

Boron isotopic discrimination for subduction-related serpentinites

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ABSTRACT

The Guatemala Suture Zone (GSZ), Guatemala, is a region that contains two distinct suture-related serpentinite mélanges straddling the Motagua fault and an ophiolitic complex paired with the northern mélange. The serpentinite matrix of the mélanges formed by subduction-fluid hydration of peridotite from the deep mantle wedge. The occurrence of serpentinite from both exhumed subduction channel mélange and ophiolite is not uncommon in paleo-suture zones, but distinguishing them and their tectonic origin can be difficult. A new method of discrimination, based on boron isotopes in serpentine from both mélanges and ophiolite, as well as on mica and pyroxene from the metamorphic and vein-rock blocks embedded within the mélanges, has been developed. The metamorphic and vein samples have mainly negative $\delta^{11}\text{B}$, ranging from -15.3‰ to $+4.3\text{‰}$, in the same range as the serpentine from the mélanges (-14.4‰ to $+9.7\text{‰}$). In addition to being the most negative $\delta^{11}\text{B}$ values ever measured in serpentinite, comparable values from vein minerals indicate that the same fluid serpentinized the overlying mantle. In contrast, serpentine samples from the ophiolite have positive $\delta^{11}\text{B}$, in the range 0‰ to $+18.0\text{‰}$, consistent with hydration by seawater-derived fluids. As the GSZ displays two mélanges whose serpentinite originated from two different deep subductions and mantle hydration, we hypothesize that the negative signature of exhumed mélange serpentinite is the norm and that the B isotopic signature can be a useful tool to discriminate the tectonic origin of serpentinization in paleo-suture zones.

INTRODUCTION

Serpentinites most commonly originate by hydration of peridotite by two different processes: (1) by a seawater source reacting with peridotite from the ocean crust, and (2) by reaction of peridotite at the base of the mantle wedge with fluids released from the slab during subduction (Evans et al., 2013). In subduction-related tectonic settings, both types of serpentinite are commonly found. A good example is in Guatemala, where type 1 is exposed in obducted ophiolite sequences overthrusting onto a margin (Dilek and Furnes, 2014), and type 2 occurs in exhumed subduction channel assemblages as serpentinite mélanges containing high-pressure–low-temperature (HP-LT) rocks such as eclogites, jadeitites, and other metabasites (Deschamps et al., 2013; Harlow et al., 2004, 2015). In many collisional tectonic settings, both types of serpentinite occur as paired belts (Harlow et al., 2014; Fig. 1), and discriminating between them can be difficult. Thus, the tectonic origin of serpentinite bodies in subduction settings remains unclear for many suture zones.

For example, serpentinites of the Western Alps associated with HP-ultrahigh-*P* rocks are interpreted as fragments of the oceanic lithosphere (Angiboust et al., 2009; Guillot et al., 2009), as mantle wedge-related mélanges (Scambelluri and Tonarini, 2012; Schwartz et al., 2000), or as a mixture of both (Deschamps et al., 2013; Guillot et al., 2015). A similar uncertainty exists for the Trinity peridotite (California, USA): it is

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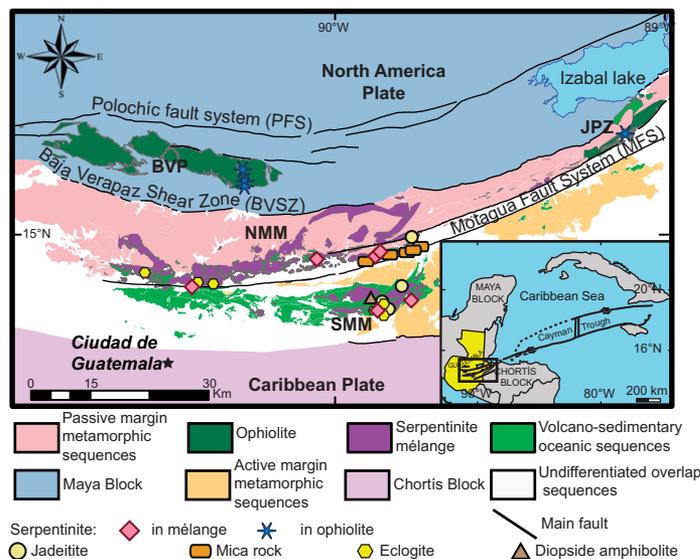


Figure 1. Geological map of the Guatemala Suture Zone (after Flores et al., 2013) showing the two serpentinite mélanges, North Motagua Mélange (NMM) and South Motagua Mélange (SMM) straddling the Motagua fault system, the disrupted ophiolite sequences, Juan de Paz (JPZ) and Baja Verapaz (BVP), and the locations of samples analyzed in our study.

interpreted as the base of an ophiolite (Quick, 1981) on the basis of field and tectonic observations, or as a slice of mantle wedge (Peacock, 1987) on the basis of petrologic observations and hydrogen geochemistry. Here we present the first *in situ* boron isotopic measurements on serpentine minerals from the Guatemala suture zone (GSZ) serpentinite mélanges and paired northern ophiolite. Comparison of mélange serpentinites (formed at 30–70 km depth) with ophiolitic serpentinites (from oceanic crust) shows a clear distinction based on B isotopic signatures. Thus, B isotopes in serpentinites may be a useful discriminant to distinguish whether hydration occurred at shallow depths (from infiltrating seawater) or at greater depths in a subduction zone (from dehydration fluids).

BORON ISOTOPES IN SUTURE AND SUBDUCTION ZONES

Boron is a highly fluid-mobile light element with two isotopes (^{10}B and ^{11}B) that are useful in the study of hydrous fluid transfer from the slab to the mantle wedge ultramafics. The low mass of B and the large relative mass difference of its isotopes allow it to fractionate easily as a function of temperature, pH, and phase partitioning (Konrad-Schmolke and Halama, 2014; Wunder et al., 2005). Interestingly, ^{11}B is preferentially partitioned in phases with trigonal coordination (fluids), whereas ^{10}B is mainly partitioned in phases with tetrahedral coordination (solids) (Peacock and Hervig, 1999), typically phyllosilicates in the absence of tourmaline (Marschall et al., 2007; Wunder et al., 2005).

Existing whole-rock B isotopic measurements of serpentinite from the oceanic crust (former abyssal peridotites; Boschi et al., 2013, and

references therein; Harvey et al., 2014b) and the Mariana forearc (sampled between 1 and 300 m below seafloor; Benton et al., 2001) display positive $\delta^{11}\text{B}$ values (Fig. 2A) in the range of +3‰ to +25‰. These values indicate that the fluid responsible for serpentinization was seawater derived ($\delta^{11}\text{B}$ of seawater \sim +40‰; Spivack and Edmond, 1987), or a mix between seawater and shallow subduction fluids. Whole-rock measurements of B isotopes on altered oceanic crust samples from Troodos (Cyprus) and Oman ophiolites yield slightly negative to positive values (Fig. 2A; Smith

et al., 1995; Yamaoka et al., 2012, 2015) with $\delta^{11}\text{B}$ ranging from -2‰ to $+17\text{‰}$. In these cases, the B isotopic signatures are the result of isotopic fractionation of B from seawater at different temperatures (25–325 °C) and depths within the oceanic crust (0–1.5 km) (Smith et al., 1995). Secondary ion mass spectrometry (SIMS) measurements of $\delta^{11}\text{B}$ on antigorite from the Trinity peridotite (interpreted as from the mantle wedge overlying subduction) yield an average value of $\delta^{11}\text{B} = -10.4\text{‰} \pm 1.2\text{‰}$ (Peacock and Hervig, 1999). Two studies reported whole-rock measurements on serpentinite samples from the oceanic mantle: the Erro Tobbio peridotite (Italy) yielded $\delta^{11}\text{B}$ ranges from +10‰ to +24‰ on low- and high-grade polytypes (Scambelluri and Tonarini, 2012), and antigorite from the Betic Cordillera (Spain) yielded $\delta^{11}\text{B}$ ranges from +21‰ to +25‰ (Harvey et al., 2014a). The $\delta^{11}\text{B}$ of blueschist, eclogite, and amphibolite from different locations was measured by SIMS in mica and amphibole, and the results ranged from -18‰ to -2‰ (e.g., Halama et al., 2014; Pabst et al., 2012; Peacock and Hervig, 1999). Whole-rock analyses by thermal ionization mass spectrometry on eclogites and amphibolites from Sulu (China) yield a $\delta^{11}\text{B}$ ranging from -9‰ to $+3\text{‰}$ (Xiao et al., 2011).

GEOLOGICAL BACKGROUND AND SAMPLE DESCRIPTIONS

Central Guatemala features a complex tectonic boundary between the North America and Caribbean plates, formerly called the Motagua Fault Zone (Harlow et al., 1994), and recently renamed the GSZ (Flores et al., 2013). Two serpentinite mélanges are found within the GSZ: the North Motagua Mélange (NMM) and the South Motagua Mélange (SMM). A dismembered ophiolite sequence is found in the northern section of the GSZ, the Baja Verapaz and Juan de Paz ophiolites (Fig. 1). The mélanges contain blocks of serpentinite, HP–LT metabasites, and HP–LT vein rocks embedded in a serpentinite matrix. The metabasite blocks (eclogite and amphibolite) are metamorphosed pieces of the subducted oceanic crust, and the veins (jadeite and mica rock) represent fluid crystallization within the subduction channel or its mantle wedge lid (Harlow, 1994; Harlow et al., 2011, 2016). Metasedimentary blocks are absent, except for a few samples within the SMM. The GSZ is an ideal place to study the relations between slab, mantle wedge, and overriding plate sequences, because the serpentinite in the mélanges and ophiolites were formed in two different paleo–subduction zones, in different tectonic settings, and at different times (Flores et al., 2013; Appendix DR1 in the GSA Data Repository¹). The SMM records a cold subduction (peak \sim 480 °C, \sim 2.6 GPa; Tsujimori et al., 2006; or \sim 520 °C, \sim 2.5 GPa; Endo et al., 2012), whereas the NMM was warmer and shallower (peak \sim 500–600 °C, $<$ 2 GPa; Flores et al., 2013; Harlow et al., 2011). For this study, two serpentinites and seven metabasites and vein rocks are from the SMM, four serpentinites and nine vein rocks and metabasites are from the NMM, and four serpentinites are from the ophiolite adjacent to the NMM (Table DR1-1 in the Data Repository). Serpentinites from the mélanges consist of antigorite, whereas those from the ophiolite contain lizardite. They are cut by secondary veins of antigorite, dolomite, or tremolite (mélange) or chrysotile (ophiolite) (Appendix DR1). Eclogites are partly retrogressed to blueschist, and locally greenschist facies, whereas garnet grains also recorded the prograde history of the samples, as evidenced by various inclusions (glaucophane, omphacite, epidote, phengite; Appendix DR1). Jadeite and phengite from vein rocks are strongly chemically zoned, indicating several fluid influxes (Tables DR1-1–DR1-3).

ANALYTICAL METHOD AND B ISOTOPE RESULTS

Boron isotopes were measured *in situ* by laser ablation–multicollector–inductively coupled plasma–mass spectrometry at Lamont Doherty

¹GSA Data Repository item 2016301, petrological description and pressure–temperature conditions, boron element and isotope results, and boron isotope fractionation, is available online at www.geosociety.org/pubs/ft2016.htm, or on request from editing@geosociety.org.

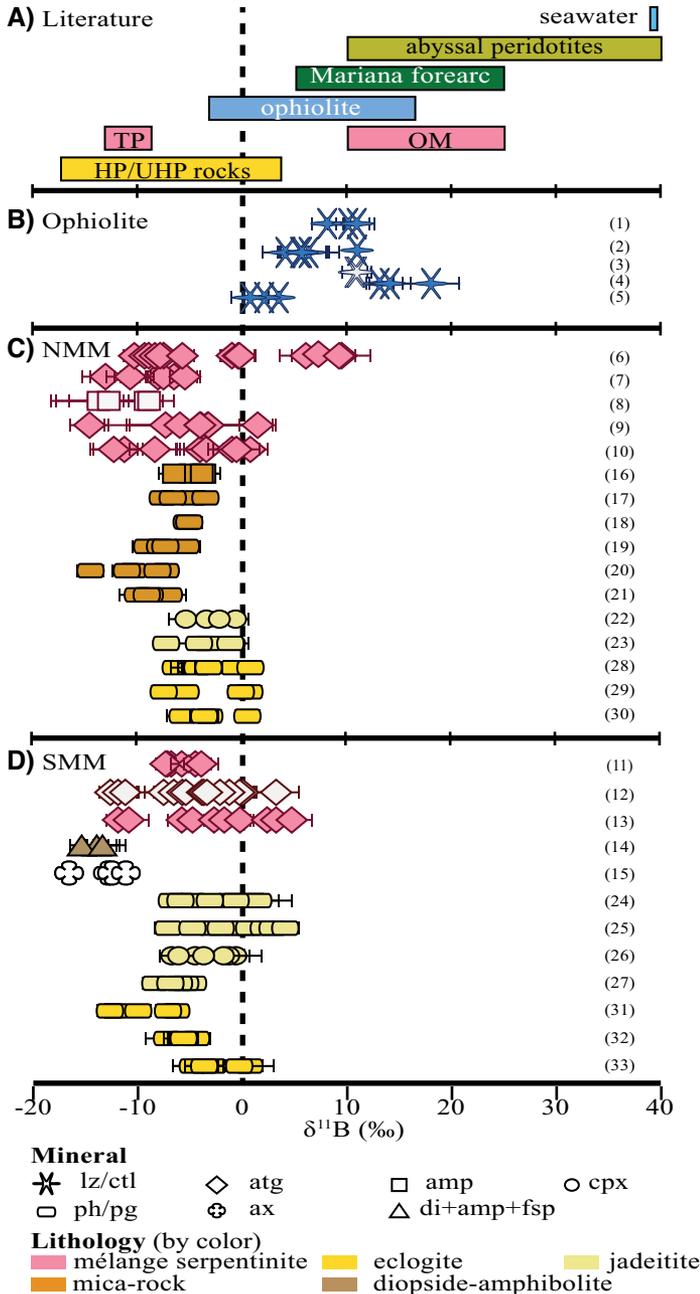


Figure 2. A: $\delta^{11}\text{B}$ values from the literature (see text for references and lithologies). OM—oceanic mantle; TP—Trinity peridotite; HP—high pressure; UH—ultrahigh. B: Comparison with *in situ* $\delta^{11}\text{B}$ measurements from ophiolites. C: Comparison with *in situ* measurements from the North Motagua Mélange (NMM). D: Comparison with *in situ* measurements from the South Motagua Mélange (SMM). Error bars are shown except where the symbol width exceeds the error. The numbers in parentheses refer to the sample listed in Table DR2-1 (see footnote 1). Open symbols represent veins. Abbreviations: lz—lizardite; ctl—chrysotile; ph—phengite; pg—paragonite; atg—antigorite; ax—axinite; amp—amphibole; di—diopside; fsp—feldspar; cpx—clinopyroxene.

Earth Observatory (New York, USA), following Martin et al. (2015), and by SIMS at the Woods Hole Oceanographic Institution (Massachusetts, USA), following Marschall and Monteleone (2015) (Appendix DR2). The serpentinite from all ophiolites have positive $\delta^{11}\text{B}$ values, from +0.8‰ to +18.0‰ (Fig. 2B), whereas all serpentinite from mélanges, both NMM and SMM, have significantly more negative $\delta^{11}\text{B}$ values: NMM from -14.4‰ to +9.7‰ (Fig. 2C), and SMM from -12.5‰ to +4.9‰ (Fig. 2D). Minerals from metamorphic and vein rocks from both NMM and SMM have negative to slightly positive $\delta^{11}\text{B}$ values that overlap the range of mélangé serpentinite. The most negative values are from the SMM metabasite MVE04-4-3, which has $\delta^{11}\text{B}$ values ranging from -15.3‰ to -13.2‰ (Fig. 2D). The mica rock samples, all from the NMM, display only negative values in mica and amphibole, from -14.5‰ to -5.0‰ (Fig. 2C). Jadeitites display the greatest range within a single sample, in both pyroxene and mica, particularly in SMM samples ($\delta^{11}\text{B}$ from -8.3‰ to +4.3‰). The $\delta^{11}\text{B}$ of mica and pyroxene from NMM jadeitites ranges from -7.3‰ to -0.5‰. The scattered $\delta^{11}\text{B}$ values may reflect multiple fluid influxes, with the positive values likely reflecting influx of fluids from different depths in the subduction channel, from different sources, or a mixture of fluids. The $\delta^{11}\text{B}$ of mica in eclogites is also scattered, but each sample displays a relatively narrow range. In the SMM eclogites, $\delta^{11}\text{B}$ ranges from -12.7‰ to +0.5‰, whereas in the NMM eclogites $\delta^{11}\text{B}$ ranges from -8.9‰ to +0.4‰. The detailed results, including the B concentrations, are provided in Appendix DR2.

TECTONIC IMPLICATION AND MANTLE HYDRATION

The *in situ* measurements of ophiolitic serpentinite overlap published whole-rock values on altered oceanic crust from other ophiolites, for both B concentrations and $\delta^{11}\text{B}$ (Fig. 3), although they are different lithologies. The positive $\delta^{11}\text{B}$ and moderate contents of B (<16 ppm) in samples from the GSZ, together with the presence of lizardite and/or chrysotile polytypes, are consistent with a seawater-derived fluid responsible for

serpentinization of abyssal peridotites. The results from mélangé samples for both NMM and SMM are consistent and overlap the single value obtained from the Trinity peridotite (-10.4‰ ± 1.2‰; Peacock and Herwig, 1999), supporting the interpretation that at least part of the Trinity peridotite represents mantle wedge hydrated during subduction (Peacock, 1987). In addition, serpentinites from NMM and SMM contain only antigorite, the HT polytype of serpentinite, supporting a deeper mantle wedge origin. Although the Erro Tobbio peridotite is noted as of mantle wedge origin, it originates from oceanic mantle, equated with abyssal peridotite serpentinized by a seawater-derived fluid, subjected to shallow subduction fluids in the alpine forearc, and then dragged down to eclogite facies depth (Scambelluri et al., 2001). Figure 3 shows that Erro Tobbio samples fit in the overlapping fields of altered abyssal peridotites and/or forearc serpentinites with a seawater-induced B signature, together with samples from the Betic Cordillera (Harvey et al., 2014a). Samples from the GSZ mélanges (hydrated mantle wedge overlying subduction) are distinctly different: not only do they have the most negative $\delta^{11}\text{B}$ values ever measured in serpentinite (to -15‰; Appendix DR2) but they also have very low B contents (mainly <10 ppm; Fig. 3; Appendix DR2).

Significantly, the $\delta^{11}\text{B}$ range in minerals from the mélangé-hosted vein-rock blocks of the GSZ is similar to that from mélangé serpentinites. The fluids released from the subducting slab that crystallized jadeitites and mica rocks also serpentinized the encapsulating mélangé ultramafics (Harlow et al., 2015). In addition, the *in situ* B isotope signatures from mica, pyroxene, and amphibole of metabasites and vein rocks overlap published $\delta^{11}\text{B}$ values from HP-LT metabasites (Figs. 2A, 2C, and 2D), and the negative signature of such rocks was described (Marschall et al., 2007, and references therein). Models and experiments on the fluids expected to be released during subduction (e.g., Wunder et al., 2005; Marschall et al., 2007; Konrad-Schmolke and Halama, 2014) conclude that their $\delta^{11}\text{B}$ values will decrease with increasing depth (in the range of 20–70 km) because of the strong fractionation of ^{11}B into the fluid phase, reaching significantly negative values (to between -15‰ and -28‰; Appendix DR3). The decrease in $\delta^{11}\text{B}$ is observed regardless of the mineralogy of the metamorphic rock (with or without mica) and pH (basic or neutral). The pH in a serpentinite environment is expected to be strongly basic, and consequently minimize the B isotopic fractionation (Scambelluri and Tonarini, 2012). The $\delta^{11}\text{B}$ values of the fluids modeled here (Appendix DR3) should therefore be close to the $\delta^{11}\text{B}$ values of the minerals precipitating from these fluids. The lowest $\delta^{11}\text{B}$ values of vein rocks and mélangé serpentinites measured in our study are in the same range as modeled fluids, consistent with the idea that the fluids released from rocks in subduction zones are responsible for both vein-rock crystallization and serpentinization of peridotite in and along the channel. Thus, tectonic settings must be considered as factors in producing B isotope fractionation, because they affect the *P-T* conditions where the rocks form and/or the fluids are expelled, as well as the origin of the fluid available for the reaction (serpentinization and precipitation of vein rocks). In this way, the discrimination of the tectonic origin of serpentinites in subduction environment based on B isotopic signature makes sense.

The distinct B signatures of the mélangé serpentinites (low B content, negative $\delta^{11}\text{B}$) represent mantle wedge hydration at significant depths, 30 to >70 km, where jadeite crystallized (Harlow et al., 2011). Moreover, the fact that both NMM and SMM samples, from different subduction systems (Flores et al., 2013), show comparable B isotopic signatures indicates that negative values of mélangé serpentinites may be the norm.

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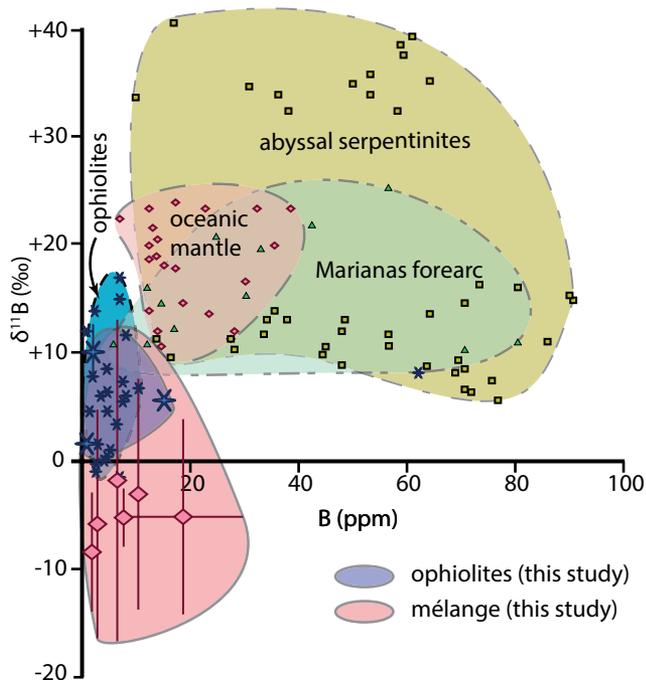


Figure 3. $\delta^{11}\text{B}$ versus B for the following serpentinite reservoirs. Squares—serpentinized abyssal peridotites; triangles—Mariana forearc; stars—ophiolites; diamonds—oceanic mantle (see text for references). All values are whole rocks, except for our study, where the values for ophiolite and mélangé serpentinites are the averages of the *in situ* isotopic values presented in Figure 2 and of the *in situ* B content in Table DR2-1 (see footnote 1).

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