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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 δ11B study of such veins in mantle xenoliths from Avachinsky and Shiveluch volcanoes, Kamchatka arc, indicates that slab-derived FMEs, including B and its characteristic high δ11B, 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 δ11B (from −16.6‰ to +9.9‰) 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 solids 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; Pflümpner et al., 2016), comprising metasomatic mineral phases such as hornblende, phlogopite, and pyroxenes (GSA Data Repository Tables DR1 and DR2). 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; Ari 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; Ari 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 δ11B (the per mil difference between the 11B/9B of a sample and NIST [U.S. Geosociety of America, 1993] B-1206)] standards) of arc volcanic rocks have been used as a proxy for mantle hydration (e.g., Tatsumi et al., 1998; Pflümpner et al., 2016). However, samples with exceptional δ11B values (+9.9‰ to +12.5‰) are common in the Kamchatka arc, which challenge this approach. Yet, B has been considered to be a suitable tracer of metasomatism because it is correlated with Li (Niesler et al., 2007; Pflümpner et al., 2016), both being highly incompatible in subarc mantle. Given the Zr-B coexistence in amphibole (Biddle and House, 1997), the unexpectedly high δ11B values would indicate an additional source of boron.

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1GSA Data Repository item 2019192, petrological descriptions, analytical methods, and data tables, is available online at http://www.geosociety.org/datarepository/2019/192/ or on request from editing@geosociety.org.

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 δ11B) 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., Marshall et al., 2017), and a wide range of δ11B 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 δ11B 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.

GOEDELOGICAL 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 δ11B 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 arc-eruptive pyroclastic flow from the 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 under 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; Yodogzinski 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; Yodogzinski 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 volcanoes (36.3 µg g–1) that have the highest δ11B of all studied Kamchatka volcanic products typically record the range of δ11B observed in Kamchatka arc volcanic rocks (B = 11.2–36.3 µg g–1; δ11B = –3.7‰ to +5.6‰; Ishikawa et al., 2001). The low B contents and δ11B of the nominally anhydrous melts and fluids 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 δ11B 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., Kepezhsikas et al., 1995; Kepezhsikas and Defant, 1996), the low B abundances and $\delta^{11}$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 mélangé 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 $^{11}$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 $\delta^{11}$B (i.e., $< -7\%e$) may have equilibrated with slab fluid released by chlorite dehydration in the AOC (Rüpké 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 (Rüpké 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 (Cannăo et al., 2015).

The higher $\delta^{11}$B (>$5\%e$) of some of the vein minerals requires at least some forearc serpen-
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