Global Ba/Nb systematics in arc magmas reflect the depths of mineral dehydration in subducted slabs

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ABSTRACT

The transfer of material from subducting slabs to the overlying mantle is one of the most important processes regulating Earth's geochemical cycles. A major part of this material cycling involves slab devolatilization and the release of sediment- and slab-derived fluids to the mantle wedge, triggering melting and subsequent arc volcanism. Previous geodynamic, geophysical, and geochemical studies have revealed many important controls on fluid fluxing to the mantle and its manifestations in arc magmas. However, it remains difficult to identify the specific mineral breakdown reactions that control element fluxes from the subducting slab into the overriding mantle. To address this challenge, we combine global arc whole-rock compositional data with geophysical information (e.g., depths to slab) and thermodynamic data. We observe three peaks in Ba/Nb in global arc magma whole-rock compositions corresponding to depths to slab of 60, 120, and >290 km. Using published thermodynamic and geodynamic models of slab evolution, we show that these peaks can be linked to the progressive breakdown of hydrous minerals (e.g., epidote, actinolite, lawsonite) in subducting slabs.

INTRODUCTION

Trace element systematics of volcanic rocks are commonly used to understand subduction processes, e.g., mantle melting, sediment melting, and/or dehydration (Hermann and Rubatto, 2009; Skora and Blundy, 2010; Turner and Langmuir, 2022a), slab devolatilization (van Keken et al., 2011; Carter et al., 2015; Hernández-Uribe et al., 2020b; Taniuchi et al., 2020), slab melting (Mungall, 2002), and subduction erosion (Straub et al., 2020). In arc magmatic settings, trace elements are typically classified as fluid-mobile or immobile. Fluid-immobile elements (e.g., Nb) are typically retained by the subducting slab, and consequently, the concentrations of these elements in arc magmas are dominated by the mantle wedge component. In contrast, the concentrations of fluid-mobile elements (FMEs; e.g., Ba, Cs, Pb, U) in arc volcanic rocks are dominated by the flux of slab-derived fluids to the mantle wedge (Elliott et al., 1997; Plank and Langmuir, 1998; Schmidt and Poli, 2014). This slab-to-mantle wedge flux causes arc magmas to have significantly higher ratios of fluid-mobile to fluid-immobile elements (e.g., Ba/Nb) compared to non-subduction-related magmas. The FMEs can be transported from the slab to the mantle wedge by supercritical fluids, aqueous fluids, or silicate melts depending on the pressure (P) and temperature (T) experienced by the subducting material (Pearce, 1982; Tatsumi et al., 1983; Brenan et al., 1995; Elliott et al., 1997; Kessel et al., 2005; Pearce et al., 2005; Hermann and Rubatto, 2009; Skora and Blundy, 2010).

Slab fluid loss is a gradual process mediated by discontinuous metamorphic reactions (Ryan and Chauvel, 2014; Schmidt and Poli, 2014; Hernández-Uribe and Palin, 2019; Holt and Condit, 2021), where the breakdown of specific hydrous phases controls the release of fluids and other elements (Ryan and Chauvel, 2014; Schmidt and Poli, 2014). However, uncertainties remain regarding which specific phases (e.g., phengite) control the trace element systematics of arc magmas. We provide new insights into the controls on the release of FMEs from the slab to the mantle wedge by combining a comprehensive global geochemical data set with modern estimates of subducting slab geometries and phase equilibria to identify which minerals contribute to FME enrichments in arc magmas. We used our igneous geochemical and tectonic compilation ArcMetals (Barber et al., 2021) based on GEOROC (https://georoc.eu/georoc) data (Sarbas and Nohl, 2008), integrated with recently published phase-equilibria thermodynamic models of phase stability and devolatilization (Hernández-Uribe and Palin, 2019; Hernández-Uribe et al., 2020b). We then compared these thermodynamic models to both ArcMetals and time-dependent geodynamic evolution models of slab dehydration (Holt and Condit, 2021). We find that globally, arc magmas show elevations in Ba/Nb at three characteristic ranges of depth to slab (DTS), and we relate each peak in Ba/Nb to specific mineral breakdown reactions that are a function of slab P-T path.

FLUID-MOBILE ELEMENT CONTENTS OF ARC MAGMAS

In Figure 1, we show Ba/Nb distributions versus DTS in a subset of arcs (Figs. 1A–1D). The data constituting these four plots represent one-quarter of the total ArcMetals data set and demonstrate that each arc has distinct Ba/Nb distributions. If we take the median Ba/Nb value for each arc, much of the underlying complex structure is lost (white stars in Figs. 1A–1D). When comparing arcs (Figs. 1E and 1F), the highest median Ba/Nb values are found in the Vanuatu, Papua New Guinea (Bismarck arc), Central America, Kamchatka (Russia), Aleutians (Alaska, USA), and Philippines subduction zones. The observed groupings on these plots do not reflect any one consistent tectonic (e.g., slab geometry) or geological (e.g., sediment cover) property. Some of these arcs share similar features: notably, there are several young and/or high-temperature island arcs (Vanuatu, Aleutians) in this group, but there are also arcs like Papua New Guinea that are overlain by much thicker crust. Furthermore, arcs with similar dips, which may reflect similar slab kinematic characteristics, are associated with volcanic rocks with vastly different Ba/Nb (Fig. 1F).

To unravel the cause of this global arc magma Ba/Nb variability, in Figure 2A we show median Ba/Nb in bins of 2 km with respect to...
DTS (methods validated in Figures S1–S7 in the Supplemental Material). A moving-average curve through these median values (Fig. 2B) was used to identify the underlying small-scale structures in the Ba/Nb data. This analysis reveals that there are three main peaks in the Ba/Nb moving average curve at DTS of 60, 120, and >290 km. We discuss the statistical validity of these peaks in the Supplemental Material. In Figure 2 and Figures S3–S5, we show that Mg# does not correlate with Ba/Nb, which demonstrates that the across-arc variations in Ba/Nb are largely unrelated to the effects of fractional crystallization (Pearce et al., 2005).

The Ba/Nb peak at 120 km corresponds to sub-arc depths where average subduction-zone magmatism takes place (Syracuse et al., 2010), whereas the 60 km and 290 km peaks by contrast represent significant fore- and back-arc magmatism, respectively. Because of the lack of data in the back-arc peak (Fig. S5), it is difficult to resolve whether the third peak is one unified peak or two smaller peaks (Fig. 2B). Hence, we focus on the largest back-arc peak at 290 km for the remainder of this discussion. These three peaks represent globally significant signals of FME enrichment, but critically, these signals would not appear together in every subduction zone, owing to variances in slab thermal structure or lithology (Holt and Condit, 2021). For example, in Figure S5, our global compilation shows that hotter subduction zones commonly have weaker back-arc peaks (Tonga), whereas colder subduction zones commonly have weaker fore-arc peaks (Honshu [Japan]).

The same statistical approach was applied to Th/U and Pb/Nd ratios. Both ratios are proxies for subduction-zone fluids (Straub et al., 2004)

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Supplemental Material. Methods and Figures S1–S11 (File S1), the schema for Ba/Nb Monte Carlo simulations (File S2), and the full data set. Please visit https://doi.org/10.1130/GEOEL.S.21183694 to access the supplemental material, and contact editing@geosociety.org with any questions.
because U and Pb are more fluid mobile than Th and Nd, respectively. The results of these analyses (Figs. S8–S11) are not as clear as those shown for Ba/Nb (Figs. 1 and 2). This complexity is attributed to the larger number of potential source processes affecting Th/U and Pb/Nd compared to the much more straightforward reservoirs hosting Ba and Nb in most arcs (see the Supplemental Material for more discussion). The sediment-derived melt and/or fluid flux would strongly influence some FMEs like Th (Plank and Langmuir, 1998; Skora and Blundy, 2010; Plank, 2014; Spencer et al., 2021) but should not greatly impact Ba (Kessel et al., 2005; Klimm et al., 2008; Schmidt and Poli, 2014; Carter et al., 2015). Some impact on Nb can be expected because Nb contents in sediments have been shown to be variable (Plank, 2014). Given that FMEs like Th are so strongly modulated by sediment, we limit our discussion to Ba/Nb patterns for the remainder of this manuscript.

**LINKING MAGMA CHEMISTRY AND SLAB MINERAL EVOLUTION**

Barium enrichments in arc lavas are typically attributed to aqueous fluid additions from the subducting slab (Pearce, 1982; Elliott et al., 1997), consistent with experimental data (Kessel et al., 2005; Klimm et al., 2008; Rustioni et al., 2021). The Ba/Nb ratio should therefore be a tracer of hydrous mineral breakdown reactions in the subducted oceanic crust and upper mantle. We investigated the extent to which mineral breakdown reaction can explain the Ba/Nb peaks observed in Figures 1 and 2 using metamorphic and geodynamic models of slab dehydration. We used a thermodynamic model (Hernández-Uribe and Palin, 2019), which determines the (1) phase assemblages, (2) degree of dehydration, and (3) density in a typical slab of normal mid-ocean ridge basal (N-MORB) composition (Gale et al., 2013) as a function of three separate metamorphic P-T paths corresponding to a high-temperature (HT) path, an average-temperature (AT) path, and a cold-temperature (CT) path (similar to subduction zones like the Cascades [western North America], Nicaragua, and Japan, respectively). We compared these theoretical data with our observed geochemical patterns; this approach prioritizes the crustal contribution of the slab to the fluid release underlying variability in Ba/Nb rather than the contributions from the deeper serpentinitized upper mantle, as the model we chose focuses only on the slab top (Hernández-Uribe and Palin, 2019).

The results of our model are presented alongside our moving average in Figure 3. In the HT model (red line, Fig. 3), a free fluid phase is stable as soon as the model begins (Hernández-Uribe and Palin, 2019). The first major change occurs when chlorite and actinolite react out, releasing a “pulse” of fluid. At this point, hornblende is the major remaining hydrous phase, accompanied by minor amounts of epidote and mica. The slab is then almost entirely devolatilized when hornblende and epidote react out. The HT path (Fig. 3) overlaps with the first Ba/Nb peak in the global data set (Fig. 2B). After this, the only remaining water and Ba should persist mainly in accessory phengite (Schmidt and Poli, 2014).

In the AT model (orange curve, Fig. 3), fluid also exists from the beginning of the slab’s evolution. Here, the first pulse of AT fluid production occurs due to gradual chlorite destabilization rather than chloride-out (Hernández-Uribe and Palin, 2019). Slab devolatilization is almost complete by sub-arc depths (110 km or ~40 kbar; Ba/Nb peak 2 in Fig. 2B), like the HT peaks. This shows that the HT fluid flux would strongly influence some FMEs like Th (Plank and Langmuir, 1998; Skora and Blundy, 2010; Plank, 2014; Spencer et al., 2021) but should not greatly impact Ba (Kessel et al., 2005; Klimm et al., 2008; Schmidt and Poli, 2014; Carter et al., 2015). Some impact on Nb can be expected because Nb contents in sediments have been shown to be variable (Plank, 2014). Given that FMEs like Th are so strongly modulated by sediment, we limit our discussion to Ba/Nb patterns for the remainder of this manuscript.

**Figure 2.** (A) Binned median Ba/Nb of all arc magmas in our ArcMetals (Barber et al., 2021) compilation within a 2 km depth-to-slab bin. Bins are displayed as colored circles, where color corresponds to median whole-rock Mg# of bin. 1σ standard deviation of Ba/Nb within each bin is shown as black error bars. (B) Moving average curve (box size 10 bins, or 20 km DTS) was calculated through the 143 bins in A.

**Figure 3.** Moving average of Ba/Nb across our global data set (black curve) with depth to slab on the x-axis. Different phase-equilibrium modeling scenarios from Hernández-Uribe and Palin (2019) described in the text are shown in red for high temperature, orange for average temperature, and blue for cold temperature; y-axis values of these curves show the amount of total bound H2O in each phase assemblage that has been released from hydrous minerals. Temp.—temperature; Avg.—average.
case (red curve, Fig. 3). However, the position of the AT curve is shifted to deeper depths relative to the HT model (Fig. 3).

The LT model (blue curve, Fig. 3) showcases a different style of behavior (Hernández-Urbie and Palin, 2019) relative to the AT and HT models because the hydrous phase assemblage in the LT slab is dominated by lawsonite. The LT curve in Figure 3 shows that the beginning of devolatilization is delayed until the slab reaches ~70 km DTS. Importantly, this pulse of LT fluid release overlaps strongly with the second Ba/Nb peak (Fig. 2B). By the time we reach the end of the LT model, both lawsonite and phengite are the major accessory minerals, and the slab still retains roughly 10% of its total starting water contents. In contrast to the HT and AT scenarios, the LT slab retains the potential to promote slab flux–related magmatism at greater DTS (>150 km). Fluid release being mainly driven by lawsonite is consistent with earlier studies of devolatilization in cold subduction zones like Japan (Nakamura and Iwamori, 2009).

These models for HT, AT, and LT slab devolatilization demonstrate the importance of specific hydrous mineral breakdown reactions (actinolite, chlorite, epidote, lawsonite) in driving the release of fluids from the subducting slab, and they successfully reproduce the first two Ba/Nb peaks observed in our global-moving-average analyses (Figs. 4A and 4B). The depths and type of reactions from thermodynamic models shown in Figures 3 and 4 are consistent with similar models (Syracuse et al., 2010; van Keken et al., 2011; Holt and Condit, 2021), with some notable differences. For example, the thermodynamic models we adopt are not time dependent or geometry dependent. This contrasts with recent efforts that combine evolving slab thermal structures with thermodynamic models to explore the variable amount of dehydration with respect to time as well as absolute P-T conditions (Holt and Condit, 2021). More importantly, the models used here (Fig. 3) only consider phase stability at the slab surface (or slab top). However, dehydration reactions are expected to proceed, albeit more slowly, as an integrated sum of the relevant P-T conditions experienced by the entire cross section of the subducting slab; i.e., from the slab top where dehydration occurs first through to the serpentinized oceanic mantle lithosphere component defining the slab base (Scambelluri and Tonarini, 2012; Holt and Condit, 2021).

In fact, slab tops have been argued to be much drier than are modeled here (Hernández-Urbie and Palin, 2019); boron isotope data (Scambelluri and Tonarini, 2012) and geodynamic models (Holt and Condit, 2021) suggest that serpentinized mantle lithosphere drives much of the fluid release from subducting plates. If this is the case, even if the lithologies driving the loss of fluids differ (Holt and Condit, 2021, their figure 3b), we would expect that drier conditions at the slab top would shift the relative position of the dehydration curves (Fig. 4) toward higher DTS (Holt and Condit, 2021). Such a shift makes tectonic sense because slabs with a high P-T path (e.g., the Cascades) are still capable of generating volcanism at sub-arc DTS, despite appearing (when only considering the slab top) as if they mostly devolatilize in the fore-arc. Furthermore, the degree of fluid release is not simply a question of which phase breakdown reactions occur, but also the particular geometric, kinematic, and thermal history experienced by the slab through its subducting lifetime (Holt and Condit, 2021). However, even under different geodynamic or lithological conditions, we would expect slab dehydration depths to overlap with our Ba/Nb peaks (e.g., the curve in Holt and Condit, 2021, their figure 3b, overlaps with peak 2 in our Fig. 2), demonstrating the spatially and temporally averaged nature of global arc magma geochemical signals and their correspondence with slab devolatilization reactions.

Future work should aim to investigate the role of slab melting (Hernández-Urbie et al., 2020a; Turner and Langmuir, 2022b), prior seafloor hydration (Hernández-Urbie et al., 2020b), and mélangé-style mass transfer (Marschall and Schumacher, 2012) in contributing to the Ba/Nb systematics described here. Slab and/or sediment melting should mobilize FMEs like Ba (Hernández-Urbie et al., 2020a; Turner and Langmuir, 2022b), but we would not expect these processes to affect the Ba/Nb patterns described here for two reasons: (1) we filtered high-SiO2 samples out of our compilation, eliminating the evolved adakites expected from MORB melting (Hernández-Urbie et al., 2020a), and (2) progressive slab and/or sediment melting would raise Nb concentrations and lower Ba concentrations in a magma, decreasing Ba/Nb (Turner and Langmuir, 2022b). Similarly, mélangé rocks like jadeitites and chlorite schists, while enriched in FMEs, would also be enriched in Nb, depressing some of the Ba/Nb signals observed here (Marschall and Schumacher, 2012).

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Figure 4. (A) Schematic diagram showing thermodynamic controls on slab dehydration in the three end-member models (described in text): high temperature (HT, red), average temperature (AT, orange), and cold temperature (CT, blue). (B) Amount of H2O contained in equilibrium hydrous phase assemblages in HT, AT, and CT models described above. Act—actinolite; Chl—chlorite; Ep—epidote; Hbl—hornblende; Laws—lawsonite.


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