

# **BORON CYCLING IN SUBDUCTION ZONES**

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**Subduction zones are among the most dramatic features on Earth, with much of the action being driven by the movement of water. The “light and lively” nature of boron coupled with the wide variation of its isotopic composition in the different players in this drama, make it an ideal tracer of the role and movement of water during subduction. The utility of boron ranges from monitoring the role of fluids expelled from the accretionary prism in influencing seawater chemistry, to the subduction of crustal material deep into the mantle and its recycling in ocean island basalts.**

**KEYWORDS:** subduction zones, water, serpentinite, phengite, recycling

## **INTRODUCTION**

At subduction zones, oceanic crust and some of its sedimentary overburden descend into the mantle (FIG. 1). Water is carried down with the slab in sediment pore water and hydrous minerals in the sediments and crust. As pressure and temperature increase in the descending slab, the pore water rapidly returns to the oceans, while some mineral-associated water is carried deeper. Eventually, pressure and temperature increase sufficiently to cause the hydrous mineral phases to release almost all their remaining water, thus hydrating the overlying mantle wedge and forming serpentinites. These may then rise as diapirs in the forearc or be dragged deeper into the subduction zone. At greater depths and temperatures, further release of hydrous fluids initiates partial melting in the overlying mantle wedge. This magma rises through the subarc mantle to form volcanoes and plutonic rocks. After it has lost almost all its water and other volatile components, the slab is subducted deep into the

Earth's mantle. It may then mingle with the deep mantle and be incorporated into the melts that form intraplate ocean island basalts (OIB).

There are several attributes of boron that make it a sensitive tracer of these processes and the role of fluids in particular. Compared to the mantle, boron is enriched in continental crust by several orders of magnitude. This enrichment is inherited by terrestrial sediments that lie on the subducted crust. Boron is also very soluble, so it is one of the few elements to have a higher concentration in seawater (4.5 ppm) than in the mantle (<0.1 ppm). Thus the pore waters that make up ~50% of the volume of the sediments on the subducted crust carry a substantial boron inventory, with some of this boron adsorbed on clay minerals. Prior to subduction, most oceanic crust has experienced millions of years of interaction with seawater circulating through the upper crust. During high temperature water-rock interaction at mid-ocean ridge crests, boron is leached from the rock. As the crust moves away from the ridge crest, the temperature of the circulating seawater drops and the behaviour of boron reverses, with seawater boron taken up into secondary hydrous minerals. The extent of this reaction is such that the concentration of boron rises from values of <1 ppm in fresh oceanic crust to up to 100 ppm in altered ocean crust that enters the subduction zone.

Boron possesses another property that enhances its utility in this setting. Namely, the ratio of the isotopes,  $^{10}\text{B}$  and  $^{11}\text{B}$ , (expressed as  $\delta^{11}\text{B}$  values) varies greatly between the components of the subduction zone (Fig. 1). For example, the  $\delta^{11}\text{B}$  of seawater is +40 ‰, compared to -7 ‰ in the mantle that is the source of mid-ocean ridge basalt (MORB) (Marschall et al., 2017), thus allowing the  $\delta^{11}\text{B}$  of solid and fluid phases to be used to further constrain boron sources and pathways in subduction zones.

The objective here is to review our understanding of boron cycling in subduction zones, including the nature of boron-hosting phases in the subducted slab and whether their stability

under the changing pressure-temperature-chemical conditions may allow crustal boron to be recycled into the mantle. This area is of particular interest because the high boron concentrations and distinct  $\delta^{11}\text{B}$  in slab phases relative to the mantle make it a potentially sensitive tracer of crustal recycling into the deep mantle.

## **THE BORON INVENTORY OF THE SUBDUCTING SLAB**

The major boron reservoir in marine sediments is clay minerals, within which boron is partitioned between a lattice-bound fraction and an adsorbed fraction derived from seawater. The boron concentration in the two fractions varies, but is typically 80-150 ppm and 10-30 ppm in the lattice-bound and adsorbed fractions, respectively. The  $\delta^{11}\text{B}$  value of the lattice-bound fraction largely reflects that of the crustal protolith (-5 to +5 ‰), whereas fractionation of seawater boron isotopes during adsorption onto clays yields typical  $\delta^{11}\text{B}$  values of +14 to +16 ‰ in this component (Spivack et al. 1987; Palmer et al. 1987; Ishikawa and Nakamura 1993).

The boron concentration of fresh MORB is <1 ppm and has a  $\delta^{11}\text{B}$  value of -7 ‰, but during interaction of ocean crust with circulating seawater at <100°C boron is taken up into secondary minerals. Again, there is large variability in the boron content and  $\delta^{11}\text{B}$  of altered oceanic crust, but compilations of ocean cores and ophiolite sections give average boron contents and  $\delta^{11}\text{B}$  value of the upper oceanic crust of ~5 ppm and +3 ‰, respectively (Smith et al. 1995). The lower, gabbroic part of the oceanic crust is less altered (Vils et al. 2009), but the upper mantle may be altered to serpentinite by circulating seawater, particularly at slow-spreading mid-ocean ridges, leading to typical boron concentrations of 20-90 ppm and  $\delta^{11}\text{B}$  values of +10 to +15 ‰ (Boschi et al. 2008).

## **SUBDUCTION ZONE PROCESSS**

### ***The Forearc Zone***

The initial stages of subduction commonly involve formation of an accretionary wedge of sediment and portions of oceanic crust scraped off the subducting plate (FIG. 1B). At shallow depths, fluids are expelled along fractures and faults in the wedge (Martin et al. 1996). Boron concentrations in these fluids can reach >10 times seawater levels, with  $\delta^{11}\text{B}$  values similar to the adsorbed fraction of boron in clays (You et al. 1995).

Not all fluids in the forearc return boron directly to the oceans. In particular, serpentinite is formed during hydration of the overlying mantle wedge by water driven off the subducting slab. Because serpentinite is buoyant, it may ascend into the accretionary prism and forearc mélange to form boron-rich serpentinite seamounts and muds (Benton et al. 2001; Savov et al. 2007). However, some serpentinite generated in the forearc is dragged deeper into the mantle (Straub and Lane, 2002). The  $\delta^{11}\text{B}$  of serpentinite minerals and the fluids from which they were derived are similar to the exchangeable component of sediments, but other chemical and isotopic signatures indicate this adsorbed fraction cannot be the major boron source. Rather, much of the boron within serpentinites formed in the subduction zone (as distinct from serpentinite formed prior to slab subduction) is derived from boron that was structurally-bound in sediments and altered oceanic crust, and then extracted by breakdown of hydrous minerals during increasing pressures and temperatures (Benton et al. 2001; Pabst et al. 2012). The  $\delta^{11}\text{B}$  of fluids released from the altered oceanic crust shows a progressive change during subduction (Peacock and Hervig 1999), with a decrease from +25 ‰ at ~100°C to +5 ‰ at 500°C, with the  $\delta^{11}\text{B}$  of the slab restite showing a corresponding decrease from -3 to -10 ‰ (Pabst et al. 2012).

### ***The Arc Magma Production Zone***

Arc volcanic rocks contain elevated boron levels and distinct  $\delta^{11}\text{B}$  values relative to the mantle, that reflect input from the subducted slab (FIG. 1C). The amount and isotopic

composition of slab-derived boron in the Izu arc varies according to the distance of the volcanic centre from subduction front and the depth to the slab (Ishikawa and Nakamura 1994). Thus, volcanoes closest to the slab have higher  $\delta^{11}\text{B}$  values and B/Nb ratios (+7 ‰ and ~40, respectively) than those that sit further back from the forearc and where the depth to the slab is greater (+1 ‰ and ~2, respectively).

Similar patterns are observed in other arcs, with a common feature that the  $\delta^{11}\text{B}$  of arc rocks extend to values that are too high (up to +18 ‰) to be derived from quantitative extraction of boron from sediments and/or altered oceanic crust. Instead, the likely source of boron with elevated  $\delta^{11}\text{B}$  is from serpentinite dehydration. There are essentially two possible sources of serpentinite-derived boron – either serpentinite that formed in the subduction zone and is then dragged down on top of the subducting slab, or serpentinite that formed prior to subduction and is located deeper in the subducting lithosphere (FIG. 1B). 3-D modelling suggests that even in NE Japan, where 130 Ma oceanic crust is subducted, the temperature at the top of the slab beneath the volcanic front is likely ~800°C (Morishige and van Keken 2014). Because antigorite undergoes virtually complete dehydration and release of boron in water-rich melts and/or silica-rich aqueous fluids at ~700°C (Harvey et al. 2014), it is therefore likely that any serpentinite-derived boron within arc rocks is derived from the base of the subducted lithosphere (FIG. 1C), where temperatures may be as low as 475°C beneath the volcanic front (Stern 2002). Importantly, boron released from the slab into the melt generation zone is quantitatively transferred to the arc rocks because boron is highly incompatible during mantle melting.

The elevated  $\delta^{11}\text{B}$  in arc rocks suggests that dehydration fluids are a major boron source, but other isotopes and trace elements (e.g.  $^{10}\text{Be}$  and Th) indicate that melting sediments supply an increasing portion of incompatible elements as the slab is subducted deeper. Indeed, the lowest  $\delta^{11}\text{B}$  values in the Izu arc (+1 ‰) lie furthest from the forearc and are more similar to

sediments. They also have B/Nb ratios (~2.5) that are closer to sediments (~1) than aqueous fluids (>100) and the mantle (0.1) (Ishikawa and Nakamura 1994). The extent to which the sediment signal comes from melting versus extraction of fluid mobile elements by deeply-sourced water is subject to debate (Stern 2002). Although enrichment of fluid-immobile species, such as  $^{10}\text{Be}$  and Th, in arc rocks requires sediment melting, most thermal models predict that subducted sediments are not heated sufficiently to melt phengite, the likely main boron host in the deeply subducted slab (Domanik and Holloway 1996).

### ***Recycling into the Deep Mantle***

The majority of boron entering the subduction zone is ultimately derived from seawater (either as sediment pore water or incorporated into hydrous minerals) and continental crust (as clastic sediments), and much of this boron is recycled into seawater during dewatering of the slab during early subduction, or recycled into arc crust in the form of arc volcanic and plutonic rocks (Moran et al. 1992). For any crustal and/or seawater boron to be recycled into the deep mantle it must be hosted in phases that are stable at greater pressures and temperatures than those within the arc magma generation zone. This either requires incorporation of boron into minerals that are stable under these conditions and/or that crustally-derived minerals in subducted sediments are not broken down during descent into the mantle.

While most of the boron in subducted altered oceanic crust and the overlying sediments is lost to fluid phases during dehydration and passes into the sub-arc mantle before the slab descends into the deep mantle, there are boron-bearing minerals that may survive beyond the volcanic front and may be subducted into the deep mantle. Of the secondary boron-bearing minerals formed in the subducted slab, the most stable is phengite, which can persist up to temperatures and pressures of >1000°C and 100 kbar, respectively (Domanik and Holloway 1996). Continued preferential extraction of high  $\delta^{11}\text{B}$  fluids leads to this phase having  $\delta^{11}\text{B}$  values as light as -18 ‰, but, importantly, it may still retain up to 50 ppm boron

(Pabst et al. 2012; Halama et al. 2014). Thus, there is the potential for boron ultimately derived from the continental crust and seawater (but with a much lighter  $\delta^{11}\text{B}$  value) to be recycled into the deep mantle.

## **SUBDUCTION ZONE BORON BUDGETS**

### ***Impact on Seawater Boron Isotopes***

Attempts to incorporate subduction zone processes into global seawater boron isotope budgets have relied on data from only a few sites, but the simplest interpretation of these data is that most of the boron expelled back into seawater at subduction zones has a  $\delta^{11}\text{B}$  of +13 ‰, compared to +40 ‰ in seawater. In addition, a plausible mass-balance can be achieved between the amount and isotopic composition of boron entering the subduction zone in pore waters and adsorbed to sediments, and that which is expelled back into seawater in forearc fluids (You et al. 1995).

The amount of boron expelled back into seawater at convergent margins depends on the amount of sediment entering the subduction zone. Thus, higher subduction rates may result in increased return of labile boron to the oceans and lower seawater  $\delta^{11}\text{B}$  values, although the long residence time of boron in the oceans (~10-20 Myr) mitigates against large and rapid changes in seawater  $\delta^{11}\text{B}$  values.

Reconstruction of seawater  $\delta^{11}\text{B}$  values over the past 50 Myr (Raitzsch and Honisch 2013) suggests that there has been an ~3 ‰ increase in seawater  $\delta^{11}\text{B}$  since the Late Eocene, superimposed on shorter term oscillations of up to 2 ‰ (FIG 2A). It is interesting to note, therefore, that over this period there appears to be a first order correlation between time-averaged subduction rates (FIG 2B) (Chen et al. 2015) and the reconstructed seawater  $\delta^{11}\text{B}$ , with peaks in the latter coinciding approximately with lower subduction rates. This apparent coincidence is not proof of a causal link between subduction rates and seawater  $\delta^{11}\text{B}$ , but the

existence of subduction rate reconstructions extending back ~180 Myr (Engebretson et al. 1992) provides a testable hypothesis if reconstructions of seawater  $\delta^{11}\text{B}$  values can be reliably extended further back in time.

### ***Recycling into the Mantle***

There is a strong correlation between budgets of fluid mobile elements, such as boron, entering subduction zones and the content of these elements in arc rocks (Plank and Langmuir 1993), but mass balance uncertainties are too large to constrain mismatches in inputs and outputs in subduction zones. The question as to whether boron is recycled into the deep mantle may be addressed, however, by searching for  $\delta^{11}\text{B}$  signatures of subduction in ocean island basalts (OIB) that are unequivocally derived from the deep mantle and have other isotope signatures (e.g., Sr, Nd and Pb) that suggest a contribution from recycled subducted slabs (White, 2015).

The first requirement is, however, knowledge of the  $\delta^{11}\text{B}$  value of the primitive mantle (PM). This has been a difficult problem to solve because the boron concentrations of mantle-derived rocks are low and easily perturbed by post-eruptive alteration of primary signatures by circulating fluids and high level assimilation of crustal material, including previously altered mantle-derived rocks. Recently, Marschall et al. (2017) undertook an ion-probe study of the boron isotope systematics of MORB and, together with consideration of other indices of alteration and assimilation, were able to determine that the  $\delta^{11}\text{B}$  value of the mantle from which MORB is derived (DMM; depleted MORB mantle) is  $-7 \pm 1$  ‰, with a boron concentration of <0.1 ppm. Comparison with other stable isotope systems (White, 2015) suggests this also likely represents the  $\delta^{11}\text{B}$  of PM (i.e. the composition of the mantle before extraction of any crust). Because MORB is likely derived from mantle previously depleted in

elements enriched in the crust (White, 2015) and boron is highly incompatible, the B concentration of PM is likely higher than that of DMM.

Relatively few OIB suites have been analysed for boron isotopes and much of the wide spread in  $\delta^{11}\text{B}$  values for individual sample suites has been ascribed to contamination of the magma source by high level assimilation of altered rocks, rather than variations in the mantle source. Thus, light  $\delta^{11}\text{B}$  values (as low as -14 ‰) in some Icelandic melt inclusions have been attributed to interaction of lavas with geothermal fluids (Brounce et al. 2012). In contrast, high level crustal assimilation of altered oceanic crust is thought to be responsible for high  $\delta^{11}\text{B}$  values (up to +12 ‰) in western Azores OIB, but lower values (-7.4 to -3.3 ‰) observed eastern Azores are considered to more closely reflect mantle source compositions (Genske et al. 2014).

A compilation of OIB data (excluding those most obviously affected by high level alteration/assimilation) is presented in FIG 3. Also shown are mixing trajectories between two potential subduction components – phengite and clastic sediments. (Fractional crystallization may yield higher B concentrations, with no change in  $\delta^{11}\text{B}$  values). Many of the low  $\delta^{11}\text{B}$  OIB data could be construed to lie on a trend from mantle  $\delta^{11}\text{B}$  values to the phengite  $\delta^{11}\text{B}$  field (FIG 3). In contrast, data from Hawaii (Tanaka and Nakamura 2005), the eastern Azores (Genske et al. 2014) and intraplate volcanic rocks from NE China (Li et al. 2016) trend to higher  $\delta^{11}\text{B}$  values than the PM. This may reflect mixing of a primitive mantle source with deeply subducted and recycled sediments, as previously suggested for the Hawaiian data (Tanaka and Nakamura 2005). Interestingly, potential mixing lines with recycled sediments (FIG 3) form a better fit to the data if the sediment endmember has  $\delta^{11}\text{B}$  values that fall to the lower end of the range observed in clastic sediments, which supports the suggestion above that any subducted and recycled boron is likely to have a lighter  $\delta^{11}\text{B}$  value than material

entering the subduction system. Further studies are required to determine whether the OIB data truly reflect mantle heterogeneities, but separating the potential role of high level assimilation/alteration processes from variations in the original mantle source will be difficult.

## **CLOSING REMARKS**

This review illustrates that boron more than lives up to its description of being “light and lively” in the upper portions of subduction zones. When it comes to deeper sections of the subducted slab, however, there are indications that there may be a more furtive side to its character, with some boron resolutely clinging onto refractory phases and returning to the deep mantle. This may be where boron behaviour in subduction zones has most promise of contributing to wider advances in Earth science, but there are several questions that must be resolved before this potential can be realised. While much information has been obtained from rocks metamorphosed under subduction zone conditions, overprinting by later fluids and boron mobility during retrograde metamorphism complicate interpretations. Experimental studies of boron partition coefficients and isotope fractionation between fluids and minerals and the amounts of these minerals formed under subduction zone conditions would help resolve these uncertainties. There is also little boron data available for OIB, particularly compared to other isotope systems, but advances in this area will likely require a combination of micro-analytical techniques and evaluation of potential contamination of mantle signatures by high level crustal assimilation and alteration.

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## Figure Captions

FIGURE 1. Schematic of subduction zone setting, with insets of specific areas. (A) Ocean crust prior to subduction, (B) fore arc, (C) magma production zone. (after Stern 2002). Boron isotope data from Palmer and Swihart (1996) and Marschall et al. (2017) (and references therein).

FIGURE 2. (A) Modelled variations in seawater  $\delta^{11}\text{B}$  values over past 50 Myr (adapted from Raitzsch and Honisch 2013), (B) Global subduction rates (Chen et al. 2015) over the past 70 Myr.

FIGURE 3.  $\delta^{11}\text{B}$  versus boron concentration data for mantle-derived rocks. Data sources: Hawaii (Tanaka and Nakamura 2005), Iceland (Brounce et al. 2012), E Azores (Genske et al. 2014), NE China (Li et al. 2016), mantle value (Marschall et al. 2017), all other data (Chaussidon and Marty 1995). Phengite data: (Pabst et al. 2012; Halama et al. 2014). Sediment data: (Palmer and Swihart 1996). FC shows fractional crystallization trend. Mixing lines show trends towards upper and lower  $\delta^{11}\text{B}$  values measured in clastic sediments (+5 and -5 ‰) and phengite (-10 and -18 ‰) using B concentrations of 100 ppm and 50 ppm, respectively. Tick marks are every 0.1‰ of sediments/phengite to a maximum of 5%.

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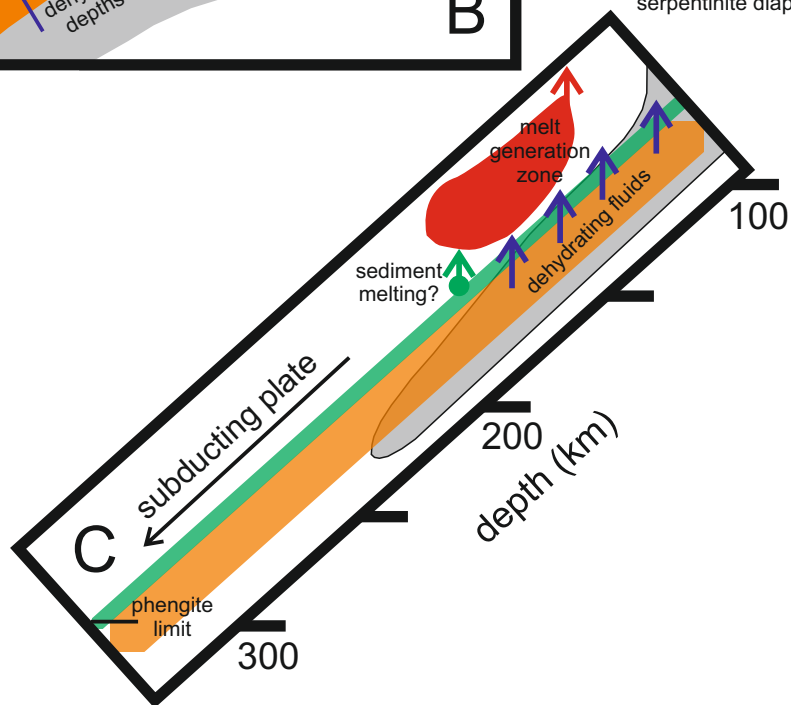
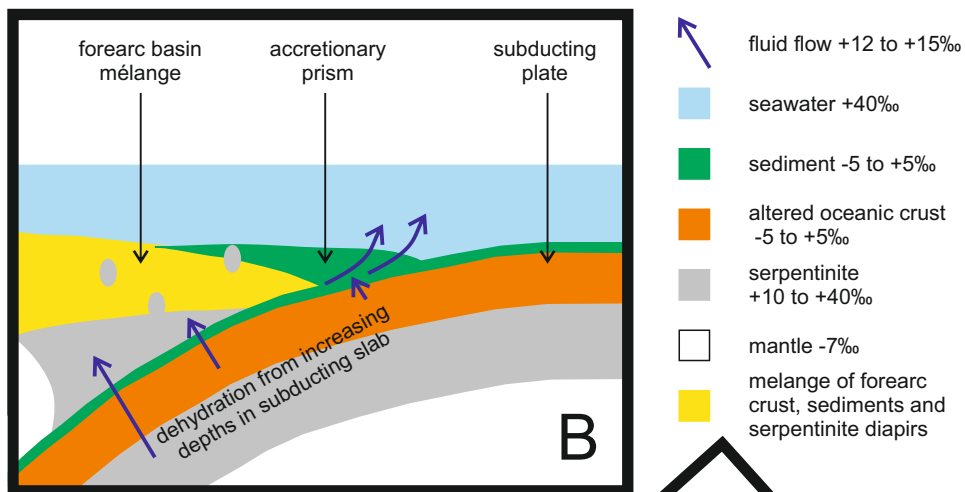
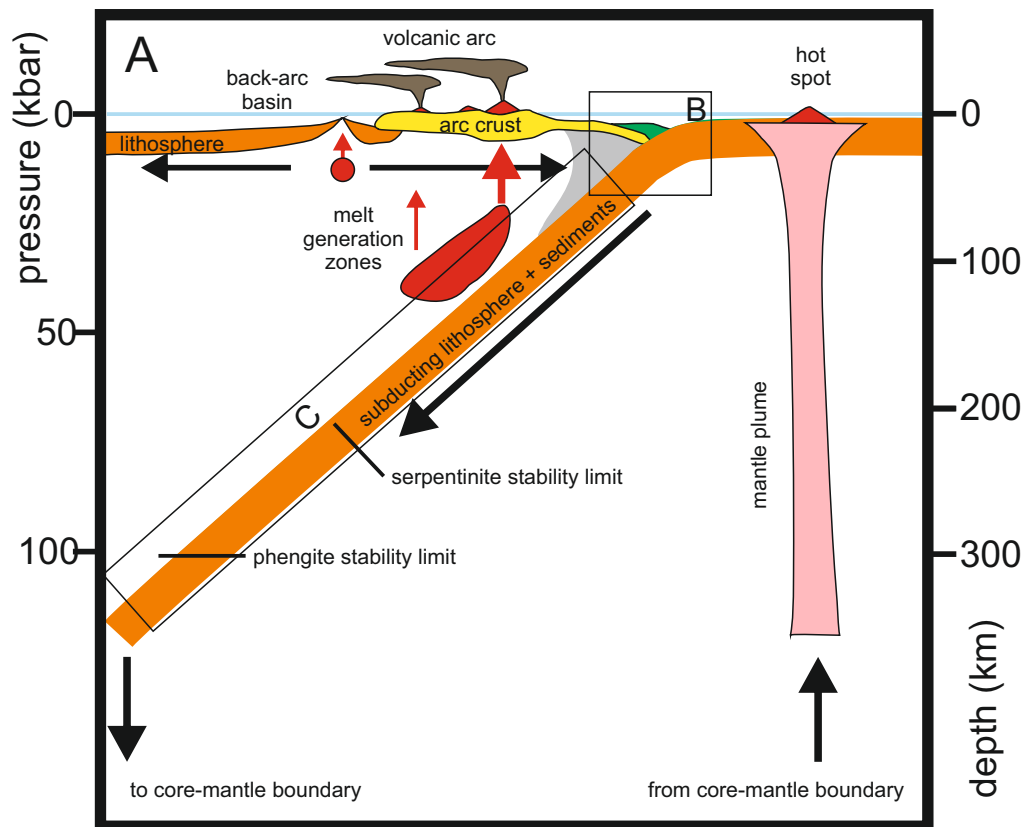
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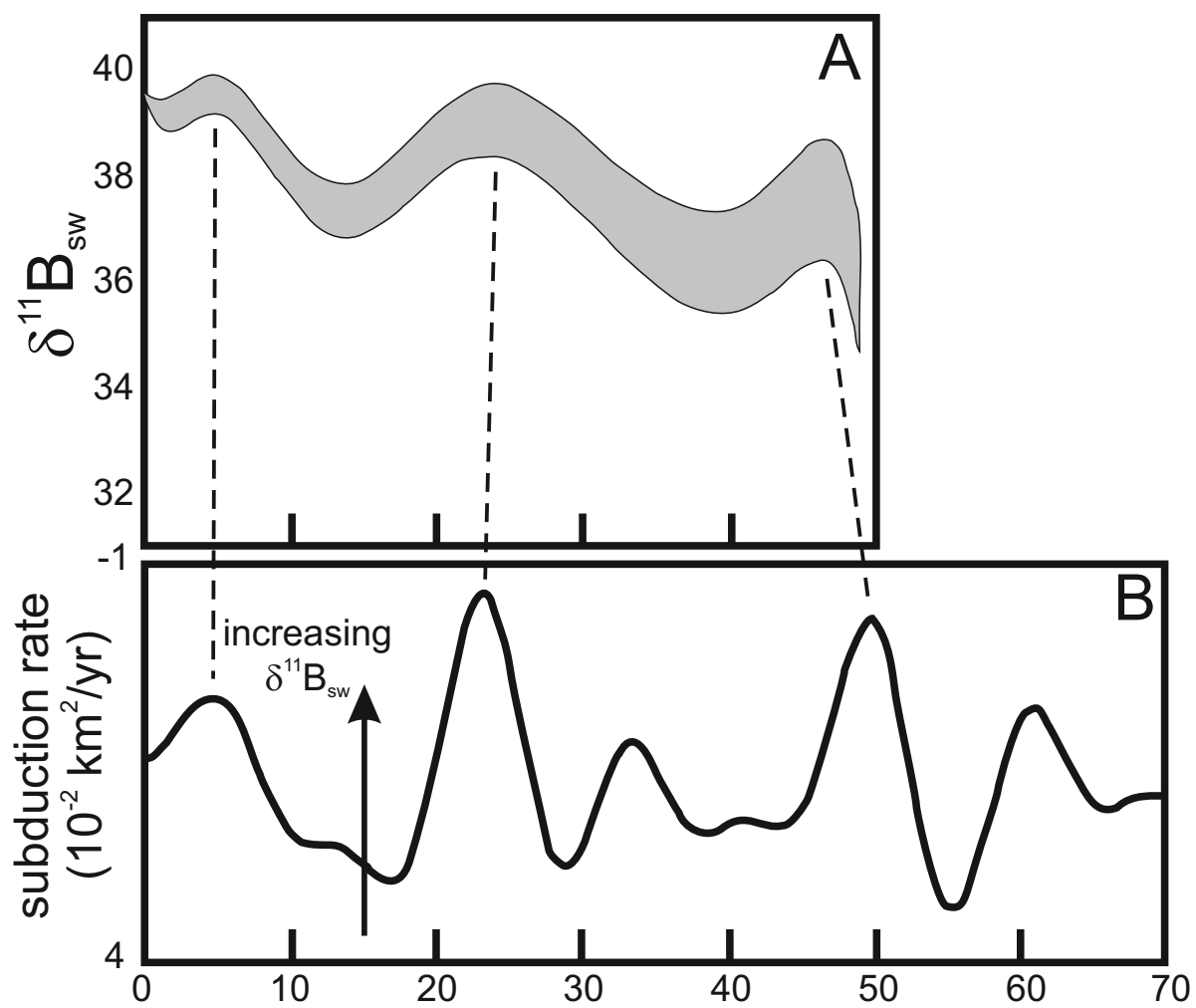
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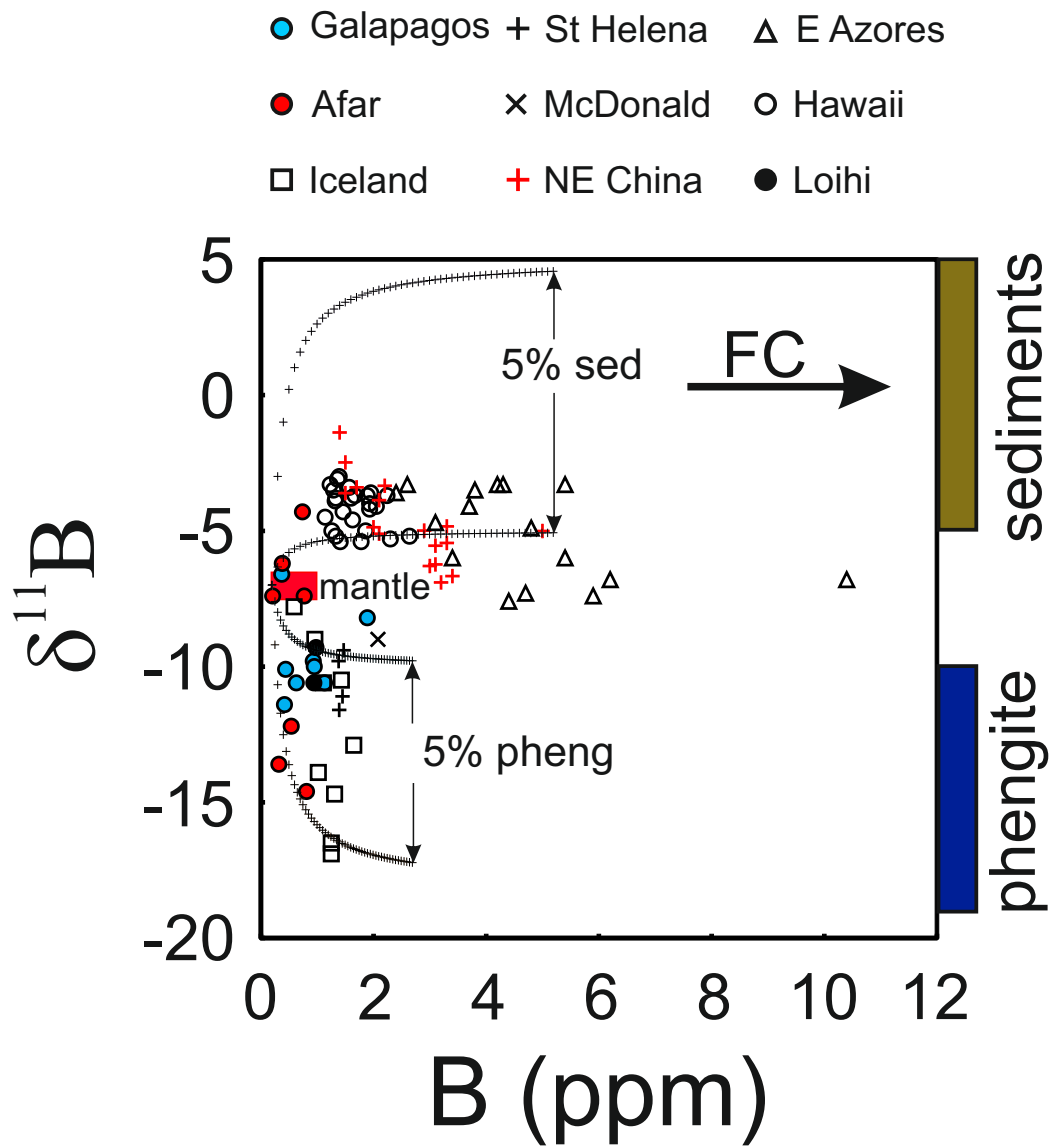
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Palmer\_fig 1



Palmer\_fig 2



Palmer\_fig 3