



## Subduction-related halogens (Cl, Br and I) and H<sub>2</sub>O in magmatic glasses from Southwest Pacific Backarc Basins



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### ARTICLE INFO

#### Article history:

Received 11 November 2013

Received in revised form 7 February 2014

Accepted 10 February 2014

Available online 7 June 2014

Editor: B. Marty

#### Keywords:

halogens

chlorine

water

subduction

mantle

backarc basin basalts

### ABSTRACT

Submarine magmatic glasses from the Manus, Woodlark, North Fiji and Lau backarc basins in the Southwest Pacific, and 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 that 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 with that of MORB indicating subduction could be a major source of halogens in the Earth's mantle.

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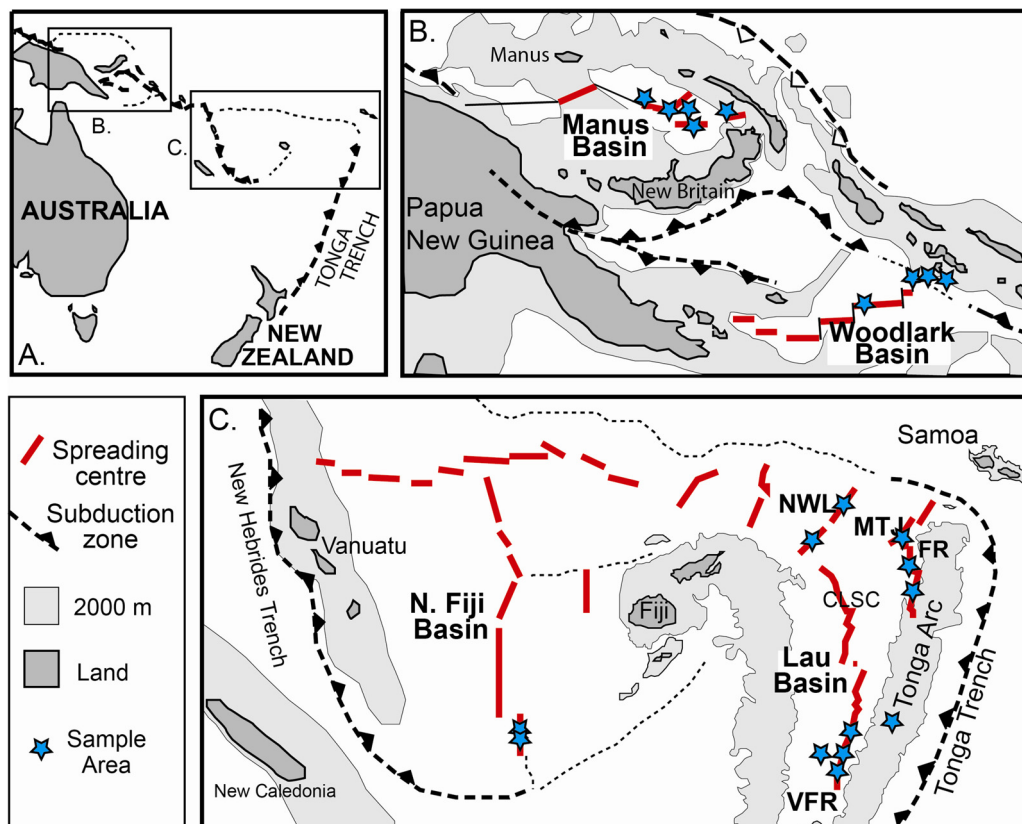
### 1. Introduction

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

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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,



**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 Solomon 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.

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 (Muramatsu 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 mechanism for iodine transport into the sub-arc mantle is 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

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