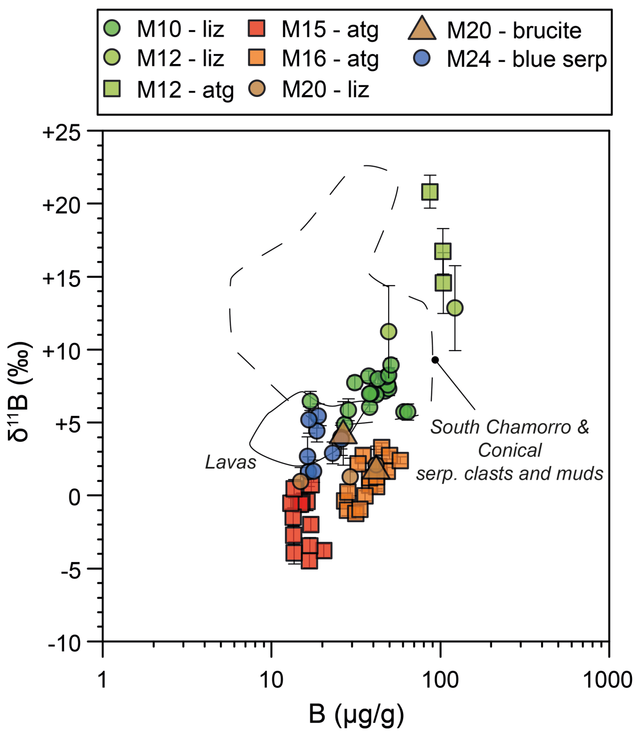


Figure 2 Relationship between δ^{11}B (‰) *vs.* B (µg/g). Data from South Chamorro (Wei *et al.*, 2005) and Conical (Benton *et al.*, 2001) seamounts, and the Mariana lavas (Ishikawa and Tera, 1999) are shown for comparison.

serpentine display overlapping δ^{11}B values, ranging between +1 and +6 ‰. Two δ^{11}B data from a serpentine-brucite mixture (sample M20) average +2.5 ± 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 δ^{11}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 δ^{11}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 δ^{11}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 δ^{11}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 δ^{11}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 δ^{11}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 δ^{11}B of +8 ‰ can reproduce the δ^{11}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 δ^{11}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 fourfold coordinated in both phases (not implemented in the proposed model). This set the basis for a newly invoked scenario to explain the measured δ^{11}B signatures. Considering an initial δ^{11}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 δ^{11}B signatures (from +12 to −5 ‰) can be achieved by flushing the suprasubduction 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 δ^{11}B signatures (Fig. 4a). Higher δ^{11}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 δ^{11}B signatures of the Conical and South Chamorro seamounts (up to +25 ‰). This model assumes a single δ^{11}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 δ^{11}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 δ^{11}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 Cannaò (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

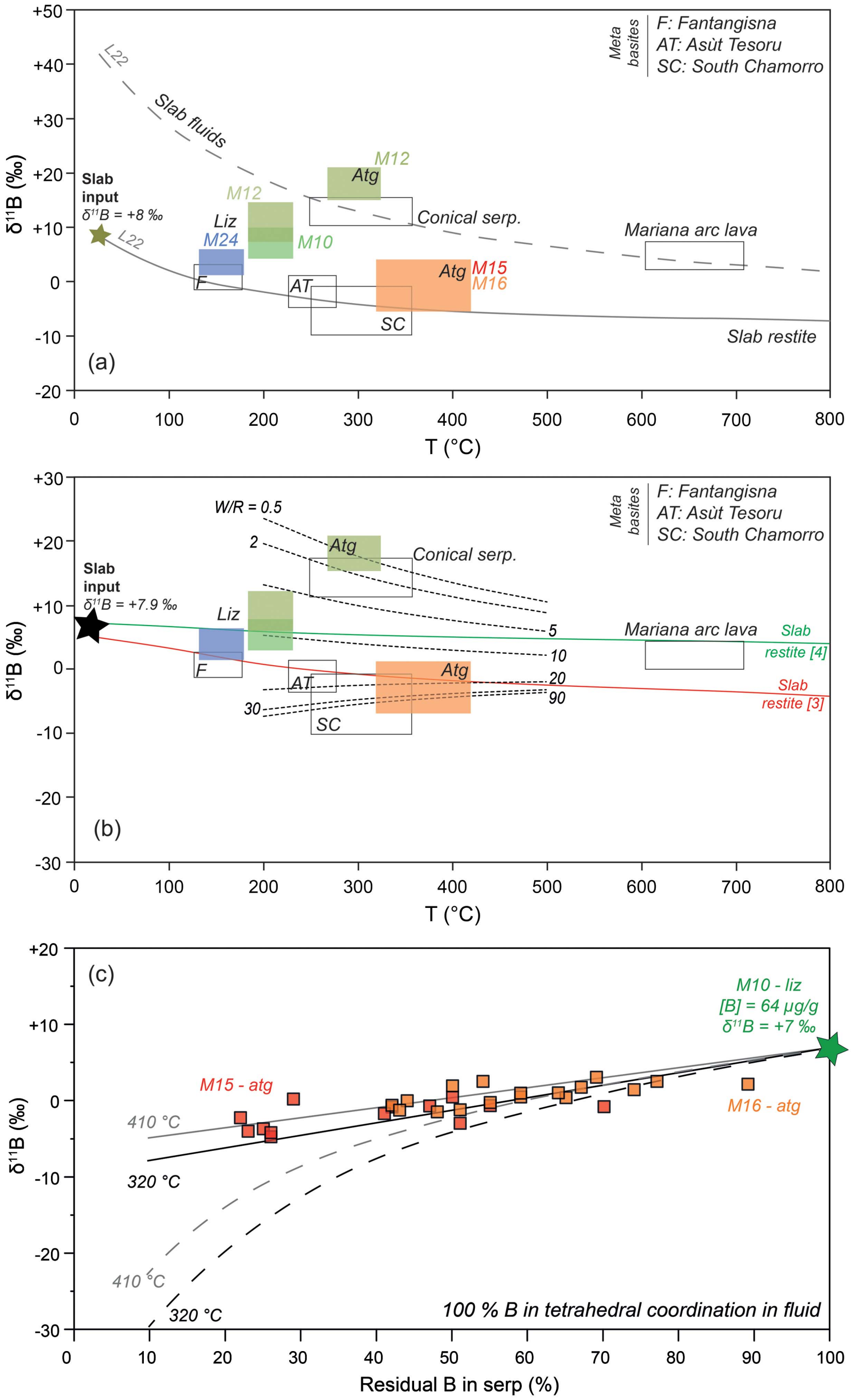


Figure 3 **(a)** Working Rayleigh dehydration modelling proposed by Liu *et al.* (2022; L22) to explain the B isotope variability in metabasites from the Fantangisña (F), Asùt Tesoru (AT) and South Chamorro (SC) seamounts (Pabst *et al.*, 2012; Liu *et al.*, 2022). Serpentinite clasts and muds from Conical (Conical serp.) are from Benton *et al.* (2001), Mariana lavas are from Ishikawa and Tera (1999); $\delta^{11}B$ data for the Asùt 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 $\delta^{11}B$ 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 $\delta^{11}B$ and B content ([B]) according to batch (solid lines) and Rayleigh (dashed lines) devolatilisations at 320 and 410 °C (black and grey, respectively) and alkaline conditions during 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 $\delta^{11}B$ signature for lizardite of +7 ‰ and 64 μg/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 $\delta^{11}B$ signatures shown by antigorite (Figs. 3c, 4b). Given the high variability of the $\delta^{11}B$ signatures in serpentine from the Conical Seamount (Benton *et al.*, 2001), if higher

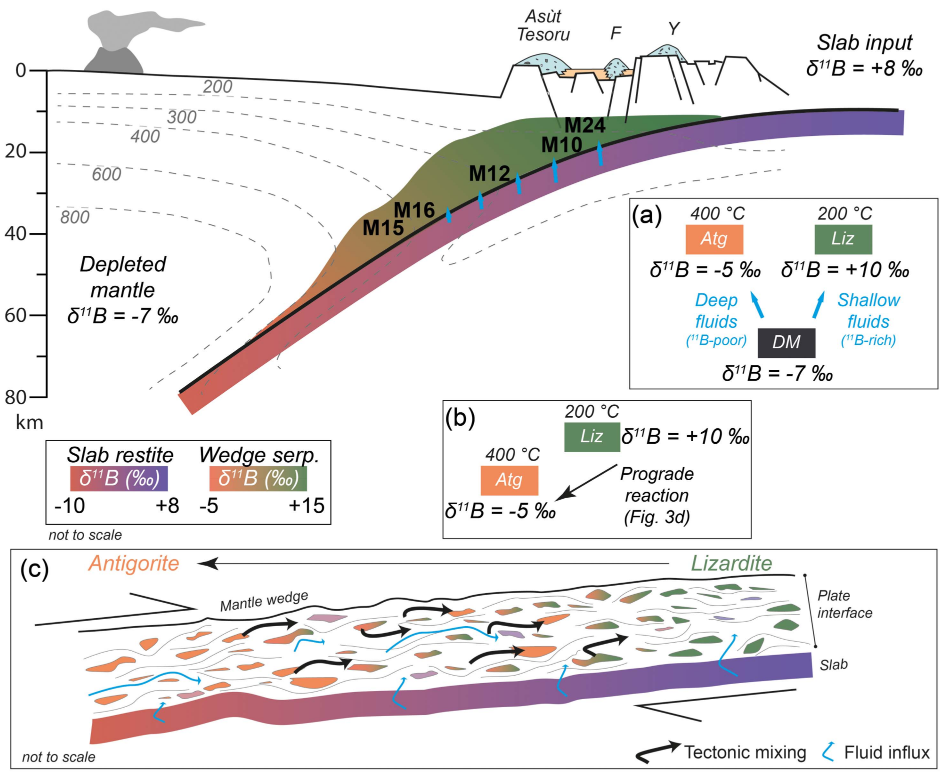


Figure 4 Cartoon illustrating the Mariana subduction setting showing the potential location of studied samples along the slab-mantle interface and the B isotope variation within the slab restite and in the wedge serpentinites. **(a)** Boron isotope composition of antigorite and lizardite flushed by deep and shallow slab fluids, respectively, according to model presented in Figure 3b. **(b)** Modification of the δ^{11}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.

δ^{11}B for the precursor lizardite is assumed (*e.g.*, δ^{11}B = +20 ‰, B = 81 μg/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 δ^{11}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 mélange domains atop the subducting slab may trigger mechanical instabilities and the formation of buoyant diapirs (Marschall and Schumacher, 2012). Such mélange materials can penetrate within the hot corner of the mantle wedge feeding island arcs contributing to the heavy δ^{11}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.*, Cannaò *et al.*, 2020). Depending on the δ^{11}B of antigorite (*e.g.*, −5 ‰ in M15 *vs.* +21 ‰ in M12), the progressive dehydration at deeper conditions of forearc serpentinites with δ^{11}B signatures comparable to the antigorite of the Asùt Tesoru will provide fluids with δ^{11}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 δ^{11}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 δ^{11}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.

Acknowledgements

This research used samples and data provided by the IODP and ODP. This work benefit funding from the Italian Ministry of University and Research (MUR) – Excellent Departments Projects. EC acknowledges the Società Italiana di Mineralogia e Petrologia (SIMP) for support through the Research Grant “Fiorenzo Mazzi” for the year 2022. Cees-Jan De Hoog is warmly thanked for providing the reference Koh-OL olivine, and Gianluca Sessa is thanked for support during the micro-analytical sessions. Constructive comments and criticisms provided by I. Savov and C.J. De Hoog significantly improved the manuscript and are greatly appreciated. Raul O.C. Fonseca is thanked for editorial handling of the manuscript.

Editor: Raúl O.C. Fonseca

Additional Information

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

Cite this letter as: Cannaò, E., Debret, B. (2024) Variable δ^{11}B signatures reflect dynamic evolution of the Mariana serpentinite forearc. *Geochem. Persp. Let.* 30, 13–19. https://doi.org/10.7185/geochemlet.2416

References

Albers, E., Kahl, W.-A., Beyer, L., Bach, W. (2020) Variant across-forearc compositions of slab-fluids recorded by serpentinites: Implications on the mobilization of FMEs from an active subduction zone (Mariana forearc). *Lithos* 364–365, 105525. https://doi.org/10.1016/j.lithos.2020.105525

Bebout, G.E., Ryan, J.G., Leeman, W.P., Bebout, A.E. (1999) Fractionation of trace elements by subduction-zone metamorphism — effect of convergent-margin thermal evolution. *Earth and Planetary Science Letters* 171, 63–81. https://doi.org/10.1016/S0012-821X(99)00135-1

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

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., Tiepolo, M., Bebout, G.E., Scambelluri, M. (2020) Into the deep and beyond: Carbon and nitrogen subduction recycling in secondary peridotites. *Earth and Planetary Science Letters* 543, 116328. https://doi.org/10.1016/j.epsl.2020.116328

Chen, Z., Chen, J., Tamehe, L.S., Zhang, Y., Zeng, Z., Zhang, T., Shuai, W., Yin, X. (2023) Light Fe isotopes in arc magmas from cold subduction zones: Implications for serpentinite-derived fluids oxidized the sub-arc mantle. *Geochimica et Cosmochimica Acta* 342, 1–14. https://doi.org/10.1016/j.gca.2022.12.005

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*. Springer, Cham, 217–247. https://doi.org/10.1007/978-3-319-64666-4_9

Debret, B., Albers, E., Walter, B., Price, R., Barnes, J.D., Beunon, H., Facq, S., Gillikin, D.P., Mattielli, N., Williams, H. (2019) Shallow forearc mantle dynamics and geochemistry: New insights from IODP Expedition 366. *Lithos* 326–327, 230–245. https://doi.org/10.1016/j.lithos.2018.10.038

Debret, B., Reekie, C.D.J., Mattielli, N., Beunon, H., Ménez, B., Savov, I.P., Williams, H.M. (2020) Redox transfer at subduction zones: insights from Fe isotopes in the Mariana forearc. *Geochemical Perspectives Letters* 12, 46–51. https://doi.org/10.7185/geochemlet.2003

Debret, B., Ménez, B., Walter, B., Bouquerel, H., Bouilhol, P., Mattielli, N., Pisapia, C., Rigaudier, T., Williams, H.M. (2022) High-pressure synthesis and storage of solid organic compounds in active subduction zones. *Science Advances* 8, eabo2397. https://doi.org/10.1126/sciadv.abo2397

Freymuth, H., Vils, F., Willbold, M., Taylor, R.N., Elliott, T. (2015) Molybdenum mobility and isotopic fractionation during subduction at the Mariana arc. *Earth and Planetary Science Letters* 432, 176–186. https://doi.org/10.1016/j.epsl.2015.10.006

Fryer, P., Lockwood, J.P., Becker, N., Phipps, S., Todd, C.S. (2000) Significance of serpentine mud volcanism in convergent margins. In: Dilek, Y., Moores, E.M., Elthon, D., Nicolas, A. (Eds.) *Ophiolites and oceanic crust: new insights from field studies and the Ocean Drilling Program*. Geological Society of America, Boulder, 35–52. https://doi.org/10.1130/0-8137-2349-3.35

Fryer, P., Wheat, C.G., Williams, T., Expedition 366 Scientists (2018) *Mariana Convergent Margin and South Chamorro Seamount*. Proceedings of the International Ocean Discovery Program, Volume 366, College Station, TX. https://doi.org/10.14379/iodp.proc.366.2018

Geilert, S., Albers, E., Frick, D.A., Hansen, C.T., von Blanckenburg, F. (2021) Systematic changes in serpentine Si isotope signatures across the Mariana forearc – a new proxy for slab dehydration processes. *Earth and Planetary Science Letters* 575, 117193. https://doi.org/10.1016/j.epsl.2021.117193

Hulme, S.M., Wheat, C.G., Fryer, P., Mottl, M.J. (2010) Pore water chemistry of the Mariana serpentinite mud volcanoes: A window to the seismogenic zone. *Geochemistry, Geophysics, Geosystems* 11, Q01X09. https://doi.org/10.1029/2009GC002674

Hyndman, R.D., Peacock, S.M. (2003) Serpentinization of the forearc mantle. *Earth and Planetary Science Letters* 212, 417–432. https://doi.org/10.1016/S0012-821X(03)00263-2

Ishikawa, T., Tera, F. (1999) Two isotopically distinct fluids component involved in the Mariana Arc: Evidence from Nb/B ratios and B, Sr, Nd, and Pb isotope systematics. *Geology* 27, 83–86. https://doi.org/10.1130/0091-7613(1999)027<0083:TIDFCI>2.3.CO;2

Li, H.-Y., Zhao, R.-P., Li, J., Tamura, Y., Spencer, C., Stern, R.J., Ryan, J.G., Xu, Y.-G. (2021) Molybdenum isotopes unmask slab dehydration and melting beneath the Mariana arc. *Nature Communications* 12, 6015. https://doi.org/10.1038/s41467-021-26322-8

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

Liu, H., Xue, Y.-Y., Yang, T., Jin, X., You, C.-F., Lin, C.-T., Sun, W.-D., Deng, J. (2022) Fluid-rock interactions at shallow depths in subduction zone: Insights from trace elements and B isotopic composition of metabasites from the Mariana forearc. *Lithos* 422–423, 106730. https://doi.org/10.1016/j.lithos.2022.106730

Marschall, H.R., Schumacher, J.C. (2012) Arc magmas sourced from mélange diapirs in subduction zones. *Nature Geoscience* 5, 862–867. https://doi.org/10.1038/ngeo1634

Marschall, H.R., Altherr, R., Rüpke, L. (2007) Squeezing out the slab — modelling the release of Li, Be and B during progressive high-pressure metamorphism. *Chemical Geology* 239, 323–335. https://doi.org/10.1016/j.chemgeo.2006.08.008

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* 207, 102–138. https://doi.org/10.1016/j.gca.2017.03.028

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

Pabst, S., Zack, T., Savov, I.P., Ludwig, T., Rost, D., Tonarini, S., Vicenzi, E.P. (2012) The fate of subducted oceanic slabs in the shallow mantle: Insights from boron isotopes and light element composition of metasomatized blueschists from the Mariana forearc. *Lithos* 132–133, 162–179. https://doi.org/10.1016/j.lithos.2011.11.010

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. *Journal of*

Geophysical Research: Solid Earth 112, B09205. https://doi.org/10.1029/2006JB004749

Spandler, C., Hermann, J., Arculus, R., Mavrogenes, J. (2003) Redistribution of trace elements during prograde metamorphism from lawsonite blueschist to eclogite facies; implications for deep subduction-zone processes. *Contributions to Mineralogy and Petrology* 146, 205–222. https://doi.org/10.1007/s00410-003-0495-5

Syracuse, E.M., van Keken, P.E., Abers, G.A. (2010) The global range of subduction zone thermal models. *Physics of the Earth and Planetary Interiors* 183, 73–90. https://doi.org/10.1016/j.pepi.2010.02.004

Tamblyn, R., Zack, T., Schmitt, A.K., Hand, M., Kelsey, D., Morrissey, L., Pabst, S., Savov, I.P. (2019) Blueschist from the Mariana forearc records long-lived residence of material in the subduction channel. *Earth and Planetary Science Letters* 519, 171–181. https://doi.org/10.1016/j.epsl.2019.05.013

Wei, W., Kastner, M., Deyhle, A., Spivack, A.J. (2005) Geochemical Cycling of Fluorine, Chlorine, Bromine, and Boron and Implications for Fluid-Rock Reactions in Mariana Forearc, South Chamorro Seamount, ODP Leg 195. In: Shinohara, M., Salisbury, M.H., Richter, C. (Eds.) *Proceedings of the Ocean Drilling Program, Scientific Results* 195, College Station, TX, 1–23. https://doi.org/10.2973/odp.proc.sr.195.106.2005