Boron isotope insights into the origin of subduction signatures in continent-continent collision zone volcanism

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Abstract

We present the first boron abundance and δ11B data for young (15-0 Ma) volcanic rocks formed in an active continent-continent collision zone. The δ11B of post-collisional volcanic rocks (~5 to +2‰) from the Armenian sector of the Arabia-Eurasia collision zone are heavier than mid-ocean ridge basalts (MORB), confirming trace element and isotope evidence for their derivation from a subduction-modified mantle source. Based on the low B/Nb (0.03-0.25 vs 0.2-90 in arc magmas), as well as low Ba/Th and Pb/Ce, this source records a subduction signature which is presently fluid-mobile element depleted relative to most arc settings. The heavier than MORB δ11B of post-collision volcanic rocks argues against derivation of their subduction signature from a stalled slab, which would be expected to produce a component with a lighter than MORB δ11B due to previous fluid depletion. Instead, the similarity of δ11B in Plio-Pleistocene post-collision to 41 Ma alkaline igneous rocks also from Armenia (and also presented in this study), suggests that the subduction signature is inherited from Mesozoic-Paleogene subduction of Neotethys oceanic slabs. The slab component is then stored in the mantle lithosphere in amphibole, which is consistent with the low [B] in both Armenian volcanic rocks and metasomatic amphibole in mantle xenoliths. Based on trace element and radiogenic isotope systematics, this slab component is thought to be dominated by sediment melts (or supercritical fluids). Previously published δ11B of metasediments suggests a sediment-derived metasomatic agent could produce the B isotope composition observed in Armenian volcanic rocks. The lack of evidence for aqueous fluids preserved over the 40 Myr since initial collision supports observations that this latter component is transitory, while the lifetime of sediment melts/supercritical fluids can be extended to >40 Myr.

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1. Introduction

Boron (B) and its stable isotopes 10B and 11B are a key tracer for the fate of slab-derived components under volcanic arcs (De Hoog and Savov, 2018; Hulet et al., 2016; Ishikawa and Nakamura, 1994; Ishikawa and Tera, 1997; Le Voyer et al., 2008; Morris et al., 1990; Palmer, 1991; Peacock and Hervig, 1999; Rose et al., 2001). This is due to a scarcity of boron in the mantle (<0.2 ppm; Chausidion and Jambon, 1994; Kamenetsky and Eggins, 2012; Marshall et al., 2017; Ryan et al., 1996) and its strong fluid partitioning, with concomitant isotope fractionation during metamorphic slab dehydration reactions which release aqueous fluids at T < 800°C (Konrad-Schmolke and Halama, 2014; Scambelluri et al., 2004; Wunder et al., 2005). B isotope fractionation is largely controlled by the preferential incorporation of 11B into trigonal over tetrahedral sites (Kakihana et al., 1977; Palmer et al., 1987). Thus B is strongly fractionated between mostly tetrahedrally co-ordinated B in silicate minerals and trigonally co-ordinated B in aqueous fluids (Peacock and Hervig, 1999; Wunder et al., 2005). This fractionation is preserved in arc magmas because later mantle melting should not lead to isotope fractionation as B is substantially tetrahedrally co-ordinated in both mantle minerals and magmas (Maner and London, 2018; Tonarini et al., 2001).

Only a handful of studies have used B to explore the impact of slab-derived components on the upper mantle (magma source) composition in regions where subduction has ceased (Agostini et al., 2008; Liu et al., 2016; Tonarini et al., 2005). We present whole-rock [B] and δ11B data for well-studied collision-related igneous
rocks from Armenia (Sokół et al., 2018; Sugden et al., 2019), in the northern part of the Arabia-Eurasia collision zone (Fig. 1a), representing the first boron isotope data for volcanic rocks from an active continent-continent collision. This collision zone is unique on Earth as a modern continental collision zone associated with widespread mantle-derived magmatism. Magmas from the southern part of the collision zone (e.g. Lake Van, Eastern Anatolia) have OIB-like (ocean island basalt) characteristics, whereas those from the north have arc-like geochemistry (Pearce et al., 1990). The arc-like geochemistry of Armenian volcanic rocks (Fig. 2, see also Table S1 in Supplementary Material) reflects a subduction-modified magma source. The [B] and δ11B data presented in this study come from 1.5-0 Ma post-collisional volcanic rocks, as well as ~41 Ma alkaline igneous rocks, the latter are used to investigate the δ11B variations in the subduction-modified mantle since the onset of continental collision. We then use these new [B] and δ11B data, alongside previously published trace element and Sr-Nd isotope data in order to investigate the nature of the slab component.

2. Geological background

The geology of Armenia is defined by the closure of the Neotethys Ocean which resulted in the Arabia-Eurasia continent-continent collision. It can be summarised as several accretion terranes overlain by younger volcanic and sedimentary units (Fig. 1b). The accretion terranes are the Mesozoic arc of the Lesser Caucasus and the South Armenian Block (SAB; a Gondwanan microcontinental fragment composed of Proterozoic metamorphic basement and its sedimentary cover; Knipper and Khain, 1980), joined at the Sevan-Akera suture zone defined by several ophiolite terranes (Rolland et al., 2009). Eventual collision was facilitated by closure of several basins along numerous subduction zones, some of the products of which formed the Mesozoic arc in NE Armenia. Closure of the Neotethys Ocean (Fig. 1) at ~70-60 Ma (Rolland et al., 2009). Subduction then jumped to the south until closure of the Southern Neotethys with the collision of Arabia with SAB-Eurasia along the Bitlis-Zagros suture (Fig. 1a) at ~50-40 Ma (Rolland et al., 2012), although some authors have posited a collision as late as ~25 Ma (Okay et al., 2010).

The investigated Plio-Pleistocene post-collisional volcanic rocks are from three volcanic highlands of distributed volcanism (Syunik, Vardenis and Gegham) and the large Aragats stratovolcano (Fig. 1b). Volcanic products have basanite to rhyolite compositions, with SiO2 between 45 and 78 wt% and MgO between 0 and 8 wt%. Most eruptions formed lava flows and/or scoria cones, although the occurrence of some ignimbrite deposits indicates that there have been larger Plinian caldera-forming eruptions in the past. All samples show characteristic negative Nb-Ta and Ti anomalies and positive spikes in Ba, K, Pb and Sr (Fig. 2a). Crustal contamination is known to have not played a role in the petrogenesis of the volcanic rocks (Sugden et al., 2019), necessitating a mantle source modified by subduction. Volcanism is attributed to melting of lithospheric mantle in response to heating due to delamination or relaxation of non-linear geothermal gradients (Sugden et al., 2019). K-Ar and Ar-Ar ages for lava flows, pumice layers and ignimbrites from Syunik, Aragats and Gegham are ~1.5 Ma (Connor et al., 2011;
In the same way as volcanic arcs, the slab component must be liberated from a subducting slab and transported by a metasomatic agent. However, because the component is inherited, it must also be stored prior to melting. Here, we use the term “slab component” to refer to both the metasomatic agent and the stored component.

3. Analytical methods

As one of the most fluid-mobile elements, B and its isotopes are extremely susceptible to surface alteration. For detailed information on sample selection, the extent of alteration in Armenian igneous rocks, and how alteration was avoided, refer to the Supplementary Material.

Most (19) of the samples were prepared for boron isotope analysis at the ICG-CNR Pisa, Italy; ∼0.2 g of sample powder was fused with K2CO3 in platinum crucibles with a 4:1 flux to sample ratio. Boron was then extracted from the fusion cakes by repeated crushing and centrifuging of the cakes in high pH B-free water. It was further purified by passing the solution through anion and cation exchange columns. Anion columns were packed with Amberlite IRA-743 boron-specific anion exchange resin, while cation-exchange columns were packed with AG 50W-X8 resin. The procedure used an anion column step, followed by a cation column step and then a final (repeat) anion column step to produce the final purified boron solution, as described by Tonarini et al. (1997).

Of those samples prepared at ICG-CNR Pisa, the B isotope composition of the mafic-intermediate Plio-Pleistocene post-collisional samples with the exception of sample 9.31B.04 were measured on a Thermo Scientific™ Neptune series multi-collector (MC)-ICP-MS in Pisa, specially tuned for 11B/10B analysis (following Foster, 2008). Samples were diluted to contain ∼20 ppb B and were then bracketed with NBS 951 boric acid standard solution of the same concentration, to correct for machine induced mass fractionation.

Within run errors are between 0.08 and 0.22‰ (2σ for this and subsequent errors). Several samples were re-prepared and re-analysed, reproducing the original value to within ±0.5‰ or better. The accuracy of the measurement was monitored as follows: 28 replicate analyses of NBS 951 gave an average δ11B of +0.01 ± 0.41‰, 7 replicate analyses of the IAEA standard B1 (seawater) gave an average δ11B of +39.38 ± 0.27‰ (accepted value ∼+38.6 ± 1.7‰; Gonfiantini et al., 2003), and 3 replicate analyses of the JB2 (basalt) gave an average δ11B of +7.25 ± 0.57‰ (accepted value +7.33 ± 0.37‰; Tonarini et al., 2003). All replicate analyses of these standards were performed after they had been processed through the full B separation procedure.

The boron concentrations of these purified boron solutions were also measured during MC-ICP-MS analysis. B solutions at variable concentrations (10, 50 and 100 ppb) were used for calibration, and analysed repeatedly to correct for instrumental drift. These concentrations were converted to sample contents using accurately measured sample weights (error < 0.1 %) and reagent volumes (error < 1 %). Sample loss during flux fusions and column chromatography is minimal (< 2 %). For both B concentration and 11B/10B measurements, analytical blanks were subtracted. Blanks were generally ∼0.2 ppb (sample/blanks > 100). Two analyses allow for the accuracy of these concentration measurements to be verified. The standard BCR-2 had a measured concentration of 3.7 ppm (accepted values 4.1 to 4.7 ppm; Menard et al., 2013). A veined gabbro which had previously been measured for [B] at the University of South Florida (sample AM20; [B] = 6.9 ppb; McCaig et al., 2018), had a measured [B] of 6.6 ppm. It is therefore reasonable to assume that concentrations are accurate to within 1 ppm.

The Tezhsar samples, as well as the one mafic sample from the Gegham volcanic highland (9.31B.04, Fig. S1) were prepared in the
same way as the Plio-Pleistocene samples. However, isotopic analyses were by thermal ionisation mass spectrometry (TIMS) using a VG Isomass 54e mass spectrometer at ICG-CNR Pisa following the methods outlined in Tomarini et al. (2001). The accuracy of these measurements was monitored by analysis of the SRM-951 boric acid standard, which had been processed through full column chemistry alongside the samples. Uncertainties on measurements are 0.4 to 0.6 \%/permil.

Boron isotopic analyses of Plio-Pleistocene obsidians from the Gegham volcanic highland (Fig. S1) were made using multiple multiplier laser ablation inductively-coupled plasma mass spectrometry (MM-LA-ICP-MS) at the Department of Terrestrial Magnetism (DTM) of the Carnegie Institution of Washington. For the full method description see Savov et al. (2009) and references therein. The accuracy of these measurements were monitored by repeated analyses of NBS 610, 612 and 614 glasses, as well as B-5 (Mt. Etna volcano basalt) and B-6 (Lipari obsidian) homogeneous glass standards (produced at DTM, P = 4 GPa), which yielded an average δ11B (-1%) of -3.58%e and -0.95%e respectively. This can be compared to respective accepted values of -3.8 ± 2%e and -1.6 ± 1.4%e (Confiandini et al., 2003), suggesting reproducibility is better than 1%, while within run uncertainties were <1%.

Boron concentrations for Tezhars and Gegham rhyolite samples were measured on a Perkin Elmer Optima 2000 DV inductively coupled Plasma-Optical Emission Spectrometer (ICP-OES) at the School of Geosciences of the University of South Florida. Samples were fluxed with Na2CO3 in platinum crucibles with lids using a furnace at 1400 °C in a boron-free clean lab environment. Sample preparation techniques followed the methods outlined in Snyder et al. (2005). The analytical blank was measured as 1.5 ppm. The blank-corrected concentration of the JB-3 (basalt) external standard was correct to within 1 ppm (18.8 ppm, vs. accepted value 18 ppm). The similar [B] for the veined gabbro sample (AM20) measured in both South Florida (6.9 ppm) and Pisa (6.6 ppm), confirms that the concentration measurements for post-collisional mafic samples can be compared directly with those of the Tezhars alkaline complex and post-collision rhyolite samples.

All measurements of boron and its isotopes were made using the same sample powders as were used to measure the major and trace element concentrations, and Sr-Nd isotope ratios (methods in Sugden et al., 2019).

4. Results

All [B] and δ11B values are shown in Table 1; δ11B ranges from −5 to +2%e (Fig. 3) for post-collisional samples, consistently heavier than mid-ocean ridge basalts (MORB; −7.1 ± 0.9%e; Marschall et al., 2017). There is no consistent variation with geographic position in the post-collision samples: samples from Aragats (−5 to −3%e), Gegham (−4 to +2%e), Vardenis (−3 to 0%e) and Syunik (−4 to +1%e) all show a similar δ11B range (Table 1), confirming previous observations that despite changes in lithospheric thickness, the slab contribution is uniform across Armenia (Sugden et al., 2019). The B/Nb in mafic samples varies from 0.03 to 0.25, i.e. lower than in any modern volcanic arc (Fig. 3; De Hoog and Savov, 2018), and in fact overlapping with the range of MORB (0.15–0.55; Marschall et al., 2017). This suggests a fluid-mobile element depleted source when compared to the sources of arc volcanism. The δ11B of the studied rocks are similar to those from hot arcs such as the Cascades (circled red in Fig. 3; −2.1 to +0.4%e; Leeman et al., 2004; Rose et al., 2001; Walowski et al., 2016), or the intraplate volcanoes of the Oregon-Snake River Plain-Yellowstone region (−8.9 to −0.8%e; Savov et al., 2007), both shown to represent melting of fluid-starved sources. B/Nb ratios are higher in the rhyolite samples by an order of magnitude (0.75-1.5; Fig. 3), but the δ11B of the rhyolites is comparable (−4 to +2%e vs. −5 to +1%e for mafic samples; Fig. 3).

Table 1

| Label | Volcano/Volcanic highland | Rock type | 87Sr/86Sr | 143Nd/144Nd | B (ppm) | Nb (ppm) | B/Nb | δ11B (%) |
|-------|---------------------------|-----------|----------|-------------|--------|--------|-------|---------|
| Plio-Pleistocene post-collision | | | | | | | | |
| 4.020.04 | Gegham | Rhyolite | 0.70479 | 0.51275 | 64.4 | 45.0 | 1.4 | −3.8 |
| 6.26.04 | Gegham | Rhyolite | 0.70416 | 0.51285 | 29.8 | 36.4 | 0.82 | +1.7 |
| 8.29B.04 | Gegham | Rhyolite | 0.70493 | 0.51279 | N.D. | N.D. | N.D. | −1.8 |
| 8.30A.04 | Gegham | Rhyolite | 0.70421 | 0.51281 | 36.7 | 50.8 | 0.72 | 0.3 |
| 9.31A.04 | Gegham | Rhyolite | 0.70422 | 0.51282 | 27.2 | 22.8 | 1.2 | −3.9 |
| 9.31B.04 | Gegham | Trachybasantian zeolite | 0.70439 | 0.51281 | N.D. | 15.7 | N.D. | −2.7 |
| 9.31D.04 | Gegham | Rhyolite | 0.70422 | 0.51282 | 28.4 | 21.5 | 1.1 | +2.1 |
| 2.708 | Syunik | Phonopahite | 0.70444 | 0.51280 | 2.7 | 30.3 | 0.090 | −2.9 |
| 2.10.08 | Syunik | Basalt | 0.70440 | 0.51283 | 2.1 | 9.4 | 0.23 | −1.9 |
| 6.26.08 | Syunik | Trachyanesite | 0.70427 | 0.51279 | 3.0 | 37.7 | 0.080 | −2.1 |
| 8.315 | Syunik | Trachybasantian zeolite | 0.70444 | 0.51279 | 2.3 | 43.0 | 0.053 | −2.4 |
| 8.515 | Syunik | Trachybasantian zeolite | 0.70462 | 0.51278 | 2.0 | 24.1 | 0.082 | −4.0 |
| 9.115 | Syunik | Trachybasantian zeolite | 0.70444 | 0.51280 | 2.1 | 31.3 | 0.068 | −2.9 |
| 10.215 | Syunik | Trachybasantian zeolite | 0.70426 | 0.51286 | 2.8 | 19.4 | 0.15 | −3.3 |
| 11.115 | Syunik | Trachybasantian zeolite | 0.70438 | 0.51281 | 2.7 | 25.6 | 0.10 | −3.0 |
| 11.415 | Syunik | Tephrite | 0.70428 | 0.51280 | 1.1 | 32.6 | 0.033 | +0.4 |
| 6.217 | Syunik | Trachybasantian zeolite | 0.70433 | 0.51279 | 2.7 | 29.6 | 0.092 | −2.7 |
| 11.35A.04 | Aragats | Rhyolite | 0.70471 | 0.51286 | 44.3 | 38.7 | 1.1 | −3.2 |
| NPP 11 | Aragats | Trachbasalt | 0.70429 | 0.51281 | 1.7 | 16.6 | 0.10 | −3.8 |
| NPP 241 | Aragats | Trachybasantian zeolite | 0.70436 | 0.51282 | 3.2 | 15.3 | 0.21 | −5.2 |
| 5.315 | Vardenis | Trachyanesite | 0.70446 | 0.51280 | 5.2 | 21.0 | 0.25 | −0.9 |
| 6.315 | Vardenis | Trachybasantian zeolite | 0.70443 | 0.51280 | 2.6 | 25.8 | 0.10 | −2.3 |

* Arteni complex: 45 km SW of Aragats summit.
† Not determined.
‡ Sr-Nd isotope ratios for Tezhars samples are initial ratios, assuming an age of 41 Ma and Rb/Sr ratios from Sokol et al. (2018).
The Tezhsar alkaline complex rocks have a similar δ¹¹B to the post-collisional rocks (Figs. 3 and 4), with one exception of a lighter δ¹¹B of ~−8.7‰ (Table 1). Tezhsar samples have higher B concentrations (4-20 ppm) and B/Nb ratios (0.2-0.8) than the post-collision samples, although B/Nb is still at the lower end for arcs generally (Fig. 3). Surprisingly, magma sources tapped at 41 Ma and <1.5 Ma have comparable Sr-Nd-B isotopic characteristics (Fig. 4) - with overlapping ¹⁴³Nd/¹⁴⁴Nd (0.51275-0.51286), and only slightly lower ⁸⁷Sr/⁸⁶Sr in Tezhsar samples (initial values 0.7040-0.7044 vs 0.7042-0.7049). The lower B/Nb and ¹⁴³Nd/¹⁴⁴Nd; and higher ⁸⁷Sr/⁸⁶Sr of these collision-related magmas when compared to arc rocks, means they define a geochemical reservoir distinct to volcanic rocks from both arcs and oceanic ridges/islands.

5. Discussion

5.1. Origin of the subduction signature

Prior to this study, Western Anatolia was the only region in the world young (17-0 Ma) volcanic rocks, which erupted after subduction ceased had been studied for B and δ¹¹B. Western Anatolia has experienced rapid geodynamic changes over the past 25 Myr, from subduction to an extensional setting (Tonarini et al., 2005), which although not a continental collision, does provide an analogue of what happens when subduction ends. Here, 23-17 Ma calc-alkaline rocks have δ¹¹B (−7.1 to −0.1‰) and B/Nb which extend from MORB to more arc-like values (Fig. 3), reflecting their formation during subduction. However, 17-14 Ma ultrapotassic rocks have very light δ¹¹B (~−15.1 to ~−12.2‰), interpreted to reflect the progressive dehydration of a stalled slab (Agostini et al., 2008), which is also shown by the gradual reduction in B/Nb (Fig. 3) (Tonarini et al., 2005). The dehydration preferentially removes ¹¹B, giving the residual slab an increasingly light δ¹¹B (Jishikawa and Tera, 1997). These samples provide a useful comparison for the likely effects of a stalled slab on δ¹¹B and B/Nb with the Armenian samples presented in this study.
The $\delta^{11}B$ of post-collisional volcanic rocks from Armenia ($-5.2$ to $+1.7\%$) is not consistent with a model in which a stalled slab progressively dehydrates during collision-related slab break-off. Instead, in Armenia $\delta^{11}B$ has exhibited consistently heavier than MORB values over the past 41 Myr, on the basis of the post-collisional ($-5.2$ to $+1.7\%$) and Tezhars alkaline complex samples ($-8.7$ to $-3\%$). Similarly, mixing with an intraplate mantle source (OIB $\sim -10\%$; Walowski et al., 2019), which had previously been underneath (and therefore unaffected by) a subducting slab would produce a lighter $\delta^{11}B$ in the post-collisional volcanic rocks compared to the older Tezhars samples. In fact, post-collision samples have slightly heavier $\delta^{11}B$ (Fig. 3). Both mixing with intraplate magmas and dehydration of a stalled slab would also result in more variable trace element and Sr-Nd isotope compositions, which is not considered.

While slab break-off is not considered a prominent process under Armenia, it could well be an important process elsewhere in the collision zone. In particular the Lake Van region of Eastern Anatolia, where alkaline magma compositions are observed, suggest of OIB-type mantle from below the slab contributing to the magma source (Keskin, 2003; Pearce et al., 1990). Volcanism in Western Anatolia continued after the eruption of the 17 BO Mts ultramafic rocks, forming two magmatic series: Na-alkaline and K-alkaline (Figs. 3 and 4). Despite the similar $\delta^{11}B$ of the Na-alkaline volcanic rocks ($-2.7$ to $-0.8\%$) to Armenian post-collisional samples (Fig. 3), their higher $87Sr/86Sr$ and lower $143Nd/144Nd$ (Fig. 4), along with their OIB-like trace element geochemistry (Innocenti et al., 2005), suggests a distinct petrogenesis. They have been interpreted as melts derived from an un-modified asthenospheric mantle (Tonarini et al., 2005). However, the $\delta^{11}B$ is inconsistent with recent estimates for the composition of the abyssal mantle ($-7$ to $-10\%$; Marschall et al., 2017; Walowski et al., 2019), suggesting there may be a minor metasomatic component contributing to the $\delta^{11}B$ of these magmas as well.

The $\delta^{11}B$ of the K-alkaline volcanic rocks from Western Anatolia changes from $-12.9\%$ at 11.5 Ma to values similar to the Armenian post-collision lavas in younger samples ($-4.1$ and $-2.6\%$ in 8 and 1 Ma samples respectively; Fig. 3). These younger K-alkaline samples have Sr-Nd-B isotope compositions, and an arclike trace element geochemistry, that are similar to the collision-related volcanic rocks from Armenia (Fig. 4; Innocenti et al., 2005). The low $\delta^{11}B$ of the older K-alkaline sample, might suggest that at this time a stalled slab is still influencing magma $\delta^{11}B$ (Agostini et al., 2008; Tonarini et al., 2005). The rebound to heavier values in the younger samples, with lower B/Nb (Fig. 3) is explained by the end of the influence of any subducting slab (Tonarini et al., 2005), such that B comes to reflect the composition of the mantle which remains. In the case of these younger K-alkaline rocks, the subduction component in their mantle source must have been inherited. The similar geochemistry of the Armenian volcanic rocks to these K-alkaline rocks suggest that they too have an inherited subduction component.

It seems most likely that the subduction signature observed in the Armenian post-collisional and Tezhars volcanic rocks, has been stored for at least 41 Myr, to be inherited during later melting events. The slab component is mostly likely to have been stored in the lithospheric mantle, where cooler temperatures (due to a conductive geotherm) stabilise metasomatic minerals able to store the slab component long after subduction has ceased (e.g. Mandler and Grove, 2016). Amphibole, rather than phlogopite, is the most likely such mineral, based on the high Ba/Rb (20-40) and low Rb/Sr (0.01-0.04) ratios of the post-collisional volcanic rocks (Sugden et al., 2019). This is because Rb is an order of magnitude more compatible in phlogopite compared to amphibole (LaTourrette et al., 1995). Temperatures of $<1100^\circ$C would be required to stabilise pargasitic amphibole (Mandler and Grove, 2016), showing that the slab component must be stored in the mantle lithosphere.

A residual amphibole phase is supported by the positive correlation between Dy/Dy* and Ti/Ti* (Fig. 5; Davidson et al., 2013). Only amphibole and clinopyroxene preferentially partition the middle rare earth elements, decreasing the Dy/Dy* ratio of any melt equilibrating with these phases. The positive correlation with Ti/Ti* confirms that amphibole must be a residual phase in the source of the post-collisional magmas because Ti is an order of magnitude more compatible in amphibole than in pyroxene (Davidson et al., 2013). Thus, amphibole is able to store slab-derived boron for $>41$ Myr, soaking up metasomatic components to be released during later melting episodes caused by partial amphibole breakdown (Sugden et al., 2019).

The low [B] of Armenian post-collisional volcanic rocks (1-5 ppm) relative to arc volcanic rocks is consistent with the low [B] observed in vein amphiboles in sub-arc mantle xenoliths from Kamchatka (0.2-3 ppm; Tomanikova et al., 2019). An amphibole source for the subduction signature would be expected to produce magmas low in B given low experimental partition coefficients for boron in amphibole (Brenan et al., 1998), explaining its low capacity for concentrating boron in its structure during the storage of a slab component. The $\delta^{11}B$ of Armenian volcanic rocks does fall within the range observed for the Kamchatka xenolith vein amphiboles ($-12$ to $+1\%$; Tomanikova et al., 2019), suggesting it is a viable reservoir.

This stored slab component is reminiscent of the “amphibole sponge” concept of Davidson et al. (2007), where it was argued that “cryptic” amphibole fractionation in the lower crust provides a hydrous filter on ascending arc magmas. It was also argued that subsequent breakdown of amphibole in these lower crustal cumulates can lead to the production of intra-crustal melts of intermediate-felsic composition (Davidson et al., 2007). However, with SiO$_2$ contents as low as 45 wt% and Sr-Nd isotope compositions on the mantle array, the Armenian post-collisional magmas are clearly mantle-derived (Sugden et al., 2019). Magma generation occurs above the lithosphere-asthenosphere boundary ($\sim$120 km; Priestley et al., 2012). This is on the basis of evidence from rare earth elements for both garnet and spinel in the melt residue,
and major element geothermobarometry revealing melting at 50-
80 km depth and at temperatures of ~1100°C, consistent with
melting in the lithosphere rather than the asthenosphere (Sugden
et al., 2019). Such temperatures are also consistent with amphibole
breakdown melting (Mandler and Grove, 2016), which is argued to
occur at both the base and interior of the mantle lithosphere (Sug-
den et al., 2019).

Hence the amphibole sponge of Armenian post-collisional mag-
matism is in the mantle lithosphere rather than in the lower
crust. Rather than arc melts, this sponge filters a slab-derived
component. Upon subsequent amphibole breakdown, melting of this
sponge creates post-collisional mafic magmas rather than felsic
intra-crustal melts.

5.1. Origin of the subduction signature in high boron post-collisional
rhyolites and Tezhsar volcanic rocks

The high B/Nb of two Tezhsar alkaline complex samples (Fig. 3),
and the lower δ31B of one Tezhsar sample (~8.7%; Fig. 3) are simi-
lar to the volcanic rocks from “hot” subduction zones (Fig. 3; Leeman
et al., 2004; Savov et al., 2009). This could suggest the subduction
signatures in the Tezhsar samples are a mixture of the component
observed in the post-collision samples, and a component
derived from contemporaneous addition of material from a
partially dehydrated slab. The Tezhsar volcanic rocks formed much
closer to the time of Mesozoic-Paleogene active slab subduction
(Mederer et al., 2013; Sokół et al., 2018), so the observation of a
second slab component only in the older Tezhsar samples is rea-
sonable. Tezhsar is analogous to the oldest of the K–alkaline lavas
from Western Anatolia (δ31B = −12.9%) when some of the de-
pleted stalled slab material was still present (Agostini et al., 2008).

Despite the higher B/Nb of the rhyolite post-collision samples,
the matching Sr-Nd-B isotope characteristics of both mafic and
felsic samples illustrates that the magma source of the parental
magma to these rhyolites is the same long-lived subduction-
modified mantle source which supplied the mafic magmas. These
isotope characteristics also confirm that crustal contamination did
not play a role in the petrogenesis of the rhyolites, meaning that
B/Nb varies with the extent of crystal fractionation. [Nb] is invari-
ant in the remaining melt during fractional crystallisation, whereas
[B] increases by an order of magnitude (Table 1). Nb must part-
ition into a crystallising phase, while B remains in the liquid. Here,
a reduction in Nb/Ta with SiO2 content in these same magmas (22-
27 in basalts vs. 6-19 in rhyolites) offers a clue. Fractionation of
magnetic rutile in the lower crust produces high Nb/Ta cumulates
(Tang et al., 2019). A small amount of rutile fractionation may be
enough for Nb to be buffered in the remaining melt, while Ta re-
 mains an incompatible element.

5.2. Nature of the slab component and its metasomatic agent

The slab signature in arc magmas is generally imparted by
aqueous fluids, melts or supercritical fluids liberated from a sub-
ducting slab and overlying sediments. Here, melts and supercritical
fluids (MSF) will be treated as interchangeable, given the similar
trace element partitioning behaviour of the two (Kessel et al.,
2005).

The [B] and δ31B of most arc rocks is dominated by aqueous
fluids derived ultimately from the subducting slab (De Hoog and
Savov, 2018, and references therein). The composition of the first
aqueous fluids released from a subducting slab is likely best repre-
sented by the heavy δ31B of fore-arc serpentinites (avg. ~+13%;
Fig. 4; De Hoog and Savov, 2018). The light δ31B in the Armenian
rocks means that an aqueous fluid source for the slab compo-
nent would have already lost a significant amount of fluid (and
hence heavy B) prior to contributing to the post-collisional man-
tle source (Konrad-Schmolke and Halama, 2014). A simple Rayleigh
fractionation model for the composition of fluid released from an
increasingly dehydrated slab is constructed (Figs. 3 and 4). Coupled
thermodynamic and thermomechanical modelling of subduct-
lithosphere can constrain the temperature of the subducting
slab, as well the phases which store B: likely to be plagioclase,
chlorite and amphibole (Konrad-Schmolke and Halama, 2014). On
this basis, a 10% fluid-residue fractionation factor is assumed (Kon-
rad-Schmolke and Halama, 2014; Wunder et al., 2005). As the slab
dehydrates, the fluids released have δ31B and B/Nb which dimin-
ish with depth (Fig. 3). The δ31B and B/Nb of arc rocks (but not the
Armenian volcanic rocks), can be explained by mixing between de-
pleted (MORB) mantle and fluids from a variably dehydrated slab
(Fig. 3). δ79Sr/86Sr and δ143Nd/144Nd would not vary during dehy-
dration (horizontal trajectories in Fig. 4). An aqueous fluid derived
from a previously dehydrated slab could explain the Sr-B isotope
composition of the post-collisional magmas (Fig. 4a), but not the
lower 143Nd/144Nd ratios (Fig. 4b).

The metasomatic agent must instead be an MSF derived from
subducted sediments or oceanic crust, in order to mobilise Nd
and modify the 143Nd/144Nd of the mantle source. Adakites are
thought to be geochemically characterised by an MSF derived from
oceanic crust. They have MORB-like Sr-Nd isotope ratios, rather
than the high δ79Sr/86Sr and low 143Nd/144Nd of the post-collisional
rocks (Fig. 4). Moreover, although Armenian post-collisional mag-
mas possess the high Sr/Y ratios (15-130) characteristic of adakites,
they lack the high primary SiO2 contents, and have higher Y and
Yb abundances (Castillo, 2012).

This leaves a sediment MSF as the carrier of the slab compo-
nent in the post-collisional rocks, supported by their low 143Nd/144Nd.
A sediment MSF is also supported by the similar Th/Rb (Fig. 6) in
the volcanic rocks (average for mafic samples ~0.16 ± 0.06 (2 SD))
and Tethyan flysch sediments (avg. 0.13 ± 0.2; Prelević et al., 2008).
For Th/Rb to reflect local subducted sediments, the metasomatic agent must be: a) derived from the sediment, and b) an MSF for Th and Rb to partition similarly
between the mobile and the residual phases, given that Th is fluid-immobile (Johnson and Plank, 2000). This is confirmed by
fluid-eclogite partitioning experiments, which show that even at
high salinities, Rb is typically enriched in the fluid by around 2 orders of magnitude more than Th (Rustioni et al., 2019). In addition, given the relatively low Th content of the oceanic crust (Kelley et al., 2003), the high Th contents of postcollisional samples (comparable to the Tethyan sediments) suggest derivation of the MSF phase from the slab sediments (Fig. 6).

The $\delta^{11}$B of this sedimentary component is likely to be in the range of −5 to +2‰ (Fig. 4) based on the $\delta^{11}$B of post-collision samples. This can be compared to the $\delta^{11}$B of metasediments. Metamorphosed terrigenous sediments (Catalina schist, California and Lago di Cignana, Italy) have much lighter $\delta^{11}$B compared to the Armenian volcanic rocks (−7 to −15‰ in tourmalines; Bebout and Nakamura, 2003). However mixed marine-terrigenous sediments from Syros, Greece, have comparable $\delta^{11}$B to the Armenian samples (−1.6 to +0.9‰ in tourmaline prograde mantles; Marshall et al., 2008). It is probably the case that there is no $\delta^{11}$B fractionation during separation of a melt phase from the residual metasediment, given the tetrahedral co-ordination of B in both magma and most silicate minerals (Maner and Halama, 2018). A melt of the mixed marine-terrigenous metasediment could produce the slab signature observed in Armenian post-collisional magmas. Release of a supercritical fluid could involve none or only limited isotope fractionation given the likely high temperatures (Konrad-Schmolke and Halama, 2014). If instead separation of a supercritical fluid did involve isotope fractionation, then the isotopically lighter, dominantly terrigenous-derived sediment could be a more viable source for the slab component’s metasomatic agent.

It is possible to construct a mixing model in an attempt to quantify the contributions of this sediment MSF and the unmodified mantle to the magma source. The proportion of boron contributed by the slab component ($F_{SC}$) is:

$$F_{SC} = \frac{\delta^{11}B_{MS} - \delta^{11}B_{UM}}{\delta^{11}B_{SC} - \delta^{11}B_{UM}}$$

(1)

$\delta^{11}B_{MS}$ is the isotope composition of the Armenian post-collision magma source - taken here as the average of post-collision samples (−2.7‰). $\delta^{11}B_{UM}$ is the composition of the unmodified mantle (−7.1‰), while $\delta^{11}B_{SC}$ is the composition of the slab component, taken as the composition of metasediments from Syros, Greece (−1.6 to +0.9‰; Marshall et al., 2008). These values suggest that between 55 and 80% of boron in the magma source is derived from the slab component. It is then possible to calculate the concentration of B in the slab component ($[B]_{SC}$):

$$F_{SC} = \frac{X_{SC}[B]_{SC}}{X_{SC}[B]_{SC} + (1 - X_{SC})[B]_{UM}}$$

(2)

$X_{SC}$ is the total mass fraction of the slab component in the magma source. Based on mixing models for Sr-Nd isotope data from post-collisional volcanic rocks in Armenia and neighbouring north-west Iran, 1% is a reasonable estimate (Allen et al., 2013; Sugden et al., 2019). [B]$_{UM}$ is the concentration of boron in the previously unmodified mantle. Given there is no evidence for a deep mantle plume in this region, the depleted mantle is a reasonable approximation here (0.077 ppm; Marschall et al., 2017). This gives $[B]_{SC}$ of between 9.3 and 30.5 ppm. This range is below the bulk-rock value for the Syros metasediment sample used to constrain $\delta^{11}$B ($\sim$94 ppm; Marschall et al., 2008). It is possible that these metasediments owe their elevated B to the influx of B-rich fluids at retrograde conditions (Marschall et al., 2008). When compared with un-metamorphosed subducting sediments, [B]$_{SC}$ is at the lower end of the range (5 to 130 ppm; Plank, 2014). This is to be expected, given that subducting sediments will release much of their B during dehydration in the fore-arc (Snyder et al., 2005), although any melting event would give a melt with a higher [B] than the source, given the incompatibility of B (D$_{solid/melt}$ ~ 0.1; Kessel et al., 2005).

It is now possible to estimate [B] of the magma source:

$$[B]_{MS} = X_{SC}[B]_{SC} + (1 - X_{SC})[B]_{UM}$$

(3)

Eq. (3) gives [B]$_{MS}$ of between 0.17 and 0.38 ppm. This can be compared with the concentrations of boron in mantle peridotite xenoliths from Kamchatka that are thought to come from subduction-modified mantle lithosphere (Tomanikova et al., 2019). Kamchatka arc lithosphere is metasomatized, but B poor, making it a good analogy for the Armenian magma source. This arc lithosphere contains B-poor amphibole (0.2 to 2 ppm), while the nominally anhydrous phases also have low B (0.25 to 1 ppm; Tomanikova et al., 2019). As such, the [B]$_{MS}$ calculated here supports a model where a sediment melt with a $\delta^{11}$B similar to the metasediments from Syros could react with the mantle lithosphere to produce the post-collisional magma source.

Ratios such as Ba/Th, Pb/Ce and U/Nb (fluid-mobile element/immobile element of similar compatibility during melting) are higher and more variable in Mesozoic-Paleogene arc rocks from Armenia and Eastern Anatolia (Fig. 7; Aydıncakir and Sen, 2013; Mederer et al., 2013) compared to the relatively young post-collision rocks

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Fig. 7. U/Nb (a) and Pb/Ce (b) vs. Ba/Th in mafic post-collisional rocks from Armenia and Mesozoic-Paleogene arc rocks from the arc of the Lesser Caucasus and the Pontides to the west. Data is sourced and filtered as in Fig. 6. MORB values after Sun and McDonough (1989).
investigated in this study. This indicates that a fluid component was present during subduction, but was not inherited by magmas formed after the continental collision. This points to the sediment MSF being much more long-lasting in the mantle, whereas the aqueous fluid component is transitory. Indeed, studies of U-Th series isotopes in Kamchatka suggest the aqueous fluid component can travel from slab to surface in 1-300 kyr, whereas a sediment component can take 350 kyr - 4 Myr to make the same journey (Turner et al., 2000). It could be the case that once the slab stalls the aqueous fluids are quickly removed, such that the subsequent slab component is dominated by sediment MSF.

6. Concluding remarks

High Ba/Th, Pb/Ce and U/Nb in Mesozoic-Paleogene Tethyan arc magmas indicate the mantle source of these magmas was modified by aqueous fluids. However, the δ11B of post-collisional volcanic rocks indicates derivation from a mantle source modified by a fluid-starved slab component. There is also no evidence for continued dehydration of a stalled slab following collision, which would be expected to produce the even lighter δ11B, as observed in the 16-17 Ma samples from Western Anatolia. Instead the similar δ11B and Sr-Nd isotope ratios in post-collisional and the Tezhsar alkaline complex volcanism indicate that the slab signature was inherited from preceding subduction. The lack of the heavy δ11B signature of aqueous fluids being a result of them being transitory and not surviving to impart their signature on post-collisional Armenian mantle sources. For this subduction component to be inherited, it needs to be stored since at least the 41 Ma volcanism recorded at Tezhsar. Amphibole is likely to be the storage repository for the slab component based on low Rb/Sr and co-variation in Dy/Dy* vs. Ti/Ti" in post-collisional volcanic rocks. This is in agreement with the low [B] in post-collisional volcanic rocks, because amphibole has a modest storage capacity for B. Higher B/Na in Tezhsar compared to post-collisional volcanic rocks (similar to B/Na in “hot” arcs) and slightly lower δ11B may suggest that an inherited slab component was mixed with a component derived from a contemporaneously subducting slab. The more clustered Sr-Nd-B isotope compositions of the post-collisional samples suggests that by the Plio-Pleistocene only the inherited slab component remains. The sediment MSF origin of the slab component suggested on the basis of trace elements and Sr-Nd isotopes may be consistent with δ11B in post-collisional volcanic rocks, given similar values for some dehydrated metasediments.

The lower 143Nd/144Nd in arc rocks compared to fore-arc serpentinites (Fig. 4) is perhaps a “smoking gun” for the presence of this sediment MSF component in all arc rocks, but their heavy δ11B is testament to it being obscured by a dominant aqueous fluid component. As a setting in which only sediment MSF metasomatizes the mantle source, volcanism in continent-continent collision zones is an ideal setting to separate the effects of slab-derived sediment MSF and aqueous fluids in subduction zones.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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