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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 δ^{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 δ^{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 $\mu g g^{-1}$) 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

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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 DR2¹). 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.

¹GSA 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 depthto-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 $\delta^{11}B$) are particularly sensitive tracers of slab-derived metasomatic agents because of the highly fluidmobile 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 $\delta^{11}B$ 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 μ g g⁻¹ and +5.58% of a single sample; Ishikawa et al., 2001). Metasomatized harzburgite xenoliths, representative of highdegree 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 adakitelike 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 vol-

Figure 2. $\delta^{11}B$ versus 1/B in vein minerals in Avachinsky (green) and Shiveluch (blue) mantle xenoliths, Kamchatka volcanic rocks (Ishikawa et al., 2001), and midoceanic-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

canic 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 $\delta^{11}B$ 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 μ g 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 $\delta^{11}B$ (-13.8% to +0.9%; Fig. 2; Table DR4). Nominally anhydrous mantle minerals have low B contents (0.3–2.1 μ g g⁻¹) and low $\delta^{11}B$ (-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 $\delta^{11}B$ 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-





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 FMEenriched arc volcanic rocks (e.g., Kepezhinskas et al., 1995; Kepezhinskas 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 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, ¹¹B depletion in silicates. Trigonally coordinated ¹¹B preferentially partitions into fluids, and tetrahedrally coordinated ¹⁰B 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 $\delta^{\rm 11}B$ (i.e., $<\!\!-7\%{\it o})$ 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 $\delta^{11}B$ (>-5%) of some of the vein minerals requires at least some forearc serpen-

tinite fluid influx ($\delta^{11}B = ~14\%$; Tonarini et al., 2011) into the subarc mantle. Vein amphiboles with the highest $\delta^{11}B$ 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 ¹¹B 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 ($\delta^{11}B$ = -5.2%; Fig. 2).

Several prior studies have established that serpentinite can host up to $80 \ \mu g \ g^{-1}$ 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 $\delta^{11}B$ 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 slabderived fluid (e.g., John et al., 2012). Large variations of $\delta^{11}B$ 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 $\delta^{11}B$ 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, slabderived 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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REFERENCES CITED

- Arai, S., Ishimaru, S., and Okrugin, V.M., 2003, Metasomatized harzburgite xenoliths from Avacha volcano as fragments of mantle wedge of the Kamchatka arc: Implication for the metasomatic agent: The Island Arc, v. 12, p. 233–246, https:// doi.org/10.1046/j.1440-1738.2003.00392.x.
- Arai, S., Abe, N., and Ishimaru, S., 2007, Mantle peridotites from the western Pacific: Gondwana Research, v. 11, p. 180–199, https://doi.org/10 .1016/j.gr.2006.04.004.
- Belousov, A.B., 1995, The Shiveluch volcanic eruption of 12 November 1964—Explosive eruption provoked by failure of the edifice: Journal of Volcanology and Geothermal Research, v. 66, p. 357–365, https://doi.org/10.1016/0377-0273 (94)00072-O.
- Bénard, A., Koga, K.T., Shimizu, N., Kendrick, M.A., Ionov, D.A., Nebel, O., and Arculus, R.J., 2017, Chlorine and fluorine partition coefficients and abundances in sub-arc mantle xenoliths (Kamchatka, Russia): Implications for melt generation and volatile recycling processes in subduction zones: Geochimica et Cosmochimica Acta, v. 199, p. 324–350, https://doi.org/10.1016/j.gca 2016 10 035
- Benton, L.D., Ryan, J.G., and Tera, F., 2001, Boron isotope systematics of slab fluids as inferred from a serpentine seamount, Mariana forearc: Earth and Planetary Research Letters, v. 187, p. 273–282, https://doi.org/10.1016/S0012-821X(01)00286-2.
- Braitseva, O.A., Bazanova, L.I., Melekestsev, I.V., and Sulerzhitsky, L.D., 1998, Large Holocene eruptions of Avacha volcano, Kamchatka (7250–3700 ¹⁴C years B.P.): Volcanology and Seismology, v. 20, p. 1–27.
- Bryant, J.A., Yogodzinski, G.M., and Churikova, T.G., 2007, Melt-mantle interactions beneath the Kamchatka arc: Evidence from ultramafic xenoliths from Shiveluch volcano: Geochemistry Geophysics Geosystems, v. 8, Q04007, https://doi.org/10 .1029/2006GC001443.
- Cannaò, E., Agostini, S., Scambelluri, M., Tonarini, S., and Godard, M., 2015, B, Sr and Pb isotope geochemistry of high-pressure Alpine metaperidotites monitors fluid-mediated element recycling during serpentinite dehydration in subduction mélange (Cima di Gagnone, Swiss Central Alps): Geochimica et Cosmochimica Acta, v. 163, p. 80–100, https://doi.org/10.1016 /j.gca.2015.04.024.
- Churikova, T., Dorendorf, F., and Wörner, G., 2001, Sources and fluids in the mantle wedge below Kamchatka: Evidence from across-arc geochemical variation: Journal of Petrology, v. 42, p. 1567–1593, https://doi.org/10.1093/petrology /42.8.1567.
- Churikova, T., Wörner, G., Mironov, N., and Kronz, A., 2007, Volatile (S, Cl and F) and fluid mobile trace element compositions in melt inclusions: Implications for variable fluid sources across the

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Kamchatka arc: Contributions to Mineralogy and Petrology, v. 154, p. 217–239, https://doi.org/10 .1007/s00410-007-0190-z.

- de Hoog, J.C.M., and Savov, I.P., 2018, Boron isotopes as a tracer of subduction zone processes, *in* Marschall, H., and Foster, G., eds., Boron Isotopes: The Fifth Element: Advances in Isotope Geochemistry: Cham, Springer International Publishing, 217 p., https://doi.org/10.1007/978 -3-319-64666-4_9.
- Gorbach, N., and Portnyagin, M.V., 2011, Geology and petrology of the lava complex of Young Shiveluch volcano, Kamchatka: Petrology, v. 19, p. 134–166, https://doi.org/10.1134 /S0869591111020068.
- Gorbach, N., Portnyagin, M., and Tembrel, I., 2013, Volcanic structure and composition of Old Shiveluch volcano, Kamchatka: Journal of Volcanology and Geothermal Research, v. 263, p. 193–208, https:// doi.org/10.1016/j.jvolgeores.2012.12.012.
- Gorbatov, A., Kostoglodov, V., and Suárez, G., 1997, Seismicity and structure of the Kamchatka subduction zone: Journal of Geophysical Research, v. 102, no. B8, p. 17,883–17,898, https://doi.org /10.1029/96JB03491.
- Halama, R., Savov, I.P., Rudnick, R.L., and Mc-Donough, W.F., 2009, Insights into Li and Li isotope cycling and sub-arc metasomatism from veined mantle xenoliths, Kamchatka: Contributions to Mineralogy and Petrology, v. 158, p. 197– 222, https://doi.org/10.1007/s00410-009-0378-5.
- Harvey, J., Garrido, C.J., Savov, I., Agostini, S., Padrón-Navarta, J.A., Marchesi, C., Sánchez-Vizcaíno, V.L., and Gómez-Pugnaire, M.T., 2014, ¹¹B-rich fluids in subduction zones: The role of antigorite dehydration in subducting slabs and boron isotope heterogeneity in the mantle: Chemical Geology, v. 376, p. 20–30, https://doi.org/10 .1016/j.chemgeo.2014.03.015.
- Hervig, R.L., Moore, G.M., Williams, L.B., Peacock, S.M., Holloway, J.R., and Roggensack, K., 2002, Isotopic and elemental partitioning of boron between hydrous fluid and silicate melt: The American Mineralogist, v. 87, p. 769–774, https://doi .org/10.2138/am-2002-5-620.
- Hirschmann, M.M., 2000, Mantle solidus: Experimental constraints and the effects of peridotite composition: Geochemistry Geophysics Geosystems, v. 1, no. 10, https://doi.org/10.1029 /2000GC000070.
- Humphreys, M.C.S., Blundy, J.D., and Sparks, R.S.J., 2006, Magma evolution and open-system processes at Shiveluch volcano: Insights from phenocryst zoning: Journal of Petrology, v. 47, p. 2303– 2334, https://doi.org/10.1093/petrology/egl045.
- Humphreys, M.C.S., Blundy, J.D., and Sparks, R.S.J., 2008, Shallow-level decompression crystallisation and deep magma supply at Shiveluch volcano: Contributions to Mineralogy and Petrology, v. 155, p. 45–61, https://doi.org/10.1007/s00410 -007-0223-7.
- Ionov, D.A., 2010, Petrology of mantle wedge lithosphere: New data on supra-subduction zone peridotite xenoliths from the andesitic Avacha volcano, Kamchatka: Journal of Petrology, v. 51, p. 327–361, https://doi.org/10.1093/petrology /egp090.
- Ionov, D.A., Bénard, A., and Plechov, P.Y., 2011, Melt evolution in subarc mantle: Evidence from heating experiments on spinel-hosted melt inclusions in peridotite xenoliths from the andesitic Avacha volcano (Kamchatka, Russia): Contributions to Mineralogy and Petrology, v. 162, p. 1159–1174, https://doi.org/10.1007/s00410-011-0645-0.
- Ionov, D.A., Benard, A., Plechov, P.Yu., and Shcherbakov, V.D., 2013, Along-arc variations in

lithospheric mantle compositions in Kamchatka, Russia: First trace element data on mantle xenoliths from the Klyuchevskoy group volcanoes: Journal of Volcanology and Geothermal Research, v. 263, p. 122–131, https://doi.org/10 .1016/j.jvolgeores.2012.12.022.

- Ishikawa, T., Tera, F., and Nakazawa, T., 2001, Boron isotope and trace element systematics of the three volcanic zones in the Kamchatka arc: Geochimica et Cosmochimica Acta, v. 65, p. 4523–4537, https://doi.org/10.1016/S0016-7037(01)00765-7.
- Ishimaru, S., Arai, S., Ishida, Y., Shirasaka, M., and Okrugin, V.M., 2007, Melting and multi-stage metasomatism in the mantle wedge beneath a frontal arc inferred from highly depleted peridotite xenoliths from the Avacha volcano, southern Kamchatka: Journal of Petrology, v. 48, p. 395– 433, https://doi.org/10.1093/petrology/egl065.
- John, T., Gussone, N., Podladchikov, Y.Y., Bebout, G.E., Dohmen, R., Halama, R., Klemd, R., Magna, T., and Seitz, H.-M., 2012, Volcanic arcs fed by rapid pulsed fluid flow through subducting slabs: Nature Geoscience, v. 5, p. 489–492, https://doi.org/10.1038/ngeo1482.
- Kakihana, H., Kotaka, M., Satoh, S., Nomura, M., and Okamoto, M., 1977, Fundamental studies on the ion-exchange separation of boron isotopes: Bulletin of the Chemical Society of Japan, v. 50, p. 158–163, https://doi.org/10.1246/bcsj.50.158.
- Kelley, K.A., Plank, T., Grove, T.L., Stolper, E.M., Newman, S., and Hauri, E., 2006, Mantle melting as a function of water content beneath back-arc basins: Journal of Geophysical Research, v. 111, B09208, https://doi.org/10.1029/2005JB003732.
- Kepezhinskas, P., and Defant, M.J., 1996, Contrasting styles of mantle metasomatism above subduction zones: Constraints from ultramafic xenoliths in Kamchatka, *in* Bebout, G.E., Scholl, D.W., Kirby, S.H., and Platt, J.P., eds., Subduction Top to Bottom: American Geophysical Union Geophysical Monograph 96, p. 307–314.
- Kepezhinskas, P., Defant, M.J., and Drummond, M.S., 1995, Na metasomatism in the island-arc mantle by slab melt–peridotite interaction: Evidence from mantle xenoliths in the north Kamchatka arc: Journal of Petrology, v. 36, p. 1505–1527, https://doi .org/10.1093/oxfordjournals.petrology.a037263.
- Kepezhinskas, P., McDermott, F., Defant, M.J., Hochstaedter, A., Drummond, M.S., Hawkesworth, C.J., Koloskov, A., Maury, R.C., and Bellon, H., 1997, Trace element and Sr-Nd-Pb isotopic constraints on a three-component model of Kamchatka arc petrogenesis: Geochimica et Cosmochimica Acta, v. 61, p. 577–600, https://doi.org /10.1016/S0016-7037(96)00349-3.
- Konrad-Schmolke, M., and Halama, R., 2014, Combined thermodynamic-geochemical modeling in metamorphic geology: Boron as tracer of fluidrock interaction: Lithos, v. 208–209, p. 393–414, https://doi.org/10.1016/j.lithos.2014.09.021.
- Levin, V., Shapiro, N.M., Park, J., and Ritzwoller, M.H., 2005, Slab portal beneath the western Aleutians: Geology, v. 33, p. 253–256, https:// doi.org/10.1130/G20863.1.
- Manea, V.C., Leeman, W.P., Gerya, T., Manea, M., and Zhu, G., 2014, Subduction of fracture zones controls mantle melting and geochemical signature above slabs: Nature Communications, v. 5, 5095, https://doi.org/10.1038/ncomms6095.
- Marschall, H.R., Wanless, V.D., Shimizu, N., Pogge von Strandmann, P.A.E., Elliot, T., and Monteleone, B.D., 2017, The boron and lithium isotopic composition of mid-ocean ridge basalts and the mantle: Geochimica et Cosmochimica Acta, v. 207, p. 102–138, https://doi.org/10.1016/j.gca .2017.03.028.

- McDonough, W.F., and Sun, S.-s., 1995, The composition of the Earth: Chemical Geology, v. 120, p. 223–253, https://doi.org/10.1016/0009-2541 (94)00140-4.
- Münker, C., Wörner, G., Yogodzinski, G., and Churikova, T., 2004, Behaviour of high field strength elements in subduction zones: Constraints from Kamchatka-Aleutian arc lavas: Earth and Planetary Science Letters, v. 224, p. 275–293, https://doi.org/10.1016/j.epsl.2004.05.030.
- Nielsen, S.G., and Marschall, H.R., 2017, Geochemical evidence for mélange melting in global arcs: Science Advances, v. 3, no. 4, p. e1602402, https://doi.org/10.1126/sciadv.1602402.
- Pabst, S., Zack, T., Savov, I.P., Ludwig, T., Rost, D., Tonarini, S., and 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, v. 132–133, p. 162– 179, https://doi.org/10.1016/j.lithos.2011.11.010.
- Peacock, S.M., and Hervig, R.L., 1999, Boron isotopic composition of subduction-zone metamorphic rocks: Chemical Geology, v. 160, p. 281–290, https://doi.org/10.1016/S0009-2541(99)00103-5.
- Peyton, V., Levin, V., Park, J., Brandon, M., Lees, J., Gordeev, E., and Ozerov, A., 2001, Mantle flow at a slab edge: Seismic anisotropy in the Kamchatka region: Geophysical Research Letters, v. 28, p. 379–382, https://doi.org/10.1029 /2000GL012200.
- Pirard, C., and Hermann, J., 2015, Focused fluid transfer through the mantle above subduction zones: Geology, v. 43, p. 915–918, https://doi.org/10 .1130/G37026.1.

- Plank, T., 2014, The chemical composition of subducting sediments, *in* Holland, H., and Turekian, K., eds., Treatise on Geochemistry Volume 4: Amsterdam, Elsevier Ltd., p. 607–629, https://doi.org /10.1016/B978-0-08-095975-7.00319-3.
- Plümper, O., John, T., Podladchikov, Y.Y., Vrijmoed, J.C., and Scambelluri, M., 2016, Fluid escape from subduction zones controlled by channelforming reactive porosity: Nature Geoscience, v. 10, p. 150–156, https://doi.org/10.1038 /ngeo2865.
- Portnyagin, M., and Manea, V.C., 2008, Mantle temperature control on composition of arc magmas along the Central Kamchatka depression: Geology, v. 36, p. 519–522, https://doi.org/10.1130 /G24636A.1.
- Prigent, C., Guillot, P.A., Lemarchand, D., Soret, M., and Ulrich, M., 2018, Transfer of subduction fluids into the deforming mantle wedge during nascent subduction: Evidence from trace elements and boron isotopes (Semail ophiolite, Oman): Earth and Planetary Science Letters, v. 484, p. 213–228, https://doi.org/10.1016/j.epsl .2017.12.008.
- Rüpke, L.H., Morgan, J.P., Hort, M., and Conolly, J.A.D., 2004, Serpentine and the subduction zone water cycle: Earth and Planetary Science Letters, v. 223, p. 17–34, https://doi.org/10.1016/j.epsl .2004.04.018.
- Ryan, W.B.F., Carbotte, S.M., and Coplan, J.O., 2009, Global multi-resolution topography synthesis: Geochemistry Geophysics Geosystems, v. 10, Q03014, https://doi.org/10.1029/2008GC002332.
- Savov, I.P., Ryan, J.G., D'Antonio, M., and 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, v. 112, B09205, https://doi.org/10 .1029/2006JB004749.

- Scambelluri, M., and Tonarini, S., 2012, Boron isotope evidence for shallow fluid transfer across subduction zones by serpentinized mantle: Geology, v. 40, p. 907–910, https://doi.org/10.1130 /G33233.1.
- Tatsumi, Y., 1989, Migration of fluid phases and genesis of basalt magmas in subduction zones: Journal of Geophysical Research, v. 94, no. B4, p. 4697– 4707, https://doi.org/10.1029/JB094iB04p04697.
- Tonarini, S., Leeman, W.P., and Leat, P.T., 2011, Subduction erosion of forearc mantle wedge implicated in the genesis of the South Sandwich Island (SSI) arc: Evidence from boron isotope systematics: Earth and Planetary Science Letters, v. 301, p. 275–284, https://doi.org/10.1016 /j.epsl.2010.11.008.
- Wunder, B., Meixner, A., Romer, R.L., Wirth, R., and Heinrich, W., 2005, The geochemical cycle of boron: Constraints from boron isotope partitioning experiments between mica and fluid: Lithos, v. 84, p. 206–216, https://doi.org/10.1016/j.lithos .2005.02.003.
- Yogodzinski, G.M., Lees, J.M., Churikova, T.G., Dorendorf, F., Wöerner, G., and Volynets, O.N., 2001, Geochemical evidence for the melting of subducting oceanic lithosphere at plate edges: Nature, v. 409, p. 500–504, https://doi.org/10 .1038/35054039.

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