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The systematics of halogen (Cl, Br and I) and H_2O abundances in magmatic glasses from Southwest Pacific Backarc Basins

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Abstract: Submarine magmatic glasses from the Manus, Woodlark, North Fiji and Lau backarc basins in the Southwest Pacific, as well as a sample from Volcano A on the volcanic front of the Tonga Arc adjacent to the Lau Basin, were investigated to characterise the Cl, Br and I elemental budgets in subduction systems. In particular we seek to determine the extent of variability in the Br/Cl and I/Cl ratios of backarc basin basalts (BABB) and evaluate if these ratios could improve constraints on the source of subducted volatile components in backarc basins worldwide. The selected glasses represent variably evolved melts of boninite, basalt, basaltic-andesite, dacite and rhyolite composition and were selected from spreading centres and seamounts located at varying distances from the associated arcs. In general the strongest subduction signatures (e.g. Ba/Nb of 100-370) occur in the samples closest to the arcs and lower more MORB-like Ba/Nb of <16 are found in the more distal samples. The glasses investigated have extremely variable halogen concentrations (e.g. 3-4200 ppm Cl), with the highest concentrations in enriched glasses with the most evolved compositions. As observed in previous studies, the K/Cl, Br/Cl and I/Cl ratios of glasses from individual settings do not vary as a function of MgO and are considered representative of the magma sources because these ratios are not easily altered by partial melting or fractional crystallisation. Systematic variations in these ratios between basins can therefore be related to mixing of halogens from different sources including: i) the mantle wedge which has MORB-like Br/Cl and I/Cl; ii) a subduction-derived slab fluid with estimated salinity of ~4-10 wt % salts and variable I/Cl; and iii) brines characterised by salinities of 55 ± 15 wt % salts and Br/Cl slightly higher than seawater, that are sometimes assimilated in crustal magma chambers. The slab fluids enriching the Woodlark Basin, North Fiji Basin and the Fonualei Spreading Centre of the Lau Basin have MORB-like I/Cl and Br/Cl overlapping the lower end of the MORB range, indicating a probable source from dehydration of altered ocean crust (AOC). In contrast, slab fluids with I/Cl ratios of up to 10 times the MORB value were detected in BABB from Manus Basin, the Valu Fa Ridge and the Tonga Arc, and in these cases the elevated I/Cl ratios are most easily explained by the involvement of fluids released by breakdown of I-rich serpentinites. The data show slab fluids vary in composition across the Tonga Arc and from north to south in the Lau Basin. However, the compositional range of subducted halogens overlaps that of MORB indicating subduction could be a major source of halogens in the Earth's mantle.

1. Introduction

The extent to which a mantle wedge contributes juvenile volatiles toward the superjacent island arc volatile flux, versus the degree to which subduction of hydrated oceanic lithosphere transports surface volatiles into and beyond the sub-arc mantle is poorly constrained (Parai and Mukhopadhyay, 2012; Rüpke et al., 2004; Staudacher and Allègre, 1988; Wallace, 2005). In contrast to lithophile elements, volatiles are lost during magma degassing and crystallisation meaning they cannot be reliably investigated in sub-aerial rocks. However, water and halogens have relatively high solubilities in silicate melts and halogens are commonly retained in melts erupted in water depths of more than about ~500 m, meaning they can be investigated in submarine glasses as well as melt inclusions (e.g. Straub and Layne, 2003; Unni and Schilling, 1978). Previous studies of volatiles in subduction-related melts have included H_2O, Cl, F, S, CO_2 and noble gases (e.g. Bach and Niedermann, 1998; Danyushevsky et al., 1993; Hahm et al., 2012; Kelley et al., 2006; Plank et al., 2013; Portnyagin et al., 2007; Sinton et al., 2003; Straub and Layne, 2003; Sun et al., 2007). The existing data show submarine backarc basin basalts (BABB) have high Cl and H_2O contents that are likely related to a flux of slab-derived fluids into the sub-arc mantle (Danyushevsky et al., 1993; Kent et al., 2002; Sinton et al., 2003; Straub and Layne, 2003; Kelley et al., 2006; Sun et al., 2007). However, the extent to which submarine magmas assimilate seawater-derived components prior to eruption is poorly known and complicates the interpretation of BABB volatile data (e.g. Bach and Niedermann, 1998; Hahm et al., 2012; Kent et al., 2002).

Combined measurement of Cl, Br and I enables the sources of volatiles in backarc basin basalts to be rigorously assessed, and the presence of assimilated seawater-derived components unambiguously identified (Kendrick et al., 2013a). This is possible because Cl, Br and I have similar compatibilities to each other and K, and these elements are not significantly fractionated by the generation of silicate melts with MgO of 1-10 wt % (Kendrick et al., 2012a; Schilling et al., 1980). Furthermore, the relative abundance ratios of Cl, Br and I are fairly uniform in the MORB mantle (Jambon et al., 1995; Kendrick et al., 2013a; Schilling et al., 1980), but vary widely in the Earth's hydrosphere and subducting oceanic lithosphere (Deruelle et al., 1992; Fehn et al., 2006; Fehn and Snyder, 2005; Kendrick et al., 2013b; Muramatsu et al., 2001). Iodine is an essential element for life that consequently has high concentrations in organic-rich sediments (Murumatsu and Wedepohl, 1998). High I concentrations and I/Cl ratios can be inherited from sediments by serpentinites formed when sedimentary marine pore fluids hydrate the mantle lithosphere and forearc mantle (Fehn et al., 2006; Kendrick et al., 2013b; Muramatsu et al., 2001; Snyder et al., 2005). In contrast, seawater has a very low I/Cl ratio (Fuge and Johnson, 1986) and can potentially be distinguished from seawater-derived brine or I-poor alteration minerals (such as amphibole), because these materials have different Br/Cl ratios (Kendrick et al., 2013a).

The current study reports the Cl, Br and I composition of submarine glasses from backarc and marginal basins in the SW Pacific, including the Manus, Woodlark, North Fiji and Lau Basins (Fig 1). The study focuses on backarc basin basalts (BABB), which vary from compositions similar to MORB, to compositions more representative of island arc basalts (Pearce and Stern, 2006). However, an island arc boninite glass from the flanks of volcano A in the Tonga Arc (Fig 1c) was included in this analysis. The aims of the study are to further characterise the Br/Cl and I/Cl composition of subducted components in SW Pacific backarc basins and to test if the primary mechanisms for iodine transport into the sub-arc mantle are via saline fluids or melts derived from sediments.

2. Sampling of SW Pacific Backarc Basins

New samples with MORB-like Ba/Nb of < 16 were selected from the Manus Basin (Fig 2a; Sinton et al., 2003). These samples were dredged during the MW8518 voyage of the RV *Moana Wave* in 1985, from the Extensional Transform Zone and Manus Spreading centre, that are more distal with respect to the New Britain Arc than the majority of the previously investigated BABB (Kendrick et al., 2012b), that came from the South and East Rifts closer to New Britain (Fig 1; see Beier et al., 2010; Binns and Scott, 1993; Kamenetsky et al., 2001; Sinton et al., 2003).

The Woodlark Basin samples were recovered during the 1982 KK820316 voyage of the RV *Kana Keoli* (Johnson et al., 1987; Muenow et al., 1991; Perfit et al., 1987). The westernmost dredge (RD26) sampled depleted MORB-like glasses from the Woodlark Spreading Centre, whereas dredges 32, 33 and 35 derive from the complex boundary area close to the current subduction zone (Fig 1; Perfit et al., 1987). Most of the Woodlark Basin is situated west of the current subduction zone, and is not in a backarc setting (Fig 1); however, rocks with BABB affinity have been dredged previously and are variously ascribed to previous episodes of subduction-related mantle enrichment prior to a reversal of subduction polarity c. 5 Ma (Perfit et al., 1987) and westward leakage of subarc mantle wedge through slab tears along the Soloman Arc (Chadwick et al., 2009).

North Fiji Basin wax core samples were recovered from the propagating rift axis of the 174° E / 21° S segment during the SS08/2006 voyage of the RV *Southern Surveyor* (Fig 1; Danyushevsky et al., 2005). Previous dredging of this segment recovered MORB-like basalts and BABB suggesting a heterogeneous mantle source (Eissen et al., 1994). The melts from the North Fiji Basin are of additional interest because the mantle wedge is unusually hot in this area (Lagabrielle et al., 1997), enabling us to investigate volatile recycling in a ‘hot subduction zone’.

Lau Basin samples recovered during voyages SS11/2004 and SS07/2008 of the RV *Southern Surveyor* and during voyages 35 and 67 of the FS *Sonne*, comprise two transects away from the Tonga Arc, one encompassing the northern Fonualei Spreading Centre and Mangatolu Triple Junction (Keller et al., 2008), and the second running along the Valu Fa Ridge but including two off axis seamounts (Fig 1; Kamenetsky et al., 1997). A boninite glass sample from Volcano A on the volcanic front of the Tonga Arc was recovered during SS07/2008, and represents the first example of active boninite volcanism in any arc globally (Fig 1; Cooper et al., 2010). Previous studies have shown basalts from these locations carry strong subduction signatures (e.g. Fig 2cd; Pearce and Stern, 2006), and the current samples were selected to test if halogen signatures vary with increasing distance from the arc front as typically observed for Ba/Nb and other trace element indicators of subduction influence (Keller et al., 2008; Haase et al., 2002; 2009). Additional halogen analyses have been reported previously for glasses from the northwest part of the Lau Basin (Kendrick et al., 2013a), which have MORB-like trace element signatures (Figs 2cd; Lytle et al., 2012), but are characterised by high $^{3}He/^{4}He$ ratios of up to 28 R/Ra (where Ra is the atmospheric $^{3}He/^{4}He$ ratio; Lupton et al., 2009), and appear to have assimilated up to 95 % of their total Cl from seawater-derived brines (Kendrick et al., 2013a).

3. Methods

The halogens (Cl, Br, I) and K were analysed in high purity glass separates of 6-30 mg using the noble gas method whereby sample irradiation converts a few parts per million of the samples Cl, Br, I and K into noble gas proxy isotopes ($^{38}Ar_{Cl}$, $^{80}Kr_{Br}$, $^{128}Xe_{I}$ and $^{39}Ar_{K}$) which are then analysed by noble gas mass spectrometry (e.g. Böhlke and Irwin, 1992; Johnson et al., 2000; Kendrick, 2012). The noble gas production ratios ($^{38}Ar/Cl$, $^{39}Ar/K$, $^{80}Kr/Br$ and $^{128}Xe/I$) are monitored using the ^{40}Ar-^{39}Ar flux monitor Hb3gr and 3 scapolite standards with precisely known Cl, Br and I abundances (cf. Kendrick, 2012; Kendrick et al., 2013a). The Fiji and Woodlark samples were irradiated in the Central Thimble facility of the USGS Triga reactor, Denver, USA (UM#53: 80 hours, 28-Nov-2012 received 6.4×10^{18} neutrons cm^{-2}). The Lau and MORB-like Manus samples were irradiated in position 5c of the McMaster nuclear reactor, Canada (UM#48: 42 hours, 15-Dec-2011, received 1.2×10^{19} neutrons cm^{-2}). Noble gas isotopes were extracted from the glasses by fusion at 1500 °C in an ultra-high vaccum resistance furnace and analysed for isotopes of Ar, Kr and Xe using the MAP-215 noble gas mass spectrometer at the University of Melbourne. Gas handling and data reduction have been described in detail by Kendrick (2012) and Kendrick et al. (2013a). The high sensitivity of noble gas mass spectrometers to noble gas isotopes provides analytical uncertainties as low as 1-2 % (2σ) for ratio and concentration measurements (internal precision). However, the external precision (accuracy) is estimated at 5 % for K, Cl and Br and 10 % for I (2σ); based on calibration of mass spectrometer sensitivity, heterogeneities in the halogen standards required for calculating Br and I, and comparison with other techniques (Kendrick et al., 2013a).

Major and trace element analyses were undertaken on Woodlark samples at the University of Melbourne; on North Fiji Basin samples at the University of Tasmania and on Valu Fa Ridge samples at the Research School of Earth Sciences, Australian National University (ANU). Each laboratory employed slightly different procedures; however, at each university major elements were measured by Cameca (SX-50 or SX-100) electron microprobes; and trace elements were measured via Agilent (7700x, 7500S or 7500cs) inductively coupled plasma mass spectrometers coupled to 193 nm excimer lasers. The beam diameters varied from 80 to 120 μm, the calibration standards were BHVO2G in Melbourne, and NIST 612 glass in Tasmania and ANU, with BCR-2G as the secondary standard in each case. Data for replicate analyses of BCR-2G analyzed with the Valu Fa Ridge samples were presented in Jenner and O'Neill (2012a). Analytical conditions typical of the Melbourne and Tasmanian laboratories have been described elsewhere (Danyushevsky et al., 2003; Woodhead et al., 2007).

Doubly polished wafers of glasses from the North Fiji Basin, and selected glasses from the Woodlark and Lau Basins were prepared for water measurement using the Bruker Vertex 70 (FT-IR) + Hyperion 2000 microscope at the University of Tasmania. In most cases the reported analyses represent the average of 3 measurements made on areas of 60×60 μm. The thickness of the glass was precisely determined for each measurement area using interference fringes on the main H_2O peak at 3550 cm^{-1}. The height of the absorbance peak was measured at 3500 cm^{-1} and 3100 cm^{-1} and converted to a H_2O concentration on the basis of empirically determined calibration factors derived from four glass standards as described in Danyushevsky et al. (1993).

A full suite of noble gases were measured in the glasses from the Woodlark Basin using the VG5400 noble gas mass spectrometer at the Australian National University following the methods of Honda et al. (2004). The instrument was calibrated using aliquots from an air bottle and a second bottle containing the helium standard of Japan (HESJ) with ^{3}He/^{4}He of 20.6 R/Ra (Matsuda et al., 2002). Noble gases were extracted by stepwise furnace heating and minor corrections were made for atmospheric blank. However, the current study reports only total fusion He isotope data obtained by combining all heating steps.

4. Results

4.1 Major and trace elements

The new major and trace element data for North Fiji, Woodlark Basin and Valu Fa Ridge glasses are summarised together with relevant compositional data from representative published studies in Table S1 of the electronic supplement and Fig 2 (Beier et al., 2010; Kamenetsky et al., 2001; Keller et al., 2008; Perfit et al., 1987; Sinton et al., 2003).

The North Fiji and Lau glasses have relatively primitive basaltic or basaltic-andesite compositions with 4.7-8.2 wt. % MgO and 49.2-55.3 wt. % SiO_2 (Table S1). In contrast, the glasses selected from the Woodlark and Manus Basins encompass a wider range of MgO and SiO_2, extending from primitive compositions of 8.1 wt. % MgO and 48.1 wt. % SiO_2 to highly evolved rhyolitic compositions with 0.6 wt. % MgO and 74.7 wt. % SiO_2 (Table S1).

The trace element data show strong subduction signatures (e.g. Ba/Nb >100 and Nb, Ta depletion) in the Tonga Arc sample and BABB glasses from Manus, Woodlark and both the Fonualei Spreading Centre and Valu Fa Ridge of the Lau Basin (Fig 2; Table S1; Cooper et al., 2010; Keller et al., 2008; Sinton et al., 2003). In comparison, the samples from the North Fiji Basin are only slightly enriched in the most incompatible trace elements (Fig 2b), the MORB-like samples from Manus are moderately depleted in trace elements (Fig 2a) and the samples from the Woodlark Spreading Centre (dredge 26) are strongly depleted in all incompatible trace elements (Fig 2b; Table S1). The full datasets for the North Fiji Basin and Valu Fa Ridge samples will be published in detail elsewhere (data of L. Danyushevsky, F. Jenner and colleagues).

4.2. Volatiles

The new Cl, Br, I and H_2O concentration data obtained in this study are given in Table S1 of the electronic supplement and summarised in Figure 3 together with halogen data from Kendrick et al. (2012b) and H_2O data from several previous studies (Kamenetsky et al., 1997, 2001; Keller et al., 2008; Shaw et al., 2012).

In general, the highest concentrations of halogens and other incompatible trace elements occur in the most evolved melts with the lowest MgO, and the samples that have the strongest subduction signatures (Figs 2 and 3). The depleted glasses from the Woodlark Basin define the minima of 3 ppm Cl, 16 ppb Br and 1.8 ppb I compared to maxima of 4200 ppm Cl, 15 ppm Br and 670 ppb I in glasses from Manus and Valu Fa (Fig 3; Table S1).

The 2σ uncertainties of most halogen measurements are smaller than the data point symbols (e.g. 1-8 %; Table S1). However, uncertainties are significantly higher for some of the Woodlark samples because of their low halogen abundances and high K/Cl of ~90 that result in a significant correction for K-derived ^{38}Ar interference on the proxy isotope used for Cl measurement (see Kendrick (2012) for data reduction). As a result, Cl is measured with a 2σ precision of 3-40%, compared to 1-17% for Br and I in these samples (Table S1).

The glasses have H_2O concentrations that vary from a minimum of 0.2 wt. % to a maximum of 1.6 wt % (Fig 3d; Table S1). The majority of our samples were erupted in water depths of more than 2000 m (Table S1), which minimises the effects of H_2O degassing. However, in contrast to the halogens that are typically strongly under-saturated in silicate melts at these conditions (Webster et al., 1999; Bureau et al., 2000), some of the H_2O concentrations are expected to be close to saturation, meaning the H_2O measurements are treated as minimum values (Fig 3d).

The Woodlark glasses have extremely variable ^{4}He concentrations that range from 10^{-6} to 7×10^{-10} cm^{3}/g (Fig S1), and ^{3}He/^{4}He isotope signatures that extend from a minimum of 1.8 R/Ra in a subduction-enriched glass to higher values that fall within the MORB range of 9 ± 2 R/Ra (where Ra is the atmospheric ^{3}He/^{4}He ratio of 1.39×10^{-6}; Graham, 2002). The variation in ^{4}He concentrations probably reflects the degree of degassing and is not correlated with either Cl concentration or the I/Cl ratio of the Woodlark samples (Fig S1).

The relative abundance ratios of Br/Cl, I/Cl and K/Cl appear unrelated to the degree of melt evolution: Br/Cl is only slightly more variable in the BABB samples investigated (±30%) than it is in MORB and OIB (Fig 3a; Kendrick et al., 2013a); and neither Br/Cl, K/Cl nor I/Cl are correlated with MgO (Figs 3e,f). These observations are consistent with previous work that has shown these elements all have very similar incompatibilities and their abundance ratios are not easily modified by partial melting or fractional crystallisation of common silicate minerals such as olivine, pyroxene or plagioclase (Kendrick et al., 2012a). In addition, whereas H_2O/Cl decreases to low MgO suggesting significant H_2O loss at MgO of < 4 wt. % (Fig S2), the lack of a relationship between halogen abundance ratios and MgO confirms the halogens where not affected by degassing. Halogen abundance ratios are therefore interpreted to reflect source composition rather than melt evolution (below).

5. Discussion

An important feature of this study is that the measurement of multiple halogens (Cl, Br and I), that all have similarly incompatibilities in the mantle (Schilling et al., 1980; Kendrick et al., 2012a), provides the potential for using halogen abundance ratios to fingerprint different volatile components present in BABB. We begin this discussion by briefly defining the limited range of Br/Cl and I/Cl in mantle reservoirs sampled by mid-ocean ridge basalts

(MORB) and ocean island basalts (OIB); and summarise how the assimilation of brine components was identified in previous studies (Kendrick et al., 2013a). We then apply this knowledge to further characterise the composition and salinity of subducted volatile components in each of the backarc basins investigated.

5.1 Defining MORB and assimilated halogen components

The ‘mantle’ Br/Cl and I/Cl fields in Figs 3 and 4 are defined by analyses of 52 glasses including MORB samples from Macquarie Island in the SW Pacific; various locations on the Mid-Atlantic Ridge (13.5°-35° N); the Juan de Fuca Ridge and East Pacific Rise (Kendrick et al., 2012a, 2013a); and ocean island glasses from the Pitcairn and Society seamounts of Polynesia which have an indistinguishable range of compositions (Kendrick et al., 2012b; 2014). Note that all the Br/Cl and I/Cl ratios reported here have been obtained using the same reference materials and the values originally reported by Kendrick et al. (2012a,b) have been recalculated using the reference material Br and I concentrations recommended by Kendrick et al. (2013a). In addition, the Macquarie Island dataset has been filtered to exclude three anomalously high I/Cl ratios that resulted from palagonite contamination (Kendrick et al., 2012a, 2013a). The range of Br/Cl is within uncertainty of 80 Atlantic and Pacific MORB and OIB glasses reported by Jambon et al. (1995) and Schilling et al. (1978, 1980). The reported range of Br/Cl and I/Cl (Fig 4a) is considered representative of variation within the Earth’s mantle because within these data sets Br/Cl, I/Cl and K/Cl form clusters (e.g. Fig 5a), whereas the assimilation of seawater-derived Cl would generate strong correlations between these ratios and mixing trends that extend to K/Cl of <<10 (see Kendrick et al. (2013a) for a detailed discussion).

Samples from the NW part of the Lau Basin that lack subduction signatures (Fig 2cd), are distinguished by strongly correlated Br/Cl, I/Cl, K/Cl and H_2O/Cl ratios, that reflect assimilation of high salinity brines in crustal magma chambers at depths of 3-5 km (see Fig S3; Kendrick et al. 2013a). Assimilation of seawater-derived Cl has been identified in a range of other locations (Coombs et al., 2004; Kent et al., 1999a; 1999b; 2002; le Roux et al., 2006; Wanless et al., 2011) and three element diagrams that use Cl as the denominator show that in every case the assimilated component is an ultra-saline brine with low K/Cl and 55 ± 15 wt % salts (Kendrick et al., 2013a). The assimilated brines are therefore probably restricted to high salinities by the relative solubilities of Cl and H_2O in silicate magmas (Kendrick et al., 2013a).

The brines assimilated by magmas from NW Lau and the Galapagos Spreading Centre are further characterised by Br/Cl of ~10-15% higher than seawater (Kendrick et al., 2013a). In contrast, condensed vapour phases venting on the seafloor can have Br/Cl ratios of up to 40 % lower than seawater (Oosting and Von Damm, 1996), consistent with a role for phase separation in generating the brines (Kendrick et al., 2013a). However, the salinity and Br/Cl of the brine is probably also influenced by preferential incorporation of H_2O>Cl>Br into hydrous minerals during crustal alteration (Kendrick et al., 2013a), and we assume that altered ocean crust is characterised by low Br/Cl. This is justified because in contrast to the suggested similar incompatible behaviour of Cl, Br and I in the mantle (Schilling et al., 1980; Kendrick et al., 2012a), Cl is expected to have a higher compatibility than the larger Br and I anions in hydrous alteration minerals such as amphibole (Svensen et al., 2000; Kendrick, 2012), which is a major reservoir of Cl in altered ocean crust (Barnes and Cisneros, 2012).

The brines identified in NW Lau (and Galapagos Spreading Centre) preserve low I/Cl ratios of close to seawater (Figs 4b and S3; Kendrick et al., 2013a) which is strongly depleted in iodine relative to the mantle and known crustal lithologies (Fuge and Johnson, 1986).

However, brines in backarc basins could potentially acquire elevated I/Cl as a result of fluid interaction with sediments (cf. You et al., 1994). Therefore melt Br/Cl ratios higher than seawater together with low K/Cl and low H_2O/Cl are considered more diagnostic of brine assimilation than low I/Cl ratios.

5.2 Defining subducted halogen components

5.2.1 Lau Basin: Fonualei Spreading Centre

The BABB from the Fonualei Spreading Centre have elevated H_2O/Ce of 1640->2400 and Cl/K of >0.2 (Table S1) that are much higher than typical MORB values of 150-250 and 0.05-0.1, respectively (Michael, 1995; Michael and Cornell, 1998; Kendrick et al., 2012a), indicating an excess (e.g. non-mantle) volatile component in these melts. The Br/Cl and I/Cl ratios of the Fonualei Spreading Centre glasses are very similar to MORB (Fig 4b); however, the highest Cl concentrations of 800-1200 ppm occur in samples with the most elevated Ba/Nb (60-160; Table S1), and the samples Br/Cl as well as Ba/Nb ratio is related to the estimated depth above the slab (Fig 5). These data suggest that most of the variation in halogen abundance ratios is related to mixing of mantle halogens with a subducted component that has I/Cl similar to MORB and Br/Cl at the lower end of the MORB range (Figs 4a and 5a).

5.2.2 Lau Basin: Valu Fa Ridge and Tofua Arc

The BABB from the Valu Fa Ridge and Tonga Arc have Ba/Nb of 109-235, elevated H_2O/Ce of 610-1880, Cl/K of 0.3-0.4 and Cl concentrations of 540-2440 ppm that indicate an excess volatile component (Figs 2 and 3; Table S1). The Valu Fa - Tonga glasses have variable I/Cl that can be interpreted as defining a binary mixture between mantle halogens and subducted volatiles with I/Cl of equal to or higher than the maximum measured I/Cl value (Fig 4b). However, I/Cl is not strongly correlated with Ba/Nb (Fig S4) suggesting the subducted component might alternatively have variable I/Cl, which is consistent with different lithologies in the subducting slab having different I/Cl ratios and contributions from specific slab lithologies vary during subduction (Peacock, 1990; Schmidt and Poli, 1998). Furthermore, halogens derived from specific lithologies are probably fractionated during subduction-related metamorphism (John et al., 2011; Kendrick et al., 2011).

The currently available data suggest these processes combine to preferentially return I (and to a lesser extent Br) to the surface reservoirs (hydrosphere) at an earlier stage of subduction than Cl, and that the I/Cl ratio of the subducted component consequently decreases across the subduction zone from the forearc to the backarc (This study; Kendrick et al., 2011; 2013b). This is supported by data from forearc serpentinites from the Marianas and Guatemala (on opposite sides of the Pacific) that have I/Cl ratios orders of magnitude higher than observed in the Tonga Arc (Kendrick et al., 2013b); and the progressive decrease in I/Cl observed from the Tonga Arc to the Valu Fa Ridge (Fig 4d). It is also consistent with systematic variations between the Br/Cl and I/Cl ratios of eclogite-facies serpentinites and serpentinite breakdown fluids preserved in eclogite facies fluid inclusions (John et al., 2011; Kendrick et al., 2011).

5.2.3 Manus Basin

The BABB from the Manus Basin have high Ba/Nb of up to 280 (Fig 2a); H_2O/Ce of up to 3400; Cl/K of up to 0.5, variable concentrations of up to 4200 ppm Cl in the most evolved melts (Table S1), and I/Cl of up to four times the MORB range (Fig 4c). These data are characteristic of a large subducted volatile component (Kamenetsky et al., 2001; Sinton et al., 2003); however, in contrast to the Valu Fa – Tonga data, the Manus data cannot be simply explained by binary mixing of a subducted component with mantle halogens.

The Manus Br/Cl and I/Cl data delineate a 'fan shaped' array with the highest Br/Cl ratios always measured in samples with low I/Cl (Fig 4c), and the MORB-like samples with <400 ppm Cl and Ba/Nb of <16 having some of the most elevated Cl/K ratios that are unlikely to result from subduction (Table S1). These data suggest mixing between multiple components including: 1) mantle-derived halogens with MORB-like abundance ratios; 2) halogens introduced with a seawater-derived brine characterised by high Br/Cl and low I/Cl (e.g. similar to the brine component in NW Lau; cf. Fig 4b); and 3) a subducted component characterised by variably elevated I/Cl (Fig 4c).

5.2.4 North Fiji Basin

The BABB from the North Fiji Basin have trace elements that lack an obvious subduction signature (Ba/Nb ~ 6-12; Fig 2b), relatively low Cl contents of 65-250 ppm and Br/Cl and I/Cl ratios that are just within the MORB range (Fig 4d). However, the North Fiji BABB have H_2O/Ce ratios of up to 560 that are at least twice the MORB value (Michael, 1995), and indicate that up to half the H_2O in these samples (e.g. ~0.35 wt %) is an excess volatile component. The uniformly low Br/Cl ratios of these glasses do not favour the assimilation of seawater-derived brines (Fig 4d), and by default the excess volatile component is therefore ascribed to a subducted origin.

5.2.5 Woodlark Basin

Woodlark Basin glasses from dredges 33 and 35 have high Ba/Nb ratios of 55-370, high halogen concentrations of 470-1200 ppm Cl, and variable ^{3}He/^{4}He signatures of 1.8-11 R/Ra that are consistent with subduction (Figs 2b and S1; Table S1). However, although the Woodlark glasses exhibit a similar range in I/Cl as the Valu Fa – Tonga glasses (cf. Figs 4b and d); the highest I/Cl ratios are not measured in the enriched samples with high Ba/Nb ratios (Fig 3a; Table S1). Rather the enriched samples have MORB-like I/Cl and Br/Cl similar to subducted components in the Fonualei Spreading Centre and North Fiji Basin, and it is the depleted MORB-like samples with 3-20 ppm Cl and 1.8-3 ppb I that have the anomalously high I/Cl ratios (Fig S1; Table S1).

The anomalously high I/Cl of samples from dredges 26 and 32 is not explained by measurement uncertainty (Table S1), nor can it be explained by degassing given that these melts would have been undersaturated with respect to halogens by more than any of the other samples investigated, and I/Cl is not correlated with ^{4}He concentration (Fig S1). However, based on their chemical compositions, the samples in dredges 26 and 33 could represent just three lava flows (Table S1) and the variable I concentration of these samples (1.8-5.2 ppb I) could therefore potentially reflect contamination by undetected palagonite alteration which can contain ppm-levels of iodine (Kendrick et al., 2013a). Great care was taken in preparing these samples and palagonite was not visible under the binocular microscope, however, their low I content renders them much more sensitive to contamination than typical glasses. Alternatively the data could indicate the strongly depleted Woodlark mantle is characterised by unusually high I/Cl ratios (Fig 4d) that might be related to an earlier episode of subduction enrichment in this complex tectonic setting (Fig 1).

5.3 Origins of the subducted components

Trace element diagrams used to differentiate subduction input of sediment melts and saline fluids include the Th/Yb versus Ba/La diagram (Fig 6; Woodhead et al., 2001). Diagrams of this type work because sediments and sediment-derived melts have characteristically high Th/Yb ratios and both elements are fluid immobile (Plank and Langmuir, 1998). In contrast, Ba is extremely mobile compared to La meaning saline fluids (irrespective of source) tend to be characterised by high Ba/La ratios (Fig 6a; Woodhead et al., 2001). The BABB in this study plot close to the x-axis in Fig 6 with low Th/Yb ratios and variable Ba/La enrichment consistent with fluxing of the sub-arc mantle with saline fluids and minimal involvement of sediment melts (Fig 6; see also Turner et al., 1997; Haase et al., 2002; Hergt and Woodhead, 2007). The importance of saline fluids is further supported by the low K/Cl ratios of the BABB (Fig 3), because whereas sediment melts could have variable or high K/Cl ratios, saline fluids (irrespective of source) have K/Cl ratios of <0.2, reflecting the predominance of the Cl^- anion and multiple cations including Na^+, Mg^{++}, Ca^{++} and Fe^{++} as well as K^+ (e.g. Phillipot et al., 1998; Scambelluri et al., 2004). As a result the involvement of saline slab fluids always generates BABB with low K/Cl (e.g. Kent et al., 2002; Sinton et al., 2003; Sun et al., 2007).

5.3.1 Slab fluid salinity and proportional input

Given saline fluids rather than sediment melts are the dominant medium for I transport in all the settings investigated (Fig 6), the H_2O/Cl ratios of the glasses investigated should provide some information about the salinity of the fluids (e.g. Kent et al., 2002). We explore this possibility using three element diagrams with a common denominator (Figs 7ab), in which mixing trends are defined by straight lines and H_2O degassing produces predictable results. This approach is complementary to, but fundamentally different from the modelling approach adopted by Kent et al. (2002).

Plots in which Cl is the denominator were previously used to identify the origin of assimilated Cl in melts from the NW part of the Lau Basin (Fig 7a; Kendrick et al., 2013a). These plots are advantageous because they help define the degree of variability in mantle K/Cl and H_2O/Cl ratio and the data converge on a single fluid component with K/Cl of <0.2 (Fig 7a; Kendrick et al., 2013a). Most of the BABB in this study have limited variation in K/Cl; however, the salinity of the aqueous slab fluids responsible for Cl-enrichment of the mantle wedges can be estimated by extending mixing lines from the MORB mantle field, through the glasses, to hypothetical fluid end-members with K/Cl of <0.2 (e.g. the dotted lines in Fig 7b).

The variation in H_2O/Cl exhibited by glasses from Manus, Valu Fa and Fonualei Spreading Centre suggests these melts have been variably affected by water degassing (Fig 7b). However, if we assume degassing was minimal for the glasses clustering at high H_2O/Cl ratios of ~20 (Fig 7b), the Cl enrichment of these BABB, would be explained by the addition of slab fluids with ~8-10 wt % salt (dotted lines in Fig 7b). In contrast, the outlying Manus sample with the highest H_2O/Cl ratio requires a slab fluid with <4 wt % salts (Fig 7b) and the North Fiji Basin samples, which appear unaffected by H_2O degassing (Figs 3), define a weak trend ($r^2 = 0.23$) consistent with a slab fluid salinity of ~6 wt % salt (Figs 7b). Similar salinities can also be estimated from a Cl/K versus H_2O/K plot, but are more sensitive to the assumed composition of the mantle end-member (Fig S5). The range of salinities suggested for slab fluids in this study (<4 to ~10 wt % salt) overlap the range of 0 to 19 wt % salt previously estimated for slab fluids enriching the Mariana Trough, Scotia Sea and different parts of the Lau Basin (Kent et al., 2002). In comparison eclogite facies fluid inclusions have salinities of 0->40 wt % salts (Phillipot et al., 1998; Scambelluri et al., 2004) suggesting considerable variation is possible.

Finally, the mixing model explored in Fig 7b provides an indication of the relative proportions of mantle derived and subducted halogens in each of the BABB investigated. The K/Cl of the MORB mantle represents the main uncertainty, however, based on a local mantle K/Cl of ~20, we can estimate that 0-65 % of the Cl in the North Fiji glasses was slab-derived (Fig 7b). In comparison, we can estimate that ~40-90% of the Cl in BABB with K/Cl of 2-6, from Manus, Valu Fa and the Fonualei Spreading Centre, would have been slab-derived, provided the local mantle sources had K/Cl of 10-30 that are typical of mantle reservoirs elsewhere (Kendrick et al., 2012a).

5.3.2 Slab fluid sources

Altered ocean crust is often assumed to be the dominant source of slab fluids because altered ocean crust has the potential to carry more chemically bound water into the subduction zone than volumetrically minor sediments which are compacted and heated earlier in the subduction cycle (e.g. Peacock, 1990; Schmidt and Poli, 1998); and the involvement of altered ocean crust is supported by trace element and isotope studies of arc volcanoes (e.g. Turner et al., 1997; Eiler et al., 2000; Haase et al., 2002; Hergt and Woodhead, 2007). Nonetheless, chemically unmodified marine fluids occupying sediment pore space (sedimentary marine pore fluids) have recently been suggested as an important source of atmospheric noble gases and halogens in the Earth’s mantle (Holland and Ballentine, 2006; Sumino et al., 2010); and serpentinites could be an important pathway for water, Cl and noble gas subduction (e.g. Rupke et al., 2004; Sharp and Barnes, 2004; Kendrick et al., 2011). In this section we examine the halogen abundance ratios of the subducted components in BABB to further evaluate these alternative hypotheses (Table 1; Fig 8).

The slab-fluid components in all the BABB investigated have Br/Cl ratios that are significantly lower than those of sedimentary marine pore fluids (Fig 8; Table 1). Furthermore, the slab fluids are suggested to have a wider range of salinities (~4-10 wt % salts), than sedimentary marine pore fluids which preserve salinities of relatively close to seawater (e.g. ~1-5 wt % salts e.g. Fehn et al., 2006; 2007; Muramatsu et al., 2001). These observations preclude a significant contribution of 'chemically unmodified sedimentary marine pore fluids' to the volatile inventory of back arc basins (cf. Holland and Ballentine, 2006; Sumino et al., 2010).

The Br and I content of altered oceanic crust is largely unknown, however, we anticipate halogens would initially be present in oceanic crust with MORB-like abundances and that altered ocean crust would evolve to lower Br/Cl and I/Cl as seawater derived Cl was introduced and stored in amphibole. If true, fluids released by dehydration of altered ocean crust could then account for the Br/Cl ratios at the lower end of the MORB range in the Fonualei Spreading Centre and North Fiji Basin samples, as well as the MORB-like composition of the most enriched glasses from the Woodlark Basin (Figs 4, 5 and 8).

Serpentinites represent the only known non-sedimentary lithology that sometimes has very high I concentrations (e.g. ppm levels) and high I/Cl ratios (Snyder et al., 2005; Kendrick et al., 2013b). Iodine-rich serpentinites can form when sedimentary marine pore fluids come into contact with either mantle lithosphere exposed at the pre-trench slab bend (Ranero et al., 2003), or when they enter the forearc mantle wedge early in the subduction cycle (e.g. John et al., 2011; Kendrick et al., 2013b; Snyder et al., 2005). Forearc serpentinites are subsequently entrained with the subducting slab and serpentine breakdown (re-)releases aqueous fluids with salinities of 0-40 wt % salts (and variable Br/Cl and I/Cl) over depths ranging from 40-250 km depending on the rate of subduction and mantle geotherm (e.g. Green II et al., 2010; Scambelluri et al., 2004; Kendrick et al., 2011; Schmidt and Poli, 1998; Ulmer and Trommsdorff, 1995). Therefore the high I/Cl ratios of subducted components in the Manus Basin and Valu Fa –Tonga is interpreted as evidence for serpentine breakdown fluids (Fig 4).

5.4 Implications for global volatile cycles

More than half of the backarc basins investigated in the SW Pacific are enriched by slab-fluids with MORB-like Br/Cl and I/Cl. Furthermore, where subducted components are initially I-rich (e.g. Valu Fa – Tonga), I is preferentially lost early in the subduction cycle with progressively more MORB-like compositions attained toward the backarc. Consequently, subduction could be the dominant source of halogens in the Earth’s mantle, and the systematics of halogen abundances support evidence from non-radiogenic noble gases that seawater is an important source of volatiles (including water and noble gases) in the mantle (Holland and Ballentine, 2006). In contrast to Holland and Ballentine (2006) and Sumino et al. (2010), however, we interpret our data as requiring the introduction of seawater through slab hydration and dehydration processes, and we expect different seawater-derived volatiles to be variably decoupled by the subduction process.

The data from this study show slab fluids vary in composition between different backarc basins and from the northern to southern parts of the Lau Basin (Fig 4). These differences could potentially reflect either the composition of the ingoing slab, which has been shown to influence along-strike variation in the chemistry of Tonga-Kermadoc arc lavas

(Castillo et al., 2009), or the thermal regimes of the different subduction zones which control the progress of metamorphic dehydration reactions (e.g. Schmidt and Poli, 1998).

The three major reservoirs for volatiles entering subduction zones are: i) sediments, ii) altered ocean crust and iii) serpentinites (e.g. Ito et al., 1983; Rupke et al., 2004; Parai and Mukhopadyay, 2012). However, serpentinites are strongly depleted in most trace elements (Kodolányi et al., 2012) meaning their involvement is difficult to fingerprint via conventional geochemical analysis. As a result, many studies have focused on fluids derived from altered ocean crust and the importance of serpentinites for generating voluminous fluids that may subsequently mobilise elements from overlying lithologies could have been underestimated (e.g. Turner et al., 1997; Woodhead et al., 2001; Haase et al., 2002). Our data show the halogens provide an almost unique potential (along with B isotopes; Scambelluri and Tonarini, 2012), for distinguishing the involvement serpentinite fluids in subduction zones which is critical to further improving constraint on subduction zone mass transfer processes (Spandler and Pirard, 2012).

6. Summary and conclusions

Southwest Pacific backarc basins have varied halogen systematics that indicate BABB contain halogens with 3 dominant origins:

i) Mantle-derived halogens with MORB-like Br/Cl and I/Cl account for ~10-50 % of Cl in BABB from Manus and the Valu Fa Ridge; 10-60% of Cl in melts of the Fonualei Spreading Centre; and 35-100 % of Cl in the North Fiji Basin glasses analysed.

ii) Assimilation of high salinity brines, with greater than seawater Br/Cl ratios, accounts for up to 95 % of the total Cl in melts from the NW part of the Lau Basin (Kendrick et al., 2013a); and perhaps 80-90 % of the total Cl in some MORB-like samples from Manus; however, brine assimilation was not detected in the samples from the Valu Fa Ridge, Fonualei Spreading Centre, Woodlark or the North Fiji Basin.

iii) Subducted halogens account for 0-65 % of the total Cl in melts from the North Fiji Basin and 40-90 % of the Cl in melts from Manus, Valu Fa and the Fonualei Spreading Centre. The dominant mechanism for recycling of subducted halogens into BABB is in fluids with estimated salinities of ~2-10 wt % salts. Slab fluids in 3/5 systems investigated have MORB-like I/Cl and Br/Cl at the lower end of the MORB range, suggesting they were released by dehydration of altered ocean crust; slab fluids in 2/5 systems investigated have elevated I/Cl ratios that favour input of fluids from serpentine breakdown.

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Table 1. Summary of the subducted components in Southwest Pacific Backarc Basins

	Salinity wt % salts	Br/Cl	I/Cl	Fluid source / other comments
Subducted component in arcs and backarc basins				
Manus	4-10	~0.002	>0.0004	High I/Cl requires I-rich source: serpentinites ?
Tonga Arc – Valu Fa Ridge	8-10	~0.003	>0.0010	High I/Cl requires I-rich source: serpentinites ?
Fonualei Spreading Centre	10-15	0.002-0.0026	~0.00006	Fluids probably derived by dehydration of altered ocean crust.
North Fiji Basin	2-6	0.0025	~0.00006-0.0001	I/Cl extends to the high end of the MORB range, but fluids probably derived by dehydration of altered ocean crust.
Woodlark	n.d.	0.0025-0.003	0.000001	The enriched samples have low I/Cl. Fluids probably derived by dehydration of altered ocean crust.
Fluids in subduction zones				
Sedimentary marine pore fluids	1-5	0.0035-0.009	0.000003-0.001	Characterised by Br/Cl of more than seawater and a very narrow range of seawater corrected Br*/I (see Fig 8)
Altered ocean crust	1->40	<0.0025	?	Poorly known but assumed to be enriched in Cl and have lower Br/Cl and I/Cl than MORB
Serpentinite breakdown fluids	1->40	<0.0035	Variable	The best known route for deep subduction of iodine.

Fig 1 (Kendrick et al., 2014)

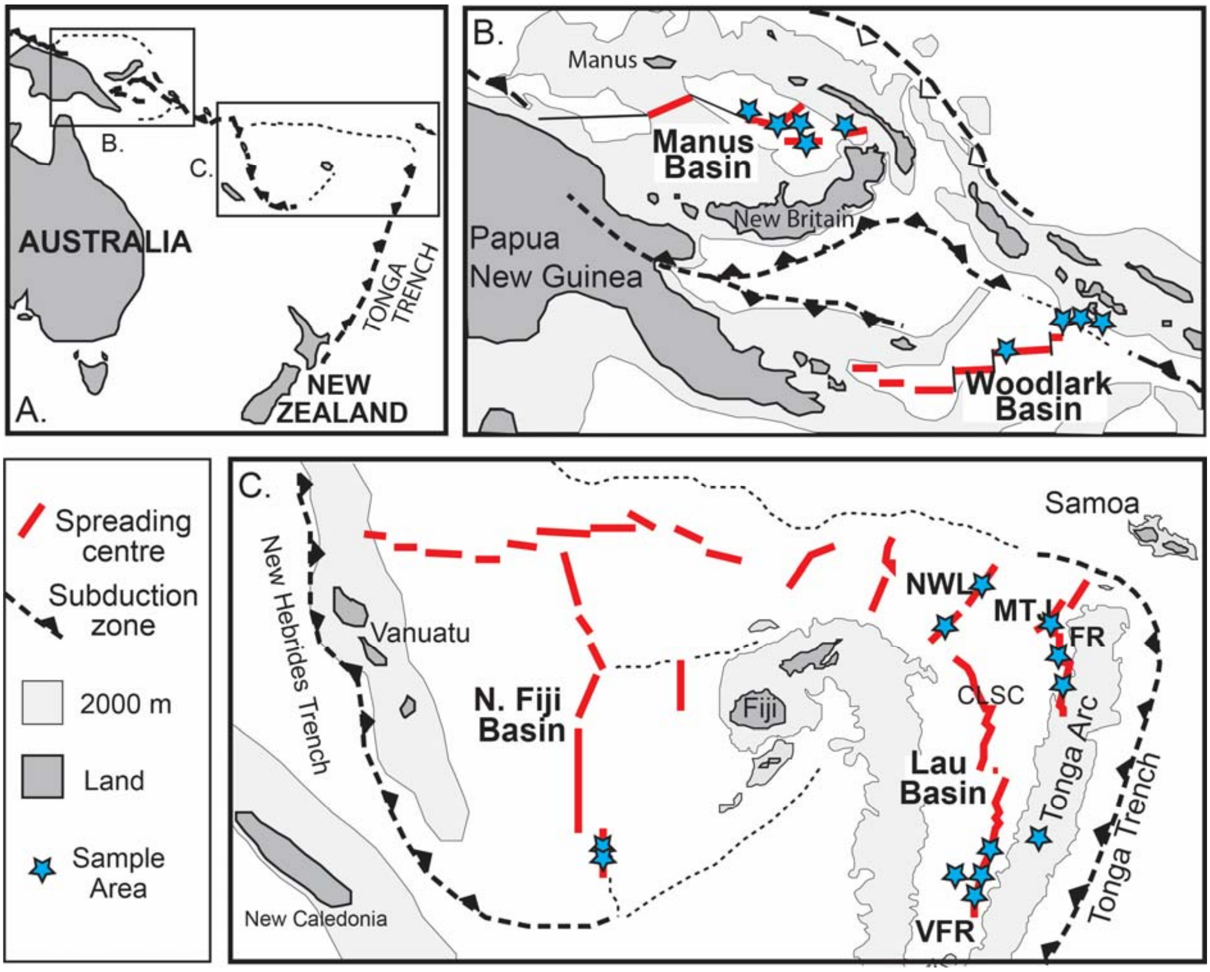

Fig 1. Map showing the positions of the Basins investigated in this study and approximate sampling areas. b) The Manus Backarc Basin is situated north of the New Britain Arc. The Woodlark Basin is situated west of the current subduction zone beneath the Soloman Arc, but is above mantle that may have been enriched by previous west-dipping subduction prior to 5 Ma. c). The North Fiji Basin is situated east of the New Hebrides Arc, while the adjacent Lau Basin is west of the Tonga (Tofua) Arc. Lau Basin abbreviations: NWL = Northwest Lau; MTJ = Mangatolu Triple Junction; CLSC = Central Lau Spreading Centre; FR = Fonualei Rifts (Spreading Centre); VFR = Valu Fa Ridge.

Fig 2 (Kendrick et al., 2014)

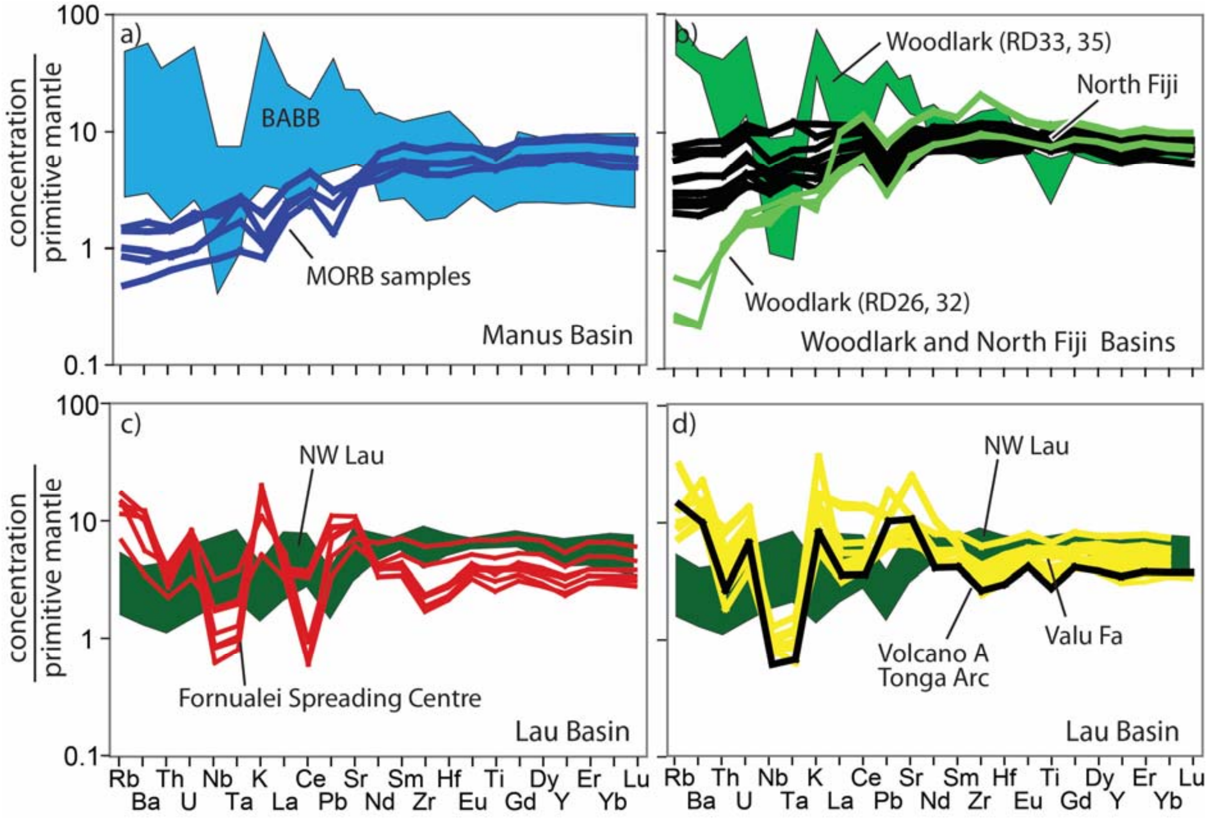

Fig 2. Spidergrams summarising trace element data for the samples included in this study. a) Manus Basin data from (Beier et al., 2010; Sinton et al., 2003). b) North Fiji and Woodlark Basin data obtained in this study, see also (Perfit et al., 1987). c) Fonualei Spreading Centre and Mangatolu Triple Junction (MTJ) samples are shown against NW Lau samples, data from (Keller et al., 2008; Lytle et al., 2012). d) Valu Fa Ridge samples are shown against NW Lau samples. Primitive mantle normalisation of McDonough and Sun (1995).

Fig 3 (Kendrick et al., 2014)

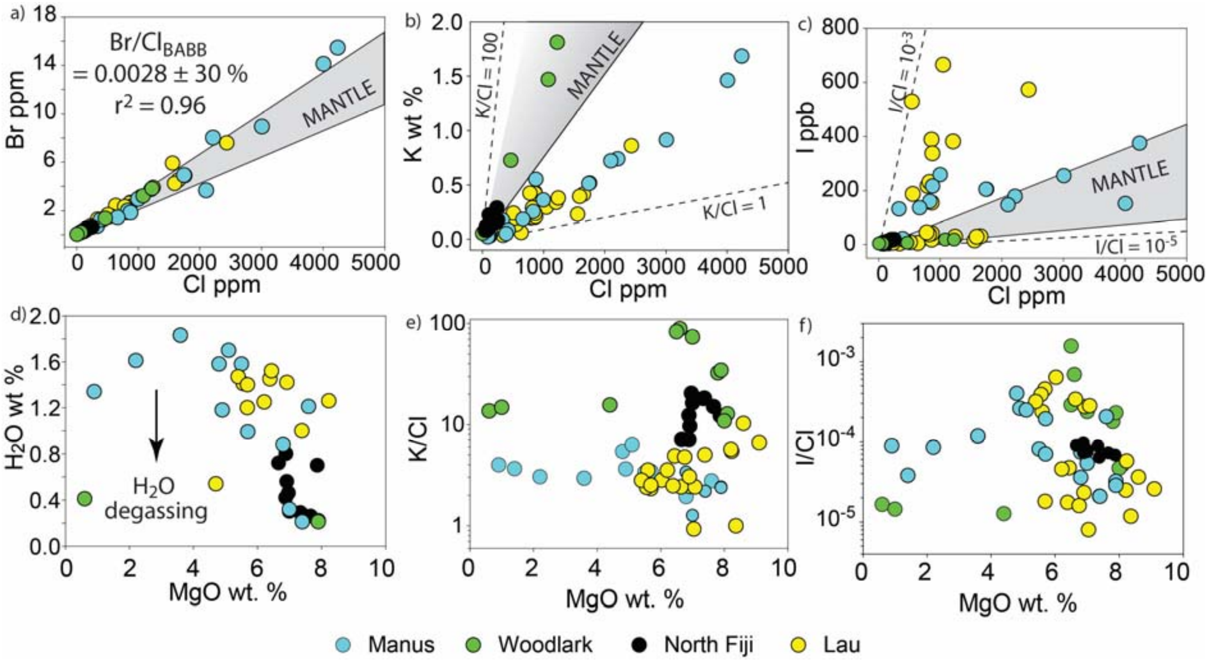

Fig 3. Concentrations of selected elements. a) Cl ppm versus Br ppm showing BABB exhibit only 30% variation in Br/Cl that is only slightly more than MORB with Br/Cl = $(2.8\pm0.6)\times10^{-3}$ (Kendrick et al., 2013a). b) Cl ppm versus K wt %, the mantle has a median K/Cl of 10 (Kendrick et al., 2012a), with lower values in BABB explained by input of slab fluids or seawater assimilation (e.g. Kent et al., 2002). c) Cl ppm versus I ppb showing some BABB are enriched in I/Cl relative to MORB/OIB samples with I/Cl of $(6\pm3)\times10^{-5}$ (Kendrick et al., 2013a). d) H_2O versus MgO. e) K/Cl versus MgO and f) I/Cl versus MgO, note that none of these ratios vary systematically as a function of MgO. Uncertainties are smaller than the symbols except for Woodlark samples, see Fig 4 (Table S1).

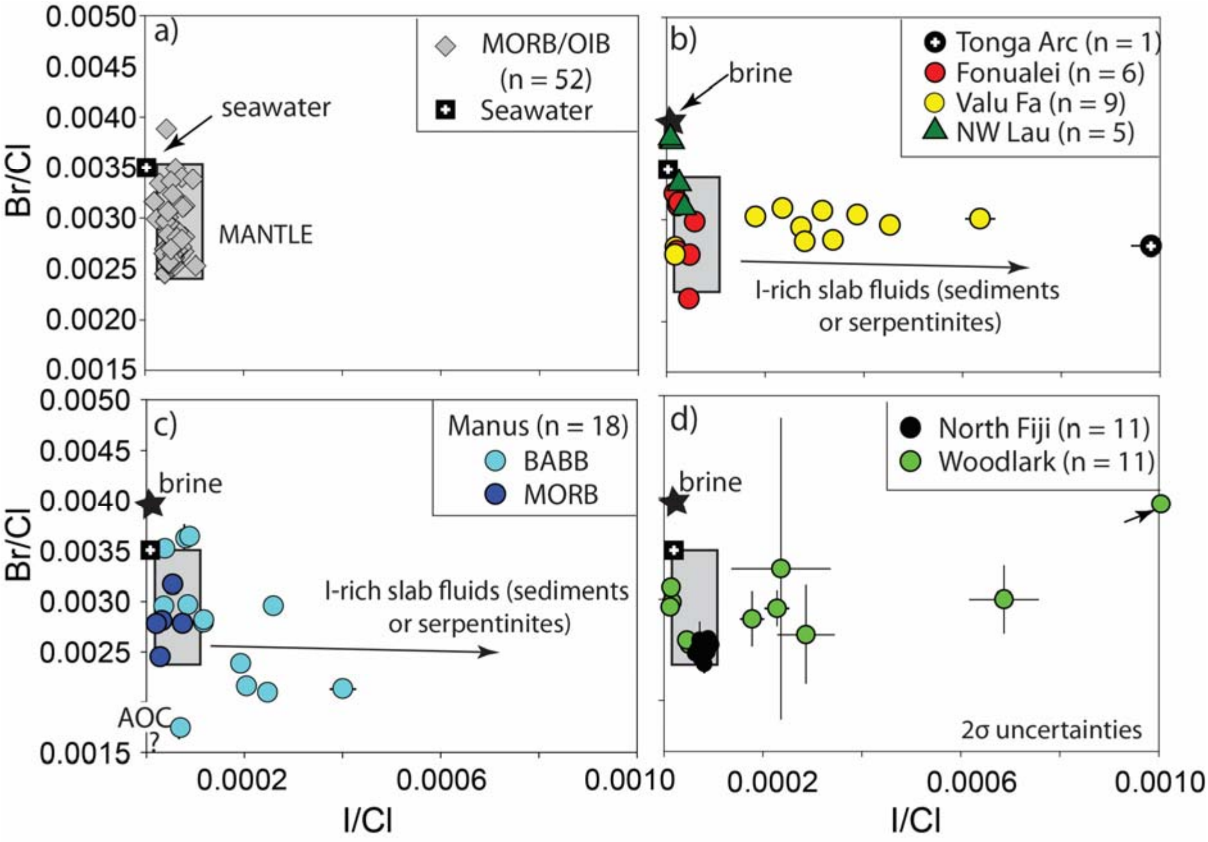

Fig 4. Halogen Br/Cl versus I/Cl three element plots for BABB glasses in this study. a) mid-ocean ridge and oceanic island glasses (Kendrick et al.,2012a; 2013a; 2014). b) Glasses from the Tonga Arc, Fonualei Spreading Centre, Valu Fa Ridge and northwest part of the Lau Basin (Kendrick et al., 2013a). c) Manus backarc basin glasses (Kendrick et al., 2012b); and d) North Fiji and Woodlark Basin glasses. The brine composition shown was determined for brines assimilated in the NW part of the Lau Basin (Kendrick et al., 2013a). Altered Ocean Crust (AOC), shown in c, is assumed to have Br/Cl lower than MORB due to the low compatibility of Br in amphibole (section 5.1). Parts b and d are available at different scales in Fig S3.

Fig 5 (Kendrick et al., 2014)

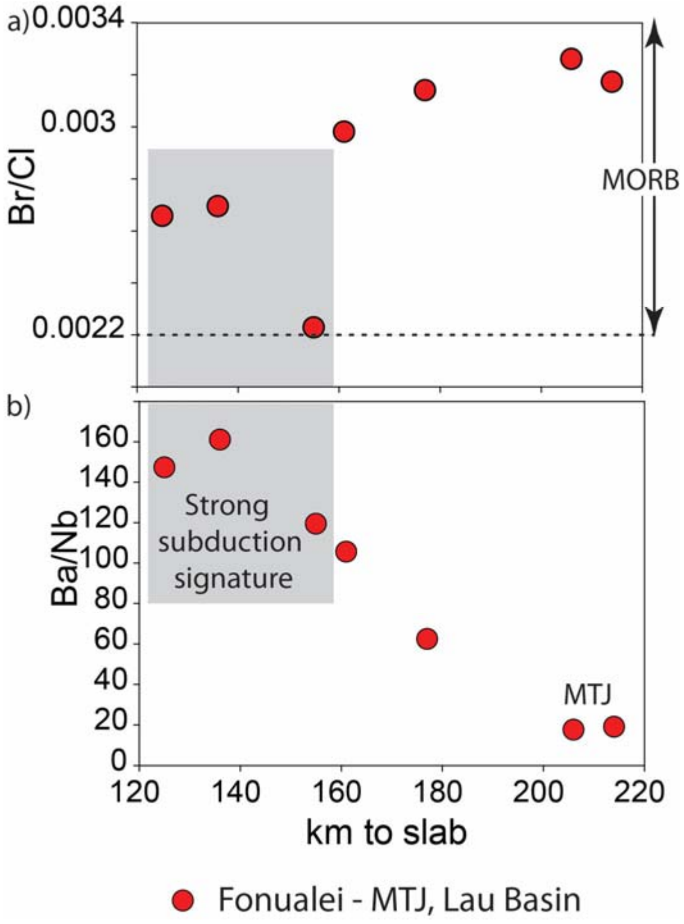

Fig 5. Halogen systematics of Lau Basin BABB. a) Fornaulei Br/Cl as a function of distance to slab and b) Fonualei Ba/Nb as a function of distance to slab. Distance to slab is from (Keller et al., 2008). MTJ = Mangatolu Triple Junction (Fig 1).

Fig 6 (Kendrick et al., 2014)

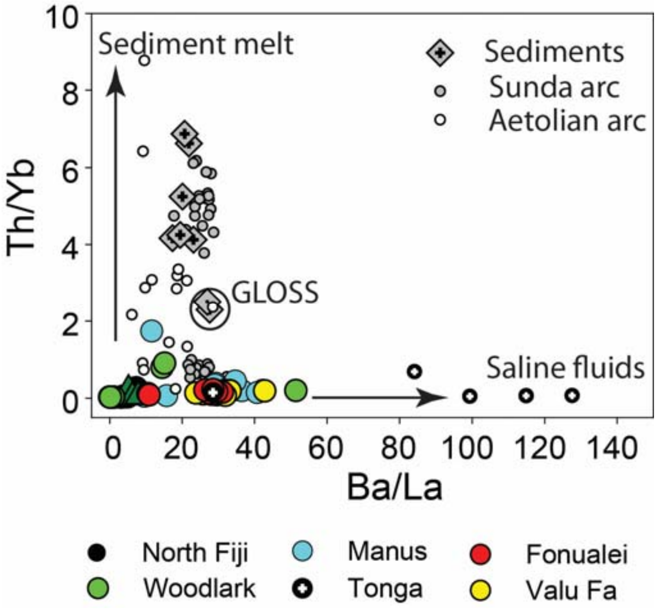

Fig 6. Th/Yb versus Ba/La four element plot used to distinguish subbduction inputs of sediment melts and saline fluids (Woodhead et al., 2001). Sediments are enriched in incompatible elements and have high Th/Yb, whereas saline fluids are enriched in fluid mobile elements like Ba. Note that the Tonga samples with the 4 highest Ba/La are from Cooper et al. (2010).

Fig 7 (Kendrick et al., 2014)

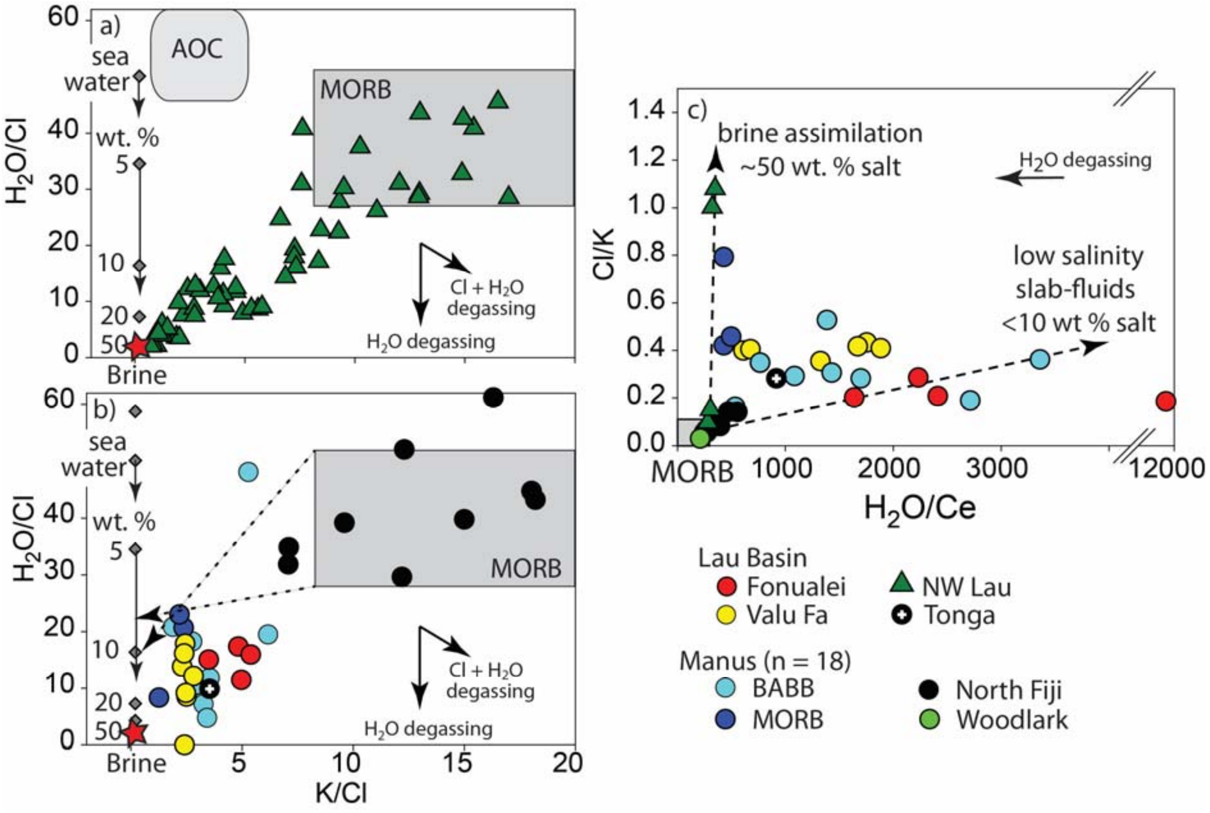

Fig 7. H_2O-Cl systematics of BABB: a) H_2O/Cl verus K/Cl data for glasses from the NW part of the Lau Basin (Lytle et al., 2012) which assimilated high salinity brines (Kendrick et al., 2013a). b) H_2O/Cl versus K/Cl for BABB in this study showing possible mixing lines between the MORB field defined in part a and slab-derived fluids with K/Cl of <0.2 (see text). c) Cl/K verus H_2O/Ce plot. Note that the composition of Altered Ocean Crust (AOC) in a is estimated from data of Ito et al. (1983) and Sano et al. (2008).

Fig 8 (Kendrick et al., 2014)

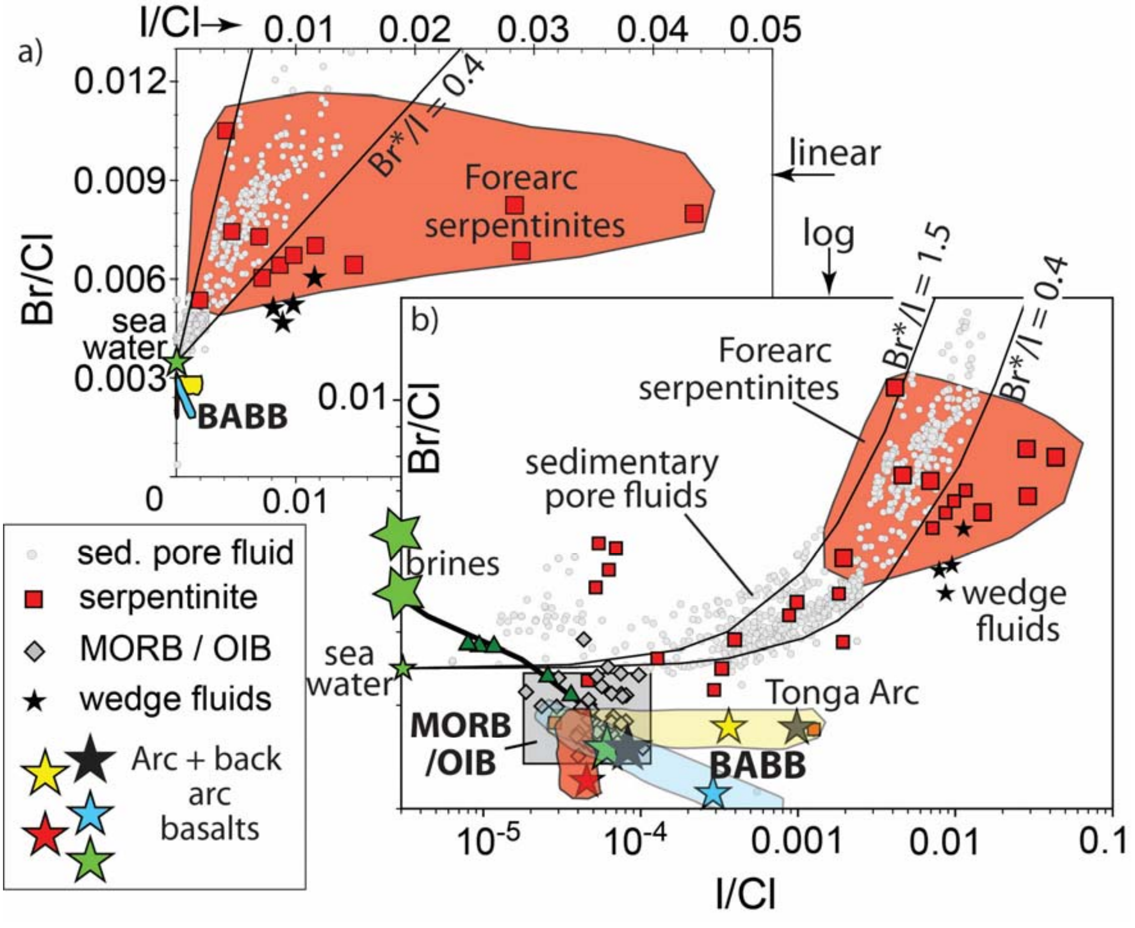

Fig 8. Summary of Br/Cl and I/Cl in subduction zone reservoirs and slab-fluids inferred from backarc basin basalts (Table 1). Selected data are shown on a linear scale (a) but the main figure (b) uses a log-log scale. Sedimentary marine pore fluids have correlated Br/Cl and I/Cl with a narrow range of seawater-corrected Br/I (indicated by black slopes with seawater intercepts in a and b; data from Murumatsu et al., 2001; Fehn et al., 2006; 2007 and references therein). Serpentinites have extremely variable Br/Cl and I/Cl overlapping sedimentary marine pore fluids (Kendrick et al., 2013b) and fluid inclusions in exhumed mantle wedge (Sumino et al., 2010). MORB (grey box) have lower than seawater Br/Cl and a relatively narrow range of I/Cl (Fig 4a; Kendrick et al., 2013a). Brines assimilatedby melts from NW Lau and Galápagos are shown in b (Kendrick et al., 2013a).*