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A limited role for metasomatized subarc mantle in the generation of boron isotope signatures of arc volcanic rocks

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ABSTRACT

Metasomatized subarc mantle is often regarded as one of the mantle reservoirs enriched in fluid-mobile elements (FMEs; e.g., B, Li, Cs, As, Sb, Ba, Rb, Pb), which, when subject to wet melting, will contribute to the characteristic FME-rich signature of arc volcanic rocks. Evidence of wet melts in the subarc mantle wedge is recorded in metasomatic amphibole-, phlogopite-, and pyroxene-bearing veins in ultramafic xenoliths recovered from arc volcanoes. Our new B and $\delta^{11}B$ study of such veins in mantle xenoliths from Avachinsky and Shiveluch volcanoes, Kamchatka arc, indicates that slab-derived FMEs, including B and its characteristically high $\delta^{11}B$, are delivered directly to a melt that experiences limited interaction with the surrounding mantle before eruption. The exceptionally low B contents (from 0.2 to 3.1 µg g^{-1}) and low $\delta^{11}B$ (from –16.6‰ to +0.9‰) of mantle xenolith vein minerals are, instead, products of fluids and melts released from the isotopically light subducted and dehydrated altered oceanic crust and, to a lesser extent, from isotopically heavy serpentinite. Therefore, melting of amphibole- and phlogopite-bearing veins in a metasomatized mantle wedge cannot alone produce the characteristic FME geochemistry of arc volcanic rocks, which require a comparatively large, isotopically heavy and B-rich serpentinite-derived fluid component in their source.

INTRODUCTION

Direct observation of the processes of element transfer and isotope fractionations associated with slab dehydration in subduction zones is not possible. However, the classic study of Tatsumi (1989) suggested that a hydrous component released from dehydrating slabs in subduction zones is responsible for the depression of the wet solidus in depleted mantle wedge harzburgite, thus generating fluid-mobile element (FME)–enriched arc volcanic rocks. Contrary to what is seen at mid-ocean ridges, elevated water contents of the subarc mantle control the extensive melting in subduction zones (Kelley et al., 2006). Subsequently, it has been suggested that a slab-derived hydrous fluid or melt percolates through the subarc mantle via an interconnected vein network (Pirard and Hermann, 2015; Plümper et al., 2016), comprising metasomatic mineral phases such as hornblende, phlogopite, and pyroxenes (GSA Data Repository Tables DR1 and DR2[1]). Previous studies (e.g., Kepezhinskas et al., 1995; Kepezhinskas and Defant, 1996) speculated that metasomatic veins could be mantle reservoirs of slab-derived elements, which, upon melting, will generate the characteristic FME-rich signature of arc volcanic rocks. In this model, the role of the subducting hydrated oceanic plate is central to the generation of FME-enriched arc volcanic rocks, since both primitive mantle and mid-oceanic-ridge basalt (MORB) source mantle contain only traces of FMEs (McDonough and Sun, 1995; Marschall et al., 2017).

Rocks from the subarc mantle are rarely exposed at Earth's surface. This, in turn, imposes constraints on our knowledge of the metasomatic processes taking place below volcanic arcs. The Kamchatka arc is exceptional because rare veined mantle xenoliths have been recovered from several volcanoes along the arc, allowing insights into the subarc mantle (Kepezhinskas et al., 1995; Kepezhinskas and Defant, 1996; Arai et al., 2003, 2007; Bryant et al., 2007; Ishimaru et al., 2007; Halama et al., 2009; Ionov, 2010; Ionov et al., 2011, 2013; Bénard et al., 2017, and references therein). Previous Kamchatka studies have demonstrated that depleted, harzburgitic, subarc mantle has been extensively metasomatized by hydrous slab-derived fluids and melts, forming amphibole- and phlogopite-bearing veins. The major- and trace-element characteristics of these veins suggest a transition from fluid-induced mantle metasomatism at the volcanic front and in the southern part of the Central Kamchatka depression (Kepezhinskas and Defant, 1996; Arai et al., 2003, 2007; Ishimaru et al., 2007; Halama et al., 2009; Ionov, 2010; Ionov et al., 2011, 2013; Bénard et al., 2017) to mostly melt-induced mantle metasomatism at its northern part (Kepezhinskas et al., 1995; Bryant et al., 2007; Ionov et al., 2013).

Boron and $\delta^{11}B$ (the per mil difference between the $^{11}B/^{10}B$ of a sample and NIST [U.S.

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[1] GSA Data Repository item 2019192, petrological descriptions, analytical methods, and data tables, is available online at http://www.geosociety.org/datarepository/2019/, or on request from editing@geosociety.org.

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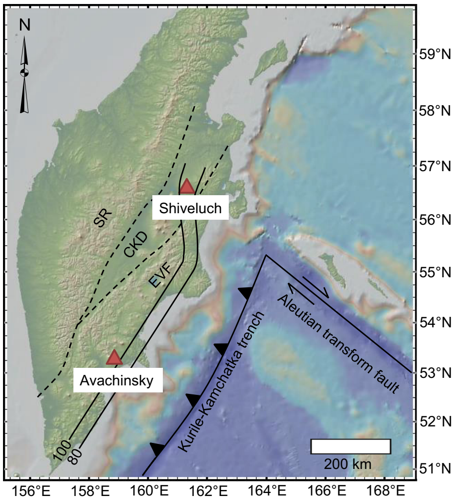

Figure 1. Avachinsky and Shiveluch volcanoes (red triangles) on the Kamchatka peninsula. Eastern volcanic front (EVF), Central Kamchatka depression (CKD), and Sredinny Range (SR) are outlined by dashed lines. Solid lines outline 80 km and 100 km depth-to-slab contours (Gorbatov et al., 1997). Figure is modified from GeoMapApp (http://www.geomapapp.org/; Ryan et al., 2009).

National Institute of Standards and Technology] 951 boric acid) have been widely used in studies of slab-derived fluids in subduction zones (de Hoog and Savov, 2018, and references therein). Boron and its isotopic composition (as δ^{11}B) are particularly sensitive tracers of slab-derived metasomatic agents because of the highly fluid-mobile nature of B (Hervig et al., 2002). Boron is enriched in subducting oceanic lithosphere relative to B-poor mantle (e.g., Marschall et al., 2017), and a wide range of δ^{11}B values (~70‰) is preserved in natural materials (e.g., de Hoog and Savov, 2018, and references therein). However, this versatile tracer has not been employed previously in the investigation of FME budgets in metasomatized (veined) subarc mantle xenoliths. Here, we report, for the first time, B and δ^{11}B measurements demonstrating that metasomatic veins formed by the percolation of hydrous melts and fluids through the subarc mantle cannot play a significant role in the generation of arc magmas.

GEOLOGICAL BACKGROUND

The Kamchatka arc extends from the Kuril Islands in the south to northern Kamchatka, where it terminates at the Aleutian transform fault (Fig. 1). It is situated on the continental margin and consists of three volcanic belts: the Eastern volcanic front (EVF), the Central Kamchatka depression (CKD), and the Sredinny Range (SR; e.g., Churikova et al., 2001; Portnyagin and Manea, 2008). For this study, we collected mantle xenoliths from the Avachinsky and Shiveluch volcanoes (for mineral major-element abundances, petrology, and geothermometry, see the Data Repository), in addition to revisiting the Shiveluch mantle xenolith suite of Bryant et al. (2007).

Avachinsky volcano is located in the EVF (Fig. 1) at a depth-to-slab of ~120 km (Gorbatov et al., 1997). It erupts mainly low-K andesites to basaltic andesites of calc-alkaline affinity (Braitseva et al., 1998) that have the highest B contents and δ^{11}B of all studied Kamchatka volcanoes (36.3 μg g^{-1} and +5.58‰ of a single sample; Ishikawa et al., 2001). Metasomatized harzburgite xenoliths, representative of high-degree partial melt residues (estimated degree of partial melting = 28%–35%; Ionov, 2010), were recovered from an andesitic pyroclastic flow from the I Av stage of volcanic activity (7500–3700 yr ago; Braitseva et al., 1998). Spinel-hosted melt inclusions from Avachinsky harzburgites record low mantle temperatures (as low as 900 °C; Ionov et al., 2011), precluding dry mantle melting in the subarc mantle underneath the volcano (Hirschmann, 2000).

Shiveluch volcano is situated in the northern CKD (Fig. 1) with a depth-to-slab of ~90 km (Gorbatov et al., 1997). It consists primarily of high-Mg# andesites (Gorbach and Portnyagin, 2011; Gorbach et al., 2013) with adakite-like geochemistry (Kepezhinskas et al., 1997; Yogodzinski et al., 2001; Münker et al., 2004). These lavas are attributed to the Kamchatka-Aleutian junction, where hot asthenospheric mantle upwells through a slab window (Peyton et al., 2001; Yogodzinski et al., 2001; Levin et al., 2005). The temperature of the subarc mantle underneath Shiveluch has been estimated to range between 1250 °C and 900 °C (Portnyagin and Manea, 2008), and an estimate of the average pre-eruptive temperature of Shiveluch andesite is ~840 °C (Humphreys et al., 2006). Like Avachinsky, Shiveluch volcanic rocks also have high concentrations of B and high δ^{11}B ratios (24.9 μg g^{-1} and +3.58‰ of a single sample; Ishikawa et al., 2001) and other FMEs, which were attributed to the subduction of the Aleutian transform fault underneath the CKD (Manea et al., 2014). Melt inclusions in Shiveluch volcanic products typically record higher B contents of 50–80 μg g^{-1} but can contain as much as 175 μg g^{-1} of B (Humphreys et al., 2008). An explosive Plinian eruption in 1964 (Belousov, 1995) brought a range of mantle xenoliths to the surface (Bryant et al., 2007), some of which are studied here (see Data Repository material).

RESULTS

Boron contents and δ^{11}B ratios of the hydrous vein minerals (amphibole and phlogopite) and nominally anhydrous mantle minerals (olivine, pyroxene, and plagioclase) were measured by secondary ion mass spectrometry (SIMS) using a Cameca 1270 ion microprobe at the University of Edinburgh (for analytical methods, see the Data Repository).

Avachinsky vein minerals are low in B (0.2–0.9 μg g^{-1}) and possess light δ^{11}B (–16.6‰ to –3.6‰), whereas B contents of Shiveluch vein minerals extend to values as high as 3.1 μg g^{-1} and higher δ^{11}B (–13.8‰ to +0.9‰; Fig. 2; Table DR4). Nominally anhydrous mantle minerals have low B contents (0.3–2.1 μg g^{-1}) and low δ^{11}B (–13.8‰ to –3.2‰; Fig. DR5). Vein minerals in Kamchatka mantle xenoliths are only slightly enriched in B relative to depleted mantle (Marschall et al., 2017), and their δ^{11}B values do not extend to the higher end of the range of δ^{11}B observed in Kamchatka arc volcanic rocks (B = 11.2–36.3 μg g^{-1}; δ^{11}B = –3.7‰ to +5.6‰; Ishikawa et al., 2001). The low B contents and δ^{11}B of the nominally anhy-

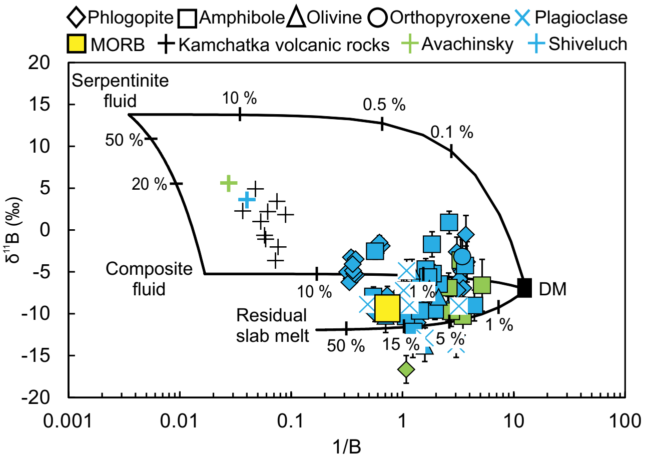

Figure 2. δ^{11}B versus 1/B in vein minerals in Avachinsky (green) and Shiveluch (blue) mantle xenoliths, Kamchatka volcanic rocks (Ishikawa et al., 2001), and mid-oceanic-ridge basalt (MORB; Marschall et al., 2017) and mixing relationships among depleted mantle (DM; Marschall et al., 2017), serpentinite fluid (Tonarini et al., 2011), composite slab fluid released at 120 km depth, and residual slab melt (calculated after Tonarini et al. [2011], with an additional dehydration stage at 25 km corresponding to 80% B loss in forearc; Savov et al., 2007). Composite fluid consists of 99% fluid released from altered oceanic crust and 1% fluid released from sediment. Detailed modeling procedure and model input parameters are provided in the Data Repository and Table DR5 therein (see text footnote). Boron concentrations and δ^{11}B of nominally anhydrous minerals are plotted in Figure DR5. All symbols are larger than error bars, unless shown.

drous mantle minerals are comparable to previous studies of mantle composition (Harvey et al., 2014, and references therein; Marschall et al., 2017) and will not be discussed further.

DISCUSSION

Contrary to earlier predictions of metasomatized mantle wedge playing a fundamental role in generating the characteristic FME-enriched arc volcanic rocks (e.g., Kepezhinskas et al., 1995; Kepezhinskas and Defant, 1996), the low B abundances and δ^{11}B values of the metasomatized subarc mantle are unexpected. The majority of vein compositions can be reproduced by mixing of variable amounts of three components: (1) isotopically light composite slab fluid, (2) residual slab melt, and (3) the depleted mantle (Fig. 2; for model input parameters, see Table DR5). Slab-derived fluids can be generated either by dehydration of mélange diapirs in the subarc mantle under the arc front (Savov et al., 2007; Nielsen and Marschall, 2017, and references therein) and/or by serpentine breakdown in the forearc, followed by dehydration of altered oceanic crust (AOC) by chlorite and amphibole breakdown under the arc front, as previously proposed in the Kamchatka subduction zone model (Konrad-Schmolke and Halama, 2014). Other hydrous minerals typically constituting the AOC, such as lawsonite and phengite, are absent in the top 10 km of the subducting slab in Kamchatka and are therefore not likely to contribute B to the subarc mantle (Konrad-Schmolke and Halama, 2014).

Dehydration of sediments and AOC, in response to rising pressure and temperature with ongoing subduction, leads to B isotopic fractionation between fluids and silicates, specifically, ^{11}B depletion in silicates. Trigonally coordinated ^{11}B preferentially partitions into fluids, and tetrahedrally coordinated ^{10}B partitions into silicate minerals and melts in low-pH environments (Kakihana et al., 1977; Peacock and Hervig, 1999; Hervig et al., 2002; Wunder et al., 2005; Pabst et al., 2012; Konrad-Schmolke and Halama, 2014). Therefore, vein amphibole and phlogopite preserving low δ^{11}B (i.e., <–7‰) may have equilibrated with slab fluid released by chlorite dehydration in the AOC (Rüpke et al., 2004; Konrad-Schmolke and Halama, 2014) or residual slab melt generated at ~90–120 km depth-to-slab, assuming vertical transport of the released fluid or melt. In cold subduction zones, fully hydrated AOC and sediments dehydrate in several steps before they are subducted to 120 km (Rüpke et al., 2004), where they release isotopically light B upon their dehydration (Fig. 2). Isotopically light fluid, however, could also have been released by dehydration of serpentinite that interacted with sediment (Cannaò et al., 2015).

The higher δ^{11}B (>–5‰) of some of the vein minerals requires at least some forearc serpentinite fluid influx (δ^{11}B = ~14‰; Tonarini et al., 2011) into the subarc mantle. Vein amphiboles with the highest δ^{11}B require up to 15% of their B contents to be derived from serpentinite and 85% from a composite lithology comprising 99% AOC and 1% sediment (Fig. 2).

Our data demonstrate a negligible contribution to the otherwise large outfluxes of boron at volcanic arcs. The veins represent a volumetrically minor mantle B end member with insufficient B concentrations to significantly skew the composition of the erupted arc volcanic rocks. Instead, a slab-derived component enriched in ^{11}B must transit relatively rapidly through the mantle wedge (Fig. 3). In Kamchatka, the limited sedimentary pile (435 m of ashy-siliceous clay; Plank, 2014) and the AOC are not likely to carry B deeper than the forearc, as more than 80% of their original boron content is released during shallow slab dehydration (Savov et al., 2007), and its further dehydration under the arc front releases isotopically light fluids (δ^{11}B = –5.2‰; Fig. 2).

Several prior studies have established that serpentinite can host up to 80 μg g^{-1} B and retain a high δ^{11}B signature of up to +25‰ in shallow subduction settings (Benton et al., 2001; Scambelluri and Tonarini, 2012; Harvey et al., 2014; de Hoog and Savov, 2018, and references therein). The results of our model suggest that fluids from dehydration of subducted forearc serpentinite and AOC, rather than metasomatized veins in the subarc mantle, are responsible for the boron elemental and isotopic signature of Kamchatka arc volcanic rocks (Fig. 2; Ishikawa et al., 2001; Churikova et al., 2007).

It has been shown that the initially high δ^{11}B value of slab fluid rapidly decreases as it moves away from the dehydration site (Prigent et al., 2018), unless the fluid flow is focused in an interconnected vein network (Fig. 3; Pirard and Hermann, 2015; Plümper et al., 2016). The fluid flow through this vein network must be rapid for only limited chemical exchange to occur between the vein minerals and the percolating slab-derived fluid (e.g., John et al., 2012). Large variations of δ^{11}B in amphibole and phlogopite in samples SHX03-18, SHX03-04, and SH98X-16 (Fig. 2; Table DR4) suggest that the veins investigated in this study sampled multiple pulses of slab-derived fluids and melts originating from different depths. Alternatively, the slab-derived fluids and melts could have been sourced by mélange diapirs in the mantle wedge (Nielsen and Marschall, 2017, and references therein) that are composed of a mixture of slab and hydrated forearc mantle lithologies with variable δ^{11}B compositions.

CONCLUSIONS

The boron contents and δ^{11}B values of vein minerals in Kamchatka arc xenoliths from Shiveluch and Avachinsky volcanoes are inconsistent with the interpretation that they provide a significant contribution to the boron budget of Kamchatka arc volcanic products. The veins record multiple pulses of fluids and melts percolating through the subarc mantle, ranging from isotopically light AOC-derived fluids and melts to isotopically heavy forearc serpentinite-derived fluids. The fluid flow appears to be focused in veins connecting either the slab dehydration sites or mélange diapirs with the magma-generation region to facilitate the rapid transport of heavy B to arc magmas, with limited interaction with the vein minerals.

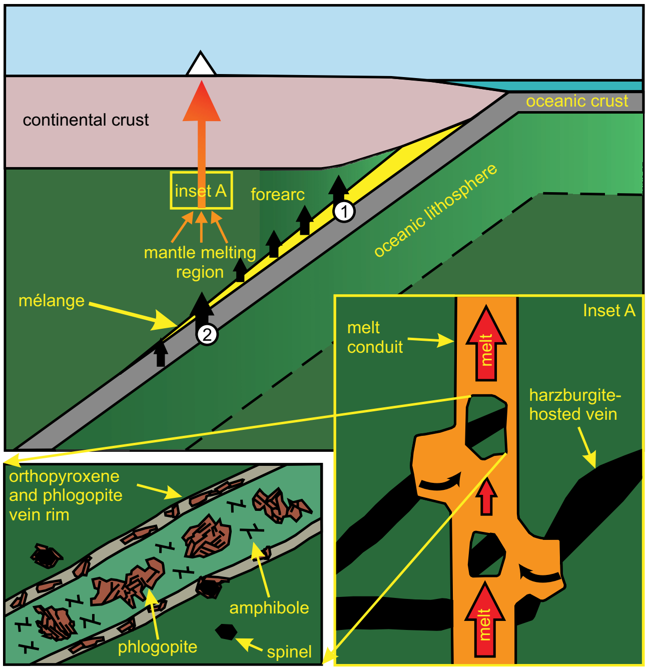

Figure 3. In Kamchatka, slab-derived fluids (black arrows) can be generated either by mélange diapir dehydration in mantle wedge (Nielsen and Marschall, 2017) or by (1) serpentine breakdown in forearc, and (2) chlorite and amphibole breakdown in altered oceanic crust (AOC) at 90–120 km depth-to-slab. B-rich, isotopically heavy, slab-derived fluid is transferred through subarc mantle by interconnected network of veins crosscutting mantle harzburgite, fragments of which are entrained into magma (orange arrows) on its way up to surface (inset A). Inset A position corresponds to depth from which xenoliths were derived (30–50 km).

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