Tracking halogens through the subduction cycle

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ABSTRACT

The flux of halogens into the Earth’s mantle at subduction zones is a critical yet poorly constrained parameter in the geochemical evolution of the planet. Here we report the first ever combined high-precision measurements of chlorine, bromine, and iodine for backarc basin basalt (BABB) and ocean island basalt (OIB) glasses. The measurements were undertaken in order to evaluate the depth and extent of the halogen subduction cycle by comparing: (1) melts formed in the Manus Basin (Papua New Guinea) proximal to a modern subduction zone, and (2) melts formed from enriched mantle (EM) reservoirs that have been linked to ancient subduction recycling [EM1 and EM2 sampled by the Pitcairn and Society seamounts (central Pacific Ocean), respectively]. As expected from previous studies, the BABBs are strongly enriched in chlorine relative to other trace elements and mid-oceanic ridge basalts (MORB); however, the combined Br/Cl and I/Cl data provide additional insights. The BABBs have I/Cl weight ratios of up to 5.3 × 10⁻⁴, that are up to five times higher than typical MORB; and the BABBs with the highest I/Cl have Br/Cl ratios of 2–3 × 10⁻⁴, that are lower than typical MORB, and significantly lower than either iodine-rich sediments or seawater-derived sedimentary pore fluids. The final breakdown of iodine-rich serpentine is considered the most likely source of the halogen enrichment in the BABB, suggesting that subduction of serpentined peridotites enables transport of strongly incompatible, fluid-mobile, volatile elements, like iodine, beyond zones of arc-magma generation. The Pitcairn and Society melts exhibit a remarkable correlation between K/Cl and σ²⁸Sr/⁸⁶Sr. The K/Cl ratios vary from MORB-like values of ~15 to maxima of ~40 in the isotopically most enriched EM end members. The trend reflects the lower subduction efficiency of halogens compared to K and other lithophile elements. Melts formed from EM and MORB mantle reservoirs have very similar Br/Cl and I/Cl weight ratios of 3.6 ± 0.8 × 10⁻⁴ and 85 ± 42 × 10⁻⁴ (2σ) respectively, that could indicate that subducted volatiles have been mixed throughout the mantle.

INTRODUCTION

The Earth’s mantle exhibits chemical heterogeneity over a range of scales (e.g., Hofmann, 2003). Much of this heterogeneity is attributed to the presence of recycled crustal materials introduced by subduction of oceanic lithosphere (e.g., Hofmann, 2003; Workman et al., 2006; Jackson et al., 2007). However, the extent to which strongly incompatible, fluid-mobile, volatile elements dissolved in seawater are incorporated into hydrous mineral phases within subducting slabs, and transferred into the deeper mantle beyond the zones of arc magma genesis, remains poorly constrained (Dixon et al., 2002; Holland and Ballentine, 2006; Sumino et al., 2010; Kendrick et al., 2011b).

Recent advances in constraining the global halogen cycle have come from variations in mantle K/Cl (Stroncik and Haase, 2004), the Cl isotope systematics of subduction zones and mantle melts (e.g., Barnes and Sharp, 2006; Bonifacie et al., 2008; John et al., 2010), cosmogenic ¹⁹⁷Au ages of recycled halogens in forearcs (Muramatsu et al., 2001; Fehn et al., 2002), and combined analysis of Cl, Br, I, and noble gases in diamond (Burgess et al., 2002), exhumed mantle wedge peridotites (Sumino et al., 2010), and subduction zone serpentinites (Kendrick et al., 2011b). However, the difficulty of measuring trace amounts of Br and I in magmatic glasses has meant that until now, the combined trace element geochemistry of Cl, Br, and I in mantle melts has received very little attention (Kendrick et al., 2012).

Earlier studies of magmatic glass were limited by measurement precision and focused exclusively on either Br and Cl (e.g., Schilling et al., 1978; Jambon et al., 1995) or I (Déruelle et al., 1992). However, because Cl, Br, and I are not strongly fractionated during partial melting or fractional crystallization of basaltic melts (Kendrick et al., 2012), their combined analysis could provide useful information about halogen sources. Marine sediments represent the Earth’s dominant iodine reservoir, and iodine is strongly depleted in seawater (Déruelle et al., 1992). Sedimentary marine pore fluids are variably enriched in organic I and Br (e.g., Martin et al., 1993; Fehn et al., 2006; Muramatsu et al., 2001, 2007), and typically have seawater-corrected Br*/I weight ratios of between ~0.4 and ~1.5 (where Br*/I = Br_total − Br_seawater and Br_seawater = 0.0035 × Cl; Kendrick et al., 2011a). These signatures can be inherited by serpentinites formed by hydration of the oceanic lithosphere, but are not preserved in slab fluids formed by serpentine breakdown (Kendrick et al., 2011b). Combined analysis of Cl, Br, and I in subduction-related mantle melts could therefore distinguish sedimentary and serpentinite sources of subducted halogens.

Figure 1. Radiogenic isotope (²⁰⁶Pb/²⁰⁴Pb vs. ⁰⁶Sr/⁰⁸Sr) systematics of glasses in this study. Glasses from Pitcairn seamounts are representative of EM1 (enriched mantle) mantle end member. Glasses from Society seamounts exemplify EM2 mantle (only Samoan ocean island basalts show stronger ²⁰⁶Pb/²⁰⁴Pb enrichment). Glasses from Manus Basin are representative of backarc basin basalts. Macquarie Island (Mac. Is.) glasses are enriched in ²⁰⁶Pb/²⁰⁴Pb, but are included to represent halogens in mid-ocean ridge basalt (MORB) (see Kendrick et al., 2012). BABB—backarc basin basalt; OIB—ocean island basalt; DMM—depleted MORB mantle. EM1, EM2, HIMU (high µ), and FOZO (focus zone) are mantle end members (Hofmann, 2003).
The previously documented Society samples were reanalyzed for trace elements (~50 mg aliquots) using an Agilent 7700 inductively coupled plasma-mass spectrometer at the University of Melbourne following the methods of Honda and Woodhead (2005). Halogen (Cl, Br, I) and K analyses were obtained by the noble gas method (Kendrick, 2012). Pristine glass chips were irradiated in position 5c of the McMaster Nuclear Reactor, Canada: irradiation UM#42 (50 h) gave a mean J-value of 0.018 ± 0.003; irradiation UM#44 (42 h) gave a mean J-value of 0.016 ± 0.001. The production ratios of noble gas proxy isotopes \( ^{39}\text{Ar}/^{38}\text{Ar} \), \( ^{38}\text{Ar}/^{37}\text{Ar} \), \( ^{88}\text{Kr}/^{84}\text{Kr} \) and \( ^{129}\text{Xe}/I \) were measured using the \( ^{39}\text{Ar}^{39}\text{Ar} \) Hb3gr flux monitor and four scapolite halogen standards (SY, SP, BB1, BB2; Kendrick, 2012). The noble gas proxy isotopes were extracted from ~1–44 mg of glass using 20 min heating steps of 300 and 1600 °C in an ultra-high vacuum tantalum resistance furnace. The extracted gases were isotopically analyzed using a MAP-215 noble gas mass spectrometer at the University of Melbourne. Halogen ratio measurements have minimum analytical uncertainty of 1%–2%. Absolute Cl concentrations have uncertainties of ~6% and absolute Br/Cl and I/Cl ratios have uncertainties of 10% (2σ). The analytical protocols were described in detail by Kendrick (2012) and Kendrick et al. (2012).

RESULTS AND DISCUSSION

The geochemical data are summarized in Table 1 and Figures 2–4 and reported comprehensively in Tables DR1–DR4 in the GSA Data Repository. The ocean island basalt (OIB) glasses contain 280–1500 ppm Cl; this is fairly typical of basaltic melts sourced from enriched mantle (EM) reservoirs (e.g., Workman et al., 2006). The BABB glasses contain 420–4200 ppm Cl, with the highest concentrations in differentiated samples with low MgO (Fig. 2; Kamenzetsky et al., 2001; Sinton et al., 2003). The samples contain 1100–4600 ppb Br and 20–830 ppb I (Table 1). Despite the varying degrees of melt differentiation, the K/Cl, Br/Cl, and I/Cl ratio measurements can be considered representative of the mantle sources because (1) they do not vary as a function of MgO (Fig. 2B; Fig. DR1), confirming they were not fractionated by either partial melting or fractional crystallization (Kendrick et al., 2012), and (2) the glasses are demonstrably free of contamination by Cl-rich crustal or seawater components, which would result in compositional outliers, or overprint the systematic behavior of the halogens in the K-Cl-Br-I plots (cf. Figs. 3 and 4; Kendrick et al., 2012).

Cosmogenic \( ^{129}\text{I} \) dating studies suggest that iodine initially present in sedimentary pore fluids, or bound to organic matter, is largely lost from subducting slabs in forearc early in the subduction cycle (e.g., at depths of ≤60 km; Muramatsu et al., 2001; Fehn et al., 2002). However, fluid inclusions trapped in the Higashiakaishi peridotite, Japan, record the escape of iodine-rich fluids through the mantle wedge at a depth of ~100 km (Sumino et al., 2010). Furthermore, the BABB glasses in this study are distinguished from MORB and OIB glasses by high I/Cl ratios of as much as 5.3 × 10^4 (Fig. 3; Table 1), demonstrating that limited quantities of iodine can be subducted beyond arc-magma generation zones and may reach the deeper mantle.

The halogen enrichment of BABB glasses (Fig. 4; Table 1) is unlikely to be explained by contamination of the mantle wedge with sedimentary material, because organic matter in sediments is characterized by seawater-corrected Br/Cl ratios of ~1–20 that are equal to or greater than those of sedimentary pore fluids (cf. Fig. 3B; Martin et al., 1993; Muramatsu et al., 2007). In contrast, saline fluids released during the final stages of serpentine breakdown are characterized by low K/Cl of 0.01–0.2, variable I/Cl and Br/Cl ratios that can be lower than those of sedimentary marine pore fluids (Fig. 3B; Kendrick et al., 2011b). Variable addition of serpentine breakdown fluids could account for the K/Cl of 2–6 in BABB, that is lower than the median MORB value of ~12 (Fig. DR2), and the negatively correlated Br/Cl and I/Cl of BABB, in which low Br/Cl ratios of 2–3 × 10^2 are associated with the most ICl enriched melts (Fig. 3B).

The importance of serpentine for deep subduction of iodine is further emphasized here because preliminary results suggest that very little iodine can be incorporated into amphibole or mica (Kendrick, 2012), and serpentine is probably unusual among hydrous minerals in its ability to incorporate significant iodine (Fig. 2B; Kendrick et al., 2011b). Furthermore, serpentine in hydrated mantle lithosphere can be subducted to greater depths than hydrous mineral phases in overlying crust (Ulmer and Trommsdorff, 1995; Schmidt and Poli, 1998).
In contrast to the BABB glasses, the Pitcairn and Society glasses all have Br/Cl of between $3.2 \times 10^{-3}$ and $4.9 \times 10^{-3}$, and I/Cl ratios of between $56 \times 10^{-6}$ and $130 \times 10^{-6}$, that are similar to MORB compositions (Fig. 3; Table 1; Schilling et al., 1978; Kendrick et al., 2012). The most important feature of the OIB data is that radiogenic isotope ratios, like $^{87}\text{Sr}/^{86}\text{Sr}$, are correlated with K/Cl (Fig. 4A). The trend can be explained by mixing similar EM-type sources with K/Cl of ~40 (representing a subducted component that recycles K to the OIB source more efficiently than Cl) and local MORB mantle with K/Cl of ~15 (Fig. 2A).

Comparison of trace element abundances in BABB and OIB melts confirms that the high K/Cl of the EM reflects a preferential enrichment of K and other lithophile elements relative to Cl (Fig. 4B; Stroncik and Haase, 2004; Workman et al., 2006); this contrasts with the relative enrichment of halogens seen in BABB (Fig. 4B). These data can be interpreted to indicate that seawater-derived volatiles, such as the halogens, are not a significant component of the EM source (e.g., Dixon et al., 2002). However, the OIB investigated have higher Cl concentrations than typical MORB (Table 1), and so we prefer to conclude only that halogens are subducted into deep EM reservoirs with much lower efficiency than K. Unless the mantle has retained a very significant component of its primordial halogens, it seems likely that subducted halogens have been mixed throughout the entire mantle to some extent. This interpretation is consistent with the presence of atmospheric noble gases throughout the convecting mantle (e.g., Holland and Ballentine, 2006).

CONCLUSIONS

The current data demonstrate that limited quantities of iodine, as well as chlorine, can be subducted past magmatic arcs to moderate depths in the Earth’s mantle (Fig. 3). Halogen abundance ratios therefore provide a useful tool for evaluating the extent to which crustal recycling influences the distribution of fluid-mobile volatile elements in the mantle. The similarity of Br/Cl and I/Cl in the MORB and EM-type OIB glasses of this study (Fig. 3B) suggests that volatile components are gradually lost from subducting slabs and may have been well mixed throughout the entire mantle. However, further characterization of Cl, Br, and I in OIB and MORB sources is required to better constrain the extent of halogen heterogeneity in the Earth’s mantle. This will enable a more quantitative evaluation of possible halogen contamination mechanisms that affect some basalt melts, and it will test if a deeply subducted volatile component can be unambiguously identified in the Earth’s mantle.

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