

Chlorine in submarine glasses from the Lau Basin: seawater contamination and constraints on the composition of slab-derived fluids

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Abstract

Measurements of chlorine concentrations in matrix glasses from 18 primitive (> 6 wt% MgO) and eight evolved lavas from active spreading centers in the Lau Basin back-arc system provide insight into the processes which control chlorine concentrations in subduction-related magmas, and can be used to investigate chlorine enrichment related to fluids derived from the underlying subducted slab. Chlorine contents of the glasses are highly variable (0.008–0.835 wt%) and generally high with respect to uncontaminated mid-ocean ridge basalt. Chlorine contents are highest in fractionated lavas from propagating ridge tips and lowest in more primitive basaltic lavas. Two different styles of enrichment in chlorine (relative to other incompatible elements) are recognized. Glasses from the Central Lau Spreading and Eastern Lau Spreading Center typically have low Ba/Nb ratios indicating minimal input of slab-derived components, and high to very high ratios of chlorine relative to K₂O, H₂O, and TiO₂. This style of chlorine enrichment is highest in the most fractionated samples and is consistent with crustal assimilation of chlorine-rich altered ocean crust material. Data from the literature suggest that contamination by chlorine-rich seawater-derived components also characterizes the Woodlark Basin and North Fiji Basin back-arc systems. The second style of chlorine enrichment reflects input from slab-derived fluid(s) to the mantle wedge from the adjacent Tonga subduction zone. Basaltic glasses from the Valu Fa Ridge and Mangatolu Triple Junction show correlations between ratios of chlorine and K₂O, H₂O, and TiO₂ and indices of slab-derived fluid input such as Ba/Nb, Ba/Th and U/Th, consistent with chlorine in these lavas originating from a saline fluid added to the mantle wedge. Within the Valu Fa Ridge the measured range of chlorine contents equates to a chlorine flux of 224–1120 kg/m/yr to the back-arc crust. Using a simple melting model and additional data from other back-arc and arc sample suites we conclude that chlorine is a major component within the slab fluids that contribute to many arc and back-arc melting systems, and probably plays an important role in regulating trace element transport by slab fluids in the mantle wedge. For the back-arc suites we have examined the estimated Cl/H₂O and Cl/K₂O ratios in the slab fluid component correlate with proximity to the arc front, suggesting that progressive dehydration of the slab and/or re-equilibration and transport within the mantle

wedge may influence the overall degree of chlorine enrichment within the slab fluid component. The degree of chlorine enrichment observed in most back-arc lavas also appears too great to be explained solely by melting of amphibole, phlogopite or apatite within the mantle source and suggests that chlorine must be present in another phase, possibly a chlorine-rich fluid. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The element chlorine is a potentially powerful tracer of interactions between mantle-derived rocks and saline aqueous fluids. Addition of even small amounts ($\ll 1$ wt%) of saline fluid (which often contains several weight percent chlorine) to mantle peridotite or basalt will substantially elevate chlorine concentrations, as the vast majority of mantle peridotite and mantle-derived melts have relatively low chlorine concentrations ($\ll 0.05$ wt%) [1–5].

One potential use for chlorine is as a tracer of saline slab-derived fluids in subduction zone-related magmas. There is abundant evidence to suggest that some fluids released during subduction by dehydration of the downgoing slab are highly saline [6–12]. Fluid inclusions in high and ultra-high pressure eclogite facies rocks show that aqueous fluids with salinities up to 84 equivalent wt% NaCl are released during dehydration and subduction metamorphism of the altered oceanic crust lithologies [6,9,10], and these may also carry significant volumes of other fluid-soluble trace elements [11]. It is also generally considered that the slab-derived fluids that contribute to magmatism within the mantle wedge are chlorine-rich [13–16], although there is less direct evidence for this. Accurate assessment of chlorine systematics in arc lavas (which are predominantly sampled subaerially) is limited by the volatile degassing of chlorine prior to eruption. However, data from melt inclusion studies show that primitive arc melts may be highly chlorine-rich, with concentrations > 1000 ppm [17–21]. Studies of back-arc lavas have also suggested that the slab fluid components that contribute to back-arc magmatism may be chlorine-rich. Kamenetsky et al. [22] identified a chlorine–lead–large-ion lithophile element (LILE)-rich component in matrix glasses and melt

inclusions from off-axis seamount lavas in the Lau Basin and related this to subduction beneath the nearby Tonga arc. Stolper and Newman [23] estimated a chlorine concentration of 1.19 wt% in the ‘H₂O-rich subduction component’ present within Mariana Trough back-arc lavas.

Knowledge of the chlorine systematics of subduction zone magmatism is also important for understanding the mass transfer processes and geochemical fluxes associated with subduction, as chlorine is likely to strongly affect the composition and transport properties of slab-derived fluids. Chloride contents strongly effect the solid–fluid partitioning behavior and/or solubility for a range of geochemically important elements (including K, Na, Cs, Sr, Ba, rare earth elements, Pb, Cu, Zn, Mo, Au, Ag, U, Th and the platinum group elements) in high pressure and temperature aqueous fluids [14,16,24–29]. Inter-element differences in solubility also suggest that local or regional variations in chloride abundance may accentuate, or even produce, some of the typical geochemical signatures of subduction zone magmas, such as elevated LILE/high field strength element and U/Th ratios [14,16,26].

In order to examine chlorine systematics in a suite of well-characterized subduction-related lavas, we have measured chlorine abundances in matrix glasses from 26 submarine lavas from the Lau Basin back-arc system in the southwest Pacific. Analysis of quenched glasses from deeply erupted submarine lavas allows us to circumvent problems associated with shallow volatile degassing. These lavas have compositions consistent with a range of ‘strengths’ of the subducted fluid signature (e.g. Ba/Nb between 5 and 355 [30,31]) and thus provide a direct means to compare chlorine with other subduction-related components. Our samples also provide the opportunity to investigate the role of assimilation of chlorine-

rich, seawater-derived components during magma ascent and storage in a suite of back-arc magmas. Previous studies have found that this process is widespread throughout the mid-ocean ridge (MOR) system as well as in some oceanic island volcanoes [3,5,32–34]. Given the similarities between MOR and back-arc magmatism, it is probable that assimilation of seawater-derived components is also common within the magmas associated with back-arc spreading centers, although the global extent of this is currently unknown.

1.1. Geology of the Lau Basin

The Lau Basin is a triangular-shaped extensional zone located between the active Tofua (Tonga) arc to the east and the Lau Ridge remnant arc to the west (Fig. 1) [35,36]. The southern portion of the basin (south of $\sim 17^\circ\text{S}$) is tectonically relatively simple and the majority of our samples come from this region. There are three major, active spreading ridges, the Central Lau Spreading Center (CLSC) to the north, the Eastern Lau Spreading Center (ELSC) and the Valu Fa Ridge (VFR) to the south. In addition, a small intermediate ridge segment, the Intermediate Lau Spreading Center (ILSC), links the CLSC and ELSC. Proximity to the Tofua arc front increases progressively to the south and lavas from the southern Lau Basin also show the strongest geochemical signatures of subduction [30,31]. Spreading rates decrease to the south, consistent with the triangular shape of the basin, ranging from 90 mm/yr full spreading rate at 18°S to 65 mm/yr at 21°S [37]. To the north the Lau Basin is more tectonically complex, with substantial offset of the Northern Lau Spreading Center (NLSC) to the west along the Peggy Ridge and development of the Mangatolu Triple Junction (MTJ; also known as the King's Triple Junction). Lavas from this region show additional chemical and isotopic components related to the Samoan plume and to subduction of sedimentary material derived from the Louisville seamounts [38,39].

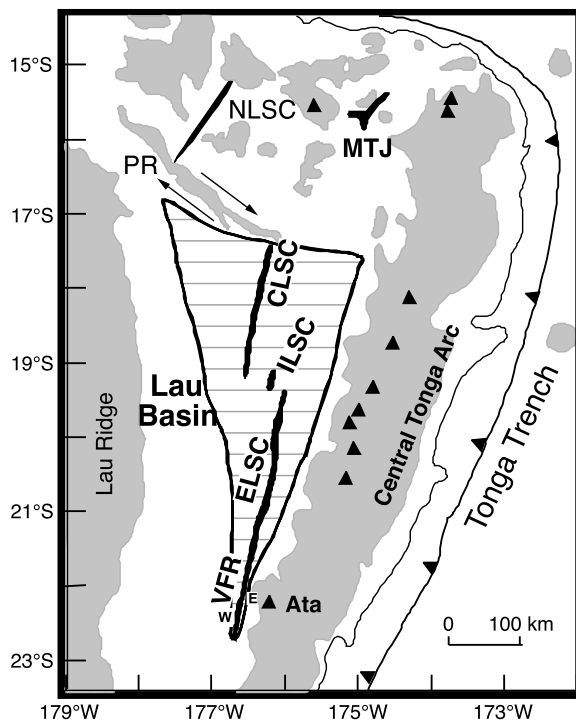


Fig. 1. Map of the Tonga–Lau Basin arc–back–arc system (after [31]). MTJ = Mangatolu Triple Junction, NLSC = Northern Lau Spreading Center, PR = Peggy Ridge, CLSC = Central Lau Spreading Center, ILSC = Intermediate Lau Spreading Center, ELSC = Eastern Lau Spreading Center, VFR = Valu Fa Ridge. Gray shading indicates water depths < 2 km, and horizontal hatched region represents new crust formed by seafloor spreading. ‘E’ and ‘W’ mark the approximate location of the eastern and western seamounts [22]. Arc front volcanoes are shown as dark triangles.

2. Samples and analytical techniques

2.1. Samples

We have analyzed naturally quenched matrix glasses from lava samples dredged from locations along the length of the Lau Basin back-arc system and the MTJ region to the north (Fig. 1). In total we present data for 26 glasses: four from the MTJ and 22 from the southern Lau Basin. Our samples represent a range of magma compositions from primitive basalt glasses to more fractionated andesite and ferrobasalt compositions (sampled from the propagating tips of the CLSC and

VFR) with MgO ranging between 3.0 and 8.4 wt% (Table 1). The large amount of prior work on these samples allows us to interpret the measured chlorine contents in light of major and trace element variations, H₂O contents (including some H₂O contents reported herein; Table 1), and Sr and U–Th isotopic compositions. Further details of the samples, including cruise information, locations and major element, volatile, trace element and isotopic compositions are given by [30,31, 40–44]. In addition to our own analyses, we have also used data for matrix glasses from four lavas dredged from the northern Lau Basin (NLB) [45], west of the NLSC and adjacent to

the Peggy Ridge (Fig. 1), and from two lavas sampled from seamounts adjacent to the VFR [22].

2.2. Analytical techniques

Glass fragments were handpicked under a microscope in order to avoid altered or devitrified material, mounted in epoxy and polished (by corundum paper and 1 μm Al₂O₃ powder) for analysis. Chlorine concentrations in glasses were determined by electron microprobe using a JEOL-8000 Superprobe at the University of Copenhagen, Denmark. Analyses were made using a

Table 1
Chlorine concentrations and representative compositions of Lau Basin glass samples

Sample	Depth (m)	Cl wt% (± 1 S.D.)	MgO	SiO ₂	K ₂ O	H ₂ O ^a	Ba/Nb
Valu Fa Ridge							
SO35/92KD-1	1975	0.130 (15)	3.84	53.41	0.35	1.58	101.6
SO35/90KD-1	1880	0.147 (8)	3.27	54.88	0.41	1.53	88.7
SO35/84KD-1	1723	0.067 (8)	7.31	50.36	0.16	1.26	130.5
SO48/114KD	1505	0.079 (16)	7.18	50.91	0.28	1.23	355.2
SO48/133GA	1620	0.175 (17)	2.96	56.70	0.44	1.36	99.6
SO48/61GC	1760	0.066 (9)	7.79	51.01	0.23	1.30	118.5
SO48/55GC	1793	0.116 (18)	4.39	53.30	0.35	1.38	64.6
Eastern Lau Spreading Center							
CD33/22-6-1	2730	0.062 (12)	7.06	51.40	0.06	<u>0.62</u>	7.8
CD33/20-5-2	2640	0.023 (8)	7.93	51.23	0.05	<u>0.38</u>	8.3
M-2239-2	2750	0.033 (13)	7.18	51.95	0.08	0.78	20.0
Intermediate Lau Spreading Center							
CD33/41-2-1	3050	0.019 (8)	8.11	50.50	0.06	<u>0.45</u>	11.4
Central Lau Spreading Center							
SO48/46GC	2280	0.021 (9)	7.05	50.03	0.06		7.4
SO48/18GA2	2260	0.042 (11)	7.10	50.23	0.06	0.27	6.4
SO48/42GC	2253	0.021 (9)	8.19	49.72	0.04	0.17	7.3
CD33/10-1-3	2260	0.231 (9)	3.30	51.50	0.17	<u>0.98</u>	5.2
CD33/11-2-1	2250	0.154 (12)	4.70	51.00	0.09	<u>0.52</u>	5.6
CD33/13-2	2255	0.552 (17)	1.42	60.38	0.39	<u>1.66</u>	7.1
CD33/12-5-2	2345	0.835 (36)	2.63	58.75	0.31	<u>1.62</u>	6.1
CD33/15-1-1	2295	0.046 (7)	7.30	50.53	0.04	<u>0.26</u>	6.9
M-2231-3	2361	0.025 (9)	7.41	50.82	0.06	0.22	6.2
M-2231-5	2410	0.049 (10)	6.42	52.52	0.24	0.30	5.3
M-2231-13	2242	0.043 (13)	6.88	51.22	0.06	0.31	5.0
Mangatolu Triple Junction							
M-2218-2	2249	0.053 (12)	6.55	52.25	0.25	1.32	23.9
M-2218-4	2234	0.011 (7)	8.41	50.53	0.11	0.38	7.9
M-2218-9	2221	0.008 (6)	8.44	49.94	0.09	0.33	6.5
M-2218-10	2217	0.023 (11)	8.19	51.05	0.19	0.83	16.8

Major element oxides and H₂O are given in weight percent. Additional major and trace element data from [31,40,41].

^a New data for H₂O from this study are shown underlined.

10 nA electron beam, defocused to 10 μm in diameter to prevent volatile element loss during long analyses, and a 15 kV accelerating voltage. Backgrounds were measured for each analysis and count time for peak and backgrounds (measured on either side of the chlorine peak) were 180 and 90 s respectively. Measured peak intensities were converted to concentrations via measurement of a natural sodalite standard. Accuracy and precision was monitored by analysis of glass LO-02-04 from Loihi seamount, Hawaii with 0.140 wt% chlorine (the chlorine concentration of this glass has been established by measurements from two separate and independently calibrated electron microprobes [3]). Repeat analysis of this glass with the Copenhagen microprobe gave a chlorine concentration of 0.139 ± 0.014 wt% (1 S.D. external reproducibility). Repeated blank measurements (made on olivine) gave an average chlorine value < 0.001 wt%. Table 1 shows the average chlorine concentrations and external reproducibility (based on 10–20 replicate analyses per sample) for these measurements. Uncertainties in chlorine concentration range between 3 and 50% (at 1 S.D.). Although some component of this uncertainty may reflect heterogeneity in the composition of analyzed glasses, relative errors correlate strongly with $1/\sqrt{\text{Cl}_m}$, (where Cl_m is the measured chlorine concentration), suggesting that counting statistics are the predominant source of uncertainty.

H₂O concentrations in glasses from eight glass samples were determined by Fourier transform infrared spectroscopy (Table 1) using the techniques described in Newman et al. [46].

3. Results

Measured chlorine contents of Lau Basin glasses are given in Table 1, together with representative elemental compositions [31,40,41,44]. Chlorine compositions measured in Lau Basin glasses range by over two orders of magnitude, from 0.008 to 0.835 wt%. Glasses from the CLSC show the highest chlorine contents and the greatest overall range of chlorine (0.021–0.835 wt%); VFR glasses have intermediate chlorine concentrations (0.066–0.175 wt%); and the

ELSC (0.023–0.062 wt%), ILSC (one sample with 0.019 wt%) and MTJ (0.008–0.053 wt%) have the lowest chlorine. Chlorine is broadly correlated with MgO (Fig. 2), and glasses with MgO > 6 wt% from the CLSC and VFR have consistently lower chlorine (< 0.10 wt%) than those with $< 6\%$ MgO. Chlorine is also generally well-correlated with other incompatible elements such as K₂O, H₂O, TiO₂, Nb and Ba (e.g. Fig. 2), although two distinct trends are apparent, with glasses from VFR and MTJ trending to higher K₂O, H₂O, Ba and Ba/Nb and lower Cl/K₂O relative to CLSC glasses, at a given chlorine concentration (Fig. 2).

4. Discussion

4.1. Sources of chlorine in Lau Basin lavas

Chlorine concentrations and the ratios of chlorine to other incompatible elements in Lau Basin glasses vary substantially (Table 1; Fig. 2). Although the most differentiated glasses have the highest chlorine concentrations, as expected given the incompatibility of chlorine during crystal fractionation of basaltic magmas, even relatively undifferentiated glasses (those with MgO > 6 wt%) have chlorine concentrations that vary by an order of magnitude.

We do not expect that chlorine loss via volatile degassing has been significant during the evolution of the submarine lavas we have analyzed. Chlorine is highly soluble in basaltic melts with relatively low H₂O concentrations ($< 3\text{--}4$ wt%) [47] and both experimental evidence and measured chlorine contents in melt inclusions suggests that the vapor exsolved by basaltic and andesitic liquids at low pressures is relatively chlorine-poor [47]. This is consistent with the observation that chlorine concentrations in mid-ocean ridge basalt (MORB) are not affected by degassing at water depths greater than ~ 700 m below sea level [48]. The majority of samples we have studied (most of those from the CLSC, ELSC, MTJ, ILSC) also have water contents that are below the solubility of water in MORB or andesitic composition magmas [49,50] at the appropriate eruption depth,

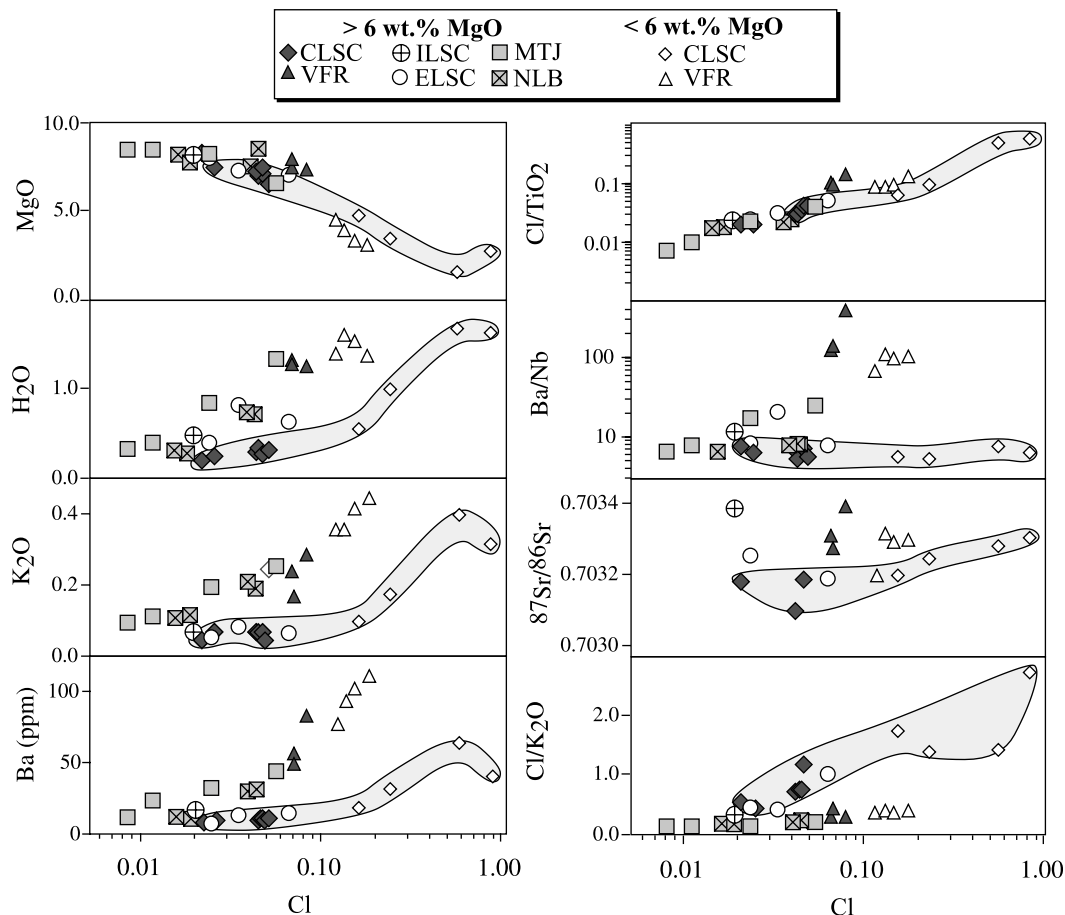


Fig. 2. Chlorine vs. selected oxide and trace element abundances and ratios for Lau Basin glasses. Unless shown otherwise concentrations are in weight percent. Symbols are as given in the accompanying legend. Data for glasses from two locations north of the Peggy Ridge [45] are described using the general term ‘Northern Lau Basin’ (NLB). The field of CLSC compositions is shown in gray in order to distinguish the different trends shown by these and other glasses.

although samples from the VFR and two from the CLSC that erupted at shallower depths (Table 1) have water contents close to the estimated solubility of H₂O in MORB magmas [50]. These lavas may have degassed some H₂O during eruption, although for those with MgO < 6 wt% the solubility of H₂O is probably somewhat greater, given the higher solubility of H₂O in more silicic melts [49]. If substantial degassing occurred then the H₂O contents of glasses with MgO > 6 wt% may be minimum estimates of magmatic H₂O contents, although the generally good correlations between H₂O and non-volatile incompatible elements (Ba, K₂O, TiO₂) for these and other Lau

Basin lavas suggest that significant amounts of water were not lost to volatile degassing.

Other factors that are likely to influence the chlorine compositions of back-arc magmas include: (i) the concentration of chlorine within the mantle source; (ii) addition of chlorine to the mantle wedge from fluids released by the adjacent subducting slab to the mantle source; (iii) the degree and nature of mantle melting and the fractionation history of each magma; and (iv) shallow assimilation of chlorine-enriched material during magma transport, storage and/or eruption in the submarine environment. These factors will all affect the chlorine concentrations

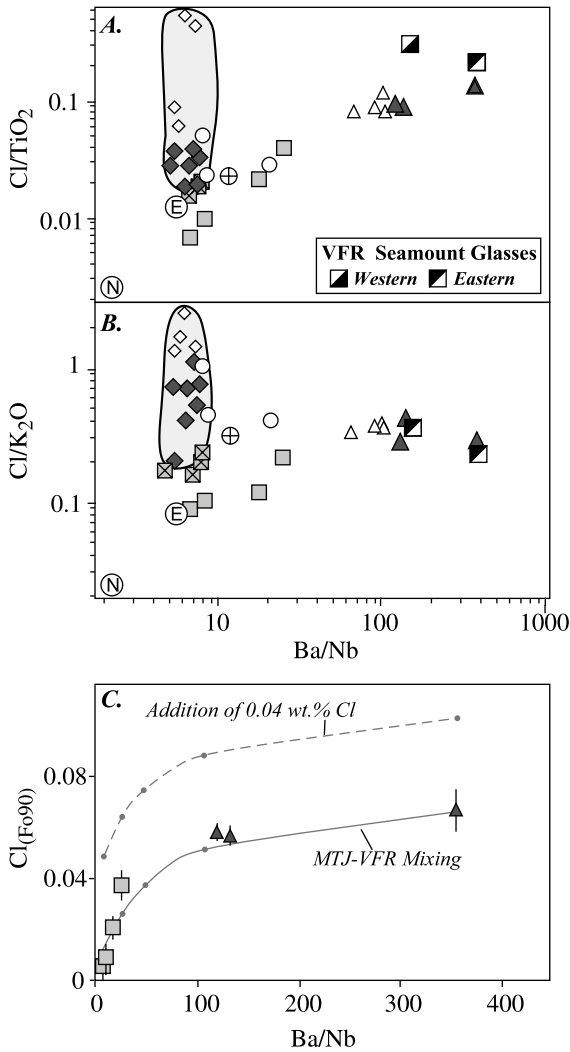


Fig. 3. (A) Ba/Nb vs. Cl/TiO₂, (B) Ba/Nb vs. Cl/K₂O and (C) Ba/Nb vs. chlorine for Lau Basin glasses. Symbols for matrix glasses from eastern and western VFR seamount samples [22] are given in the accompanying legend. Other symbols are as for Fig. 2 and circles containing 'N' and 'E' represent the composition of depleted and enriched MORB melts [4]. The field of CLSC compositions is shown in gray in A and B. Chlorine abundances shown in C have been corrected for crystal fractionation by incremental addition of olivine in FeO–MgO exchange equilibrium (using $K_{D(\text{olivine-melt})}$ for FeO/MgO=0.30) with the matrix glass composition until the recalculated compositions were in equilibrium with olivine of Fo₉₀ composition. The solid lines in C represent mixing between MTJ lava (M-2218-9) with the lowest Ba/Nb and the VFR glass with highest Ba/Nb (48/114KD). The dashed line represents addition of a fixed 0.04 wt% chlorine (approximately the amount required to produce the highest Cl/TiO₂ ratio in CLSC glasses with MgO >6 wt%) to the range of compositions represented by the solid line. For VFR glasses this amount of chlorine represents the addition of ~50% extra chlorine, and within the 1 S.D. errors bars shown, suggests that assimilation has added no more than ~10% extra chlorine to MTJ and VFR lavas. The gray field in A and B highlights the trends shown by CLSC glasses.

in back-arc magmas to some extent, however in this discussion we focus on the role of chlorine-rich fluids in the generation and eruption of back-arc basin magmas.

Assimilation of seawater-derived components by basaltic magma may be recognized by chlorine concentrations beyond those reasonably expected from melting and fractionation, as well as marked enrichment in chlorine with respect to other elements (such as K₂O and H₂O) that have broadly similar incompatibility during fractionation and mantle melting [3,5,32,34]. In back-arc magmas such an interpretation may be complicated by contributions of chlorine-rich slab-derived fluids

to the mantle wedge source. However, it is possible to differentiate between these different chlorine sources (seawater contamination vs. slab fluid) if chlorine derived from slab fluids correlates with other indices of the input of slab material (providing that these have not been significantly altered by passage through the mantle wedge [23,51]). On the plots of Cl/K₂O and Cl/TiO₂ vs. Ba/Nb shown in Fig. 3 glasses from the Lau Basin lie on two distinct trends diverging from MORB-like compositions. Glasses from the VFR, MTJ, ILSC, one sample from the ELSC as well as from VFR off-axis seamounts [22] define a trend to high Ba/Nb at a given Cl/K₂O, Cl/H₂O and Cl/TiO₂ ratio. We suggest that this trend represents addition of slab fluid components, as in addition to high Ba/Nb ratios, both MTJ and VFR samples show other chemical signatures associated with addition of slab-derived fluids, including enrichment in LILE, high U/Th, and for VFR glasses ²³⁰Th/²³⁸U activity ratios < 1 [22,30,31].

In contrast, glasses from the CLSC and two from the ELSC show a larger range in the ratios of chlorine to H₂O, K₂O and TiO₂ but have consistently lower, MORB-like, Ba/Nb ratios, consis-

tent with minimal slab input [22,30,31]. The enrichment of chlorine over K_2O , H_2O and TiO_2 in these glasses is similar to that observed in MORB and ocean island basalt (OIB) lavas contaminated by seawater or seawater-derived components [3,5,32,34]. From this we suggest that chlorine enrichment in CLSC and two ELSC glasses is also the result of shallow assimilation of seawater-derived chlorine-rich material. This interpretation is consistent with other compositional features of these glasses. In particular, the broad trend to higher degrees of chlorine enrichment over K_2O , H_2O and TiO_2 with decreasing MgO (Table 1) suggests that chlorine enrichment is not the product of an inherently chlorine-rich mantle source (or to the type of deep fluid–mantle interaction proposed by Nielsen et al. [33]), but occurs progressively throughout the fractional crystallization of these magmas.

Glasses from the NLB [45] show little evidence for substantial chlorine enrichment beyond that associated with crystal fractionation, with Cl/ K_2O ratios that range from 0.16 to 0.2, higher than typical MORB ratios [4], but substantially lower than CLSC glasses with similar chlorine abundance (Fig. 2). These glasses also have low Ba/Nb ratios (4.5–7.8) consistent with minimal input of subduction-related material.

In summary, the compositions of lavas from the Lau Basin, as well as other back-arc systems, show evidence for two distinct processes of enrichment in chlorine over other incompatible elements: (i) addition of seawater-derived components to magmas during melt storage, transport and eruption in the submarine environment; and (ii) addition of slab-derived fluid components to the mantle wedge source from which magmas derive. In the following discussion we examine each of these processes in more detail.

4.2. Assimilation of seawater-derived components

To our knowledge our study is the first time that the assimilation of chlorine-rich seawater-derived components has been comprehensively documented from a back-arc spreading system, although this process is widely recognized in MORB and some OIB lavas [3,5,32,34]. Previous

studies have also proposed that assimilation of altered oceanic crust may account for some of the stable and radiogenic isotope and noble gas compositions of Lau Basin lavas [31,52,53]. In addition, Muenow et al. [54] noted the similarity between chlorine-enrichment in glasses from the Woodlark Basin (see below) and seawater-contaminated MORB.

Chlorine– H_2O – K_2O systematics, simple mixing calculations and comparison between Cl/ K_2O ratios and other contamination-sensitive chemical signatures (e.g. $^{87}Sr/^{86}Sr$, $\delta^{18}O$) provide a means to examine both the amount and composition of assimilate involved [3,52]. In Fig. 4A we show mixing relationships between a MORB-like melt composition (with 0.01 wt% chlorine, 0.1 wt% H_2O and K_2O) and four potential chlorine-rich contaminants (altered basalt, seawater, and fluids of 15 and 50 wt% NaCl) on a plot of Cl/ K_2O vs. H_2O/K_2O . Glasses from the CLSC and the two ELSC glasses we believe to be contaminated all lie above the expected trends for addition of seawater and bulk addition of altered basalt, with CLSC glasses with MgO > 6 wt% falling close to the trajectory expected for assimilation of a 15 wt% NaCl brine. The more fractionated CLSC lavas have compositions consistent with an assimilate (or assimilants) with higher salinities (15–50 wt% NaCl), although the Cl/ H_2O and H_2O/K_2O ratios in these samples may also reflect extensive fractional crystallization [30]. One ELSC glass also lies close to the 15% NaCl trend (although requiring addition of slightly more contaminant), the other requires a contaminant with salinity only slightly higher than seawater.

Similar observations have been made regarding contaminated MORB and OIB lavas, and have led to suggestions that selective assimilation of small amounts of chlorine-rich brines and/or minerals (e.g. Fe-hydroxychloride, halite, amphibole), rather than bulk assimilation of altered oceanic crust, may best explain chlorine enrichment in these lavas [3,32,34]. In contrast, despite their elevated Cl/ K_2O ratios, CLSC glasses also show evidence for bulk assimilation of altered oceanic crust material, with a broad correlation evident between Cl/ K_2O and $^{87}Sr/^{86}Sr$ in CLSC lavas (and with the highest $^{87}Sr/^{86}Sr$ evident in the most frac-

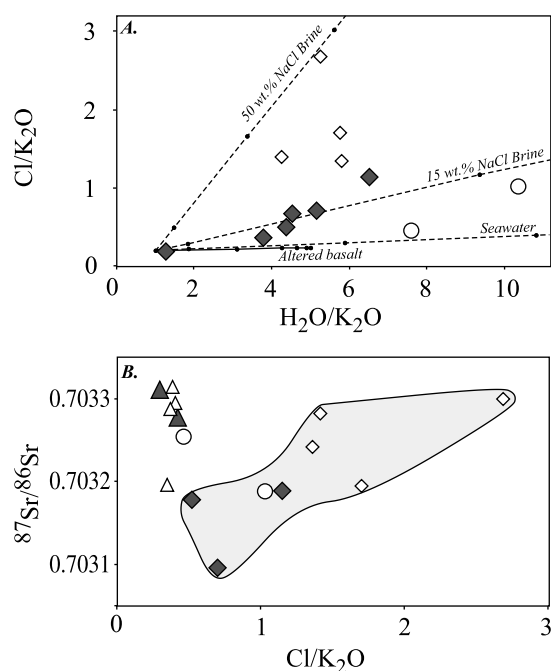


Fig. 4. (A) Cl/K₂O vs. H₂O/K₂O for glasses from the CLSC, ELSC and NLB (only the two ELSC glasses with highest Cl/H₂O are shown). (B) ⁸⁷Sr/⁸⁶Sr vs. Cl/K₂O for glasses from the CLSC and ELSC (additional data from Peate et al. [31]). Symbols as given in Figs. 2 and 5. Also shown in A are lines representing mixing between a MORB-like composition (0.01 wt% chlorine, 0.06 wt% K₂O, 0.1% H₂O) and four potential contaminants: seawater, 15% NaCl brine, 50% NaCl brine and altered basalt [3]. Points marked along mixing trajectories for brine and seawater represent 0.1, 0.5, and 1% addition of assimilant by weight, and for the altered basalt represent 10% incremental addition of assimilant. Although the altered basalt compositions used for our mixing calculations is not based directly on the compositions of altered Lau Basin basalts, the chlorine composition of the altered basalt endmember (0.1 wt%) is much higher than typical for altered ocean floor basalts and other ocean floor lithologies (<0.05 wt% [34]), and thus emphasizes the chlorine-rich nature of the assimilant phase. The gray field in B highlights the trends shown by CLSC glasses.

tionated lavas [31]; Fig. 4B). Many CLSC lavas (including three with high Cl/K₂O from this study) also have ¹⁸O-depleted glass and phenocryst compositions (with respect to typical mantle compositions) consistent with assimilation of low ^δ¹⁸O ocean crust [52]. Strontium and oxygen isotope compositions most likely reflect bulk assimilation of altered ocean crust, as the strontium and oxygen contained within the very small

amounts of brine or chlorine-rich minerals required to explain chlorine enrichment would be insufficient to substantially alter ⁸⁷Sr/⁸⁶Sr and ^δ¹⁸O. Macpherson and Matthey [52] estimated that CLSC lava ¹⁸O compositions represented up to 15% assimilation (by weight) of altered oceanic crust. Simple calculations show that assimilation of a similar amount of altered basalt or gabbro could also produce the increase in ⁸⁷Sr/⁸⁶Sr, but this material would also have to contain several weight percent chlorine to produce the highest Cl/K₂O ratios measured in CLSC glasses. This is several orders of magnitude greater than the typical concentration of chlorine in ocean floor lithologies [34], and thus the most likely assimilant may be altered basalt and/or gabbroic material from deep within seafloor hydrothermal systems that also contained significant amounts of chlorine-rich brine and/or hydrothermal minerals.

Lavas from the VFR and MTJ show no indication of chlorine enrichment other than that which correlates with slab fluid indices (Fig. 3). It is unlikely that the apparent lack of contamination in VFR and MTJ glasses simply reflects intrinsically higher magmatic chlorine contents (and corresponding lower sensitivity of Cl/K₂O, Cl/H₂O and Cl/TiO₂ ratios to addition of chlorine). Overall contamination by ocean crust material appears to have been minor or absent along the VFR [31,52] and, in contrast to CLSC lavas, primitive basalts from the VFR have similar ⁸⁷Sr/⁸⁶Sr ratios to highly fractionated ferrobasalts (although VFR lavas have systematically elevated ⁸⁷Sr/⁸⁶Sr with respect to primitive CLSC basalts; Fig. 4). MTJ lavas with low Ba/Nb also have distinctively low chlorine contents and lower Cl/K₂O ratios than contaminated CLSC glasses (Figs. 2 and 3). The mixing calculations shown in Fig. 3C, which model the effect of addition of a constant amount of chlorine to magmas with a range of primary chlorine contents, also suggest that, if any assimilated chlorine is present in VFR lavas, then it represents less than ~10% of the total chlorine present (see figure caption). We also note, however, that the VFR western seamount glass [22] has higher ratios of chlorine to K₂O, H₂O and TiO₂ as well as lower Ba/Nb than VFR and eastern seamount glasses, and thus

may also have been contaminated by seawater-derived components, or contains a slab fluid component of different composition.

In contrast to some OIB magmas, there also appears to be no relation between the extent of atmospheric noble gas contamination and high chlorine in contaminated Lau Basin samples (cf. [32]). Some lavas from the CLSC that have assimilated significant seawater-derived material have lower heavy noble gas abundances than VFR lavas and distinctly non-atmospheric $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios [42,43]. Heavy noble gas abundances in Lau Basin glasses correlate positively with both H_2O and Ba/Nb , and thus may also derive from the subducted slab [42].

Finally, in order to examine the global significance of chlorine enrichment in back-arc magmas we have compiled available data from the literature for submarine glasses from other back-arc systems [23,45,54,55]. Results are shown in Fig. 5 where we have plotted $\text{H}_2\text{O}/\text{TiO}_2$ vs. $\text{Cl}/\text{K}_2\text{O}$ for glasses from the Marianas Trough, Scotia Sea, Woodlark Basin and North Fiji Basin (all lavas plotted have $\text{MgO} > 6$ wt%). These data confirm that magmas from other back-arc systems also have chlorine concentrations and $\text{Cl}/\text{K}_2\text{O}$ ratios in excess of typical MORB values (Fig. 5), and two distinct chlorine enrichment trends are again apparent. Glasses from the Scotia Sea and Marianas Trough form an array with positive slope extending to high $\text{Cl}/\text{K}_2\text{O}$ and $\text{H}_2\text{O}/\text{TiO}_2$ (with the exception of sample ALV 1846-9 from the Marianas Trough with anomalously low TiO_2 and $\text{H}_2\text{O}/\text{TiO}_2$ [23]), similar to that shown by the VFR and MTJ glasses from the Lau Basin. Mariana Trough glasses also have trace element compositions indicative of the addition of slab fluid components [23] and we suggest that this trend represents addition of slab-derived H_2O and chlorine to the mantle wedge (see below). In contrast, glasses from the Woodlark and North Fiji basins have generally lower $\text{H}_2\text{O}/\text{TiO}_2$ and form arrays that extend to high $\text{Cl}/\text{K}_2\text{O}$, similar to CLSC glasses, consistent with addition of chlorine via assimilation of chlorine-rich seawater-derived material (as also suggested by Muenow et al. [54] for the Woodlark Basin). Woodlark and North Fiji Basin glasses also have compositions suggest-

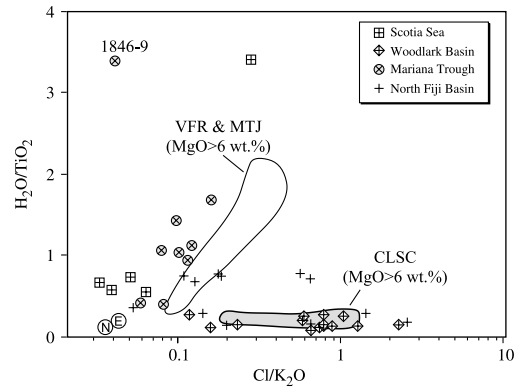


Fig. 5. $\text{H}_2\text{O}/\text{TiO}_2$ vs. $\text{Cl}/\text{K}_2\text{O}$ for submarine glasses from the Scotia Sea, Woodlark Basin, Mariana Trough and Fiji Basin. Symbols are given in the accompanying legend and circles containing 'N' and 'E' represent the composition of depleted and enriched MORB [4]. Fields for VFR and MTJ (combined), and CLSC glass compositions from this study are also shown for reference.

ing lesser input from slab-derived material (e.g. $\text{Ba}/\text{Nb} < 15$) [45,54]. A subset of the North Fiji Basin glasses have slightly higher $\text{H}_2\text{O}/\text{TiO}_2$ than Woodlark basin and CLSC lavas (Fig. 5), however these glasses also trend to high $\text{Cl}/\text{K}_2\text{O}$ values (from 0.11 up to 0.64) with little change in $\text{H}_2\text{O}/\text{TiO}_2$, suggesting that assimilation of chlorine-rich seawater-derived material exerted the major control over chlorine systematics.

Recognition of the widespread assimilation of seawater-derived components within back-arc magmas provides further evidence for the global importance of assimilation of chlorine-rich, seawater-derived components in oceanic magmatism. This process has now been recognized in all major oceanic magmatic environments (MOR, OIB and back-arcs).

4.3. Chlorine within the slab fluid component

Correlations between indices of slab-derived contribution and chlorine enrichment in uncontaminated Lau Basin samples (Fig. 3) clearly show that the slab-derived fluid component contributing to magmatism within the back-arc system is chlorine-rich. Our data can be used to characterize this component further: VFR samples offer the best opportunity for this, as they appear

largely unaffected by contamination and show a strong subduction-related signature, consistent with their closer position to the arc front [30]. In addition, although MTJ samples may be also affected by inputs related to the Samoan plume [39], these lavas form well-defined trends with VFR lavas (e.g. Fig. 3) suggesting that chlorine enrichment is also controlled by slab-related inputs.

We have used a simple melting model to estimate the Cl/H₂O and Cl/K₂O ratios of the slab fluid component (Cl/H₂O_{Slab} and Cl/K₂O_{Slab}) that contributed to VFR and MTJ glass compositions. We have chosen these two ratios in order to monitor both the salinity of the slab fluid component (which can be calculated in equivalent wt% NaCl from the Cl/H₂O_{Slab} ratio) and to monitor enrichment in chlorine with respect to another fluid-soluble incompatible element. Using a similar approach and the $D_{\text{solid/melt}}$ values of Stolper and

Newman [23] ($D_{\text{Cl}} = 0.001$; $D_{\text{H}_2\text{O}} = 0.012$, $D_{\text{K}_2\text{O}} = 0.0028$), we derived a starting mantle composition by taking the most MORB-like lava sample analyzed (MTJ lava M-2218-9) with the lowest chlorine, K₂O and H₂O contents and assuming this was the product of 5% batch melting. From this we calculated starting mantle chlorine, H₂O and K₂O contents (0.0004, 0.02 and 0.0047 wt%), which are within the range of enriched to depleted MORB source compositions estimated by Michael [4] and are a factor of 1.5–2 smaller than

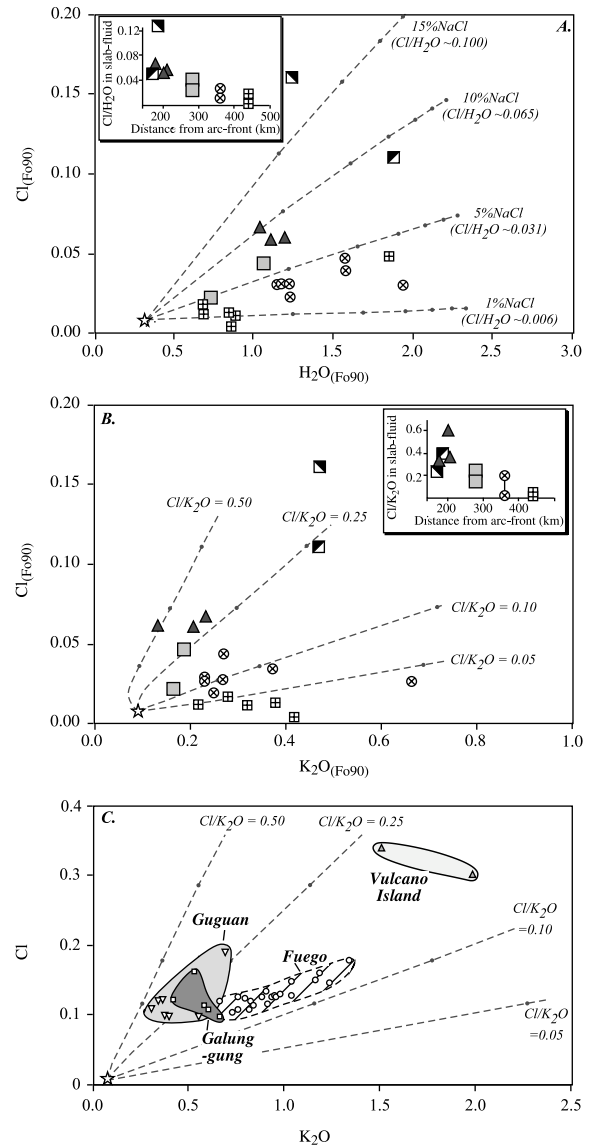


Fig. 6. (A) Chlorine vs. H₂O and (B) chlorine vs. K₂O for Lau Basin, Scotia Sea and Mariana arc samples [22,23,55] and (C) chlorine vs. K₂O for arc melt inclusion from Galunggung, Guguan, Fuego and Vulcano Island [18–21]. Symbols as given in Figs. 2, 3 and 5. All glass compositions shown in A and B have been corrected for olivine fractionation by the method given in the caption for Fig. 3 (although estimates of Cl/H₂O and Cl/K₂O ratios should not be sensitive to crystal fractionation in primitive basalts). Chlorine, H₂O and K₂O abundances are in weight percent. Lines shown in A represent addition of fluid containing 1, 5, 10 and 15 equivalent wt% NaCl to the mantle source, calculated by the method described in the text. Lines in B and C represent addition of a 5 wt% NaCl fluid with Cl/K₂O ratios of 0.05, 0.10, 0.25 and 0.50. Insets in A and B show the relation between distance from the arc front and ranges of Cl/H₂O and Cl/K₂O estimated for the slab fluid component for data from the VFR, MTJ, Scotia Sea and Marianas Trough. Markers on lines of constant Cl/H₂O in A represent addition of 0.1% fluid and on lines of constant Cl/K₂O in B addition of 0.1, 0.2 and 0.5% of a 5 wt% NaCl fluid with Cl/K₂O as given. Lines in C represent addition of 0.5, 1 and 2% of a 5 wt% NaCl fluid. The star in all figures represents the MORB-like starting composition used for calculations (see text). Only the MTJ lavas with Ba/Nb > 10 are plotted in A and B. Note that we do not show data in C for melt inclusions from Mt. Etna and Agrigan Island, Marianas [20,21] as the source for Mt. Etna magmas may also contain a large input from an OIB mantle source [21] and the subduction-related component at Agrigan appears dominated by sediment melt, not fluid [20,60].

the starting composition used by Stolper and Newman [23]. We then calculated the compositions of batch melts produced by mixtures of this source and fluids of varying salinities (from 1–15 equivalent wt. % NaCl) by assuming a linear relation between melt fraction and source H₂O content, with 5% melting at 0.02 wt% H₂O (the mantle starting composition) through to 25% melting at 0.5 wt% H₂O. We have also calculated the effect of progressively adding a 5 wt% NaCl fluid with Cl/K₂O of 0.05, 0.1, 0.25 and 0.5 to our source composition. Although this fluid has an arbitrary Cl/H₂O ratio, changes in the salinity alter the mixing proportions, but have minimal effect on the apparent Cl/K₂O_{Slab}.

Our estimates of the Cl/H₂O_{Slab} ratio (as well as the corresponding salinity for this ratio) and Cl/K₂O_{Slab} ratio within VFR and MTJ lavas, as well as to glasses from VFR seamount lavas [22], are shown in Fig. 6 and summarized in Table 2. Note that we have not used the two MTJ glasses (M-2218-4 and M-2218-9) with minimal slab fluid signature (i.e. Ba/Nb < 10) for our estimates. In Fig. 6A,B we plot the fractionation-corrected chlorine, H₂O and K₂O concentrations of primitive VFR and MTJ glasses along with lines representing constant Cl/H₂O_{Slab} and Cl/K₂O_{Slab}. Although our model involves several simplifying assump-

tions regarding the melting process, we believe it provides a meaningful estimate of Cl/H₂O_{Slab} and Cl/K₂O_{Slab}. Variation in the degree of melting away from the simple melting relation we have used will not overly alter Cl/H₂O_{Slab} and Cl/K₂O_{Slab} estimates, as these ratios are relatively insensitive to variations in the melt fraction after ~5% batch melting (using the partition coefficients given above). In addition, although we have used the same MORB source composition as the basis for estimates from different sample suites, variations in source composition should not affect our estimates of Cl/H₂O_{Slab} and Cl/K₂O_{Slab} for other suites if the magmatic chlorine, H₂O and K₂O contents are dominated by slab-derived inputs. It is also unlikely that residual volatile-bearing phases within the mantle wedge affect chlorine–H₂O–K₂O systematics as the degree of melting in back-arc and arc lavas is typically high enough to exhaust these trace phases [56]. Finally, the estimated Cl/H₂O_{Slab} and Cl/K₂O_{Slab} ratios for data from Mariana Trough glasses (see below) agree well with the composition of the Mariana Trough ‘H₂O-rich subduction component’ calculated independently by Stolper and Newman [23] (Table 2).

Overall, our data provide strong evidence that chlorine is a major component (present at weight

Table 2

Estimated Cl/H₂O_{Slab}, salinity and Cl/K₂O_{Slab} for back-arc and arc lava glass and melt inclusion suites

Location ^a	Estimated Cl/H ₂ O	Equivalent salinity (wt% NaCl)	Estimated Cl/K ₂ O
<i>Back-arc lavas</i>			
VFR	0.051–0.065	7–10	0.31–0.58
MTJ ^b	0.041–0.025	4–6.5	0.15–0.25
VFR Eastern Seamount	0.050	9	0.23
VFR Western Seamount	0.130	19	0.34
Mariana Trough	0.015–0.28	2.5–4.5	0.02–0.20
Mariana Trough ^c	0.027 ± .003	4.3 ± 0.4	0.14 ± 0.02
Scotia Sea	0–0.019	0–3	0–0.05
<i>Arc melt inclusion suites</i>			
Fuego	0.015–0.15	2.5–22	0.11–0.18
Guguan	–	–	0.16–0.41
Galunggung	0.18–0.74	25–70	0.14–0.30
Vulcano Island	–	–	0.15–0.22

^a See text for additional data sources.

^b Estimated only from the two MTJ glasses (M-2218-10 and M-2218-2) with Ba/Nb > 10.

^c Composition of H₂O-rich subduction component from [23].

percent levels) in the slab fluid(s) that contributes to magmatism within the Lau Basin back-arc system. The slab fluid component is also enriched in chlorine with respect to both H_2O and K_2O above the levels expected simply from melting of MORB-like mantle sources: estimated $\text{Cl}/\text{H}_2\text{O}_{\text{Slab}}$ and $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ in VFR and MTJ lavas are in the range of 0.04–0.065 and 0.15–0.58, and the lowest $\text{Cl}/\text{H}_2\text{O}_{\text{Slab}}$ and $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ are greater than $\text{Cl}/\text{H}_2\text{O}$ and $\text{Cl}/\text{K}_2\text{O}$ values of typical N-MORB (~ 0.014 and 0.032) – although they approach or overlap the values for enriched MORB (~ 0.05 , 0.08) [4]. Estimated slab fluid compositions for glasses from VFR-related seamounts [22] are also consistent with a chlorine-rich slab fluid (with $\text{Cl}/\text{H}_2\text{O}_{\text{Slab}}$ from 0.05–0.13 and $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ from 0.15–0.45), although we caution that the highest estimate, which is from the western seamount lava, should be considered a maximum given the possibility of seawater contamination in this sample (see above).

In addition to the Lau Basin, we have estimated the $\text{Cl}/\text{H}_2\text{O}_{\text{Slab}}$ and $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ for submarine lavas and melt inclusions in a number of other back-arc and arc-related suites, using data available in the literature. This includes submarine glasses from the Mariana Trough and the Scotia Sea back-arc systems (which appear unaffected by seawater contamination – see above) and melts trapped as melt inclusions in arc-related lavas from Fuego, Guatemala, the island of Guguan in the Mariana Arc, Galunggung, Indonesia, and Vulcano Island, Italy (Fig. 6C) [18–21,23,55]. We have only used compositions where the slab fluid signature is relatively strong ($\text{Ba}/\text{Nb} > 10$ and/or $\text{H}_2\text{O}/\text{TiO}_2 > 0.5$), and for arc-related melt inclusions suites we have relied on chlorine– K_2O systematics. Although the estimated $\text{Cl}/\text{H}_2\text{O}_{\text{Slab}}$ values for arc melt inclusions range up to those equivalent to salinities of ~ 70 wt% NaCl (Table 2) we are not confident that these represent actual slab fluid components. The H_2O contents of melt inclusions may be influenced by degassing prior to trapping and/or by diffusive re-equilibration between inclusions and the surrounding magma through the walls of the host mineral phase [57]. For the melt inclusion suites where H_2O measurements are available

[18,19] there is a higher degree of scatter in chlorine– H_2O systematics, compared to chlorine– K_2O , consistent with alteration of the H_2O contents of melt inclusions, either before or after inclusion formation.

Mariana Trough and Scotia Sea back-arc suites have estimated $\text{Cl}/\text{H}_2\text{O}_{\text{Slab}}$ and $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ values that are again consistent with addition of significant chlorine to the mantle wedge via a slab fluid, but are typically lower than those estimated for VFR and MTJ lavas Table 2; Fig. 6A,B). Available data from arc-related melt inclusion suites also suggest that the slab fluid components that contribute to many arc lavas also contain substantial chlorine (Fig. 6C). Estimated $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ ratios for all arc melt inclusion suites show broadly similar ranges, with estimated $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ ratios generally greater than MORB (with maximum $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ of 0.18–0.41 (Fig. 6C).

In addition to the Lau Basin, our results suggests that chlorine is present at weight percent levels in the slab fluid components which contribute to the many arc and back-arc magmas. Although it is generally considered that slab-derived fluids transferred to the mantle wedge are saline to some degree [13,14,16,25–27] our study is one of a relatively small number that actually demonstrate the presence of slab-derived chlorine within subduction-related magmas [20,22,23] and the first to quantitatively investigate this in a number of back-arc and arc lava suites. The range of estimated $\text{Cl}/\text{H}_2\text{O}$ ratios for back-arc lavas is equivalent to salinities between ~ 1 and 10 wt% NaCl within the slab fluid component in back-arcs (with the exception of the one Scotia Sea sample that exhibits no apparent chlorine enrichment; Fig. 6), and the similar ranges of $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ estimated from back-arc glasses and arc melt inclusion suites suggest that correspondingly high chlorine contents are also present in the slab fluid components which contribute to many arc magmas. This amount of chlorine is sufficient to exert a major influence over the solute transport properties of high temperature aqueous fluids [14,16,25–29], and from this we suggest that chlorine plays a major role in regulating the transport of fluid-soluble elements both from the subducted

slab to the mantle wedge (and probably also within the wedge itself). Models of fluid-mediated mass transfer in subduction zones should take the effect of high (and variable) chloride contents into account.

However, we also stress that the $\text{Cl}/\text{H}_2\text{O}_{\text{Slab}}$ and $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ ratios we estimate for arc and back-arc magmas apply only to the slab fluid component that actually contributes to magmatism, and that this may be significantly fractionated both during release of fluid from the downgoing slab and/or during subsequent equilibration between fluids and the mantle wedge [6,27,51,58]. Estimated $\text{Cl}/\text{H}_2\text{O}_{\text{Slab}}$ ratios for back-arc suites are equivalent to salinities only at the low end of the range observed in eclogite fluid inclusions [6,9,10], suggesting that all chlorine mobilized during slab dehydration does not contribute to subduction zone magmatism. Compositional fractionation of slab-derived fluids may also occur during reaction between fluid and mantle wedge peridotite [18,59] to form hydrous mantle minerals (e.g. amphibole, phlogopite, apatite). However, while the H_2O contents of back-arc and arc basalts may be controlled by melting of these minerals within the mantle wedge [18], this does not appear to be the case for chlorine. The $\text{Cl}/\text{H}_2\text{O}_{\text{Slab}}$ and $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ values we estimate for arc and back-arc suites range up to values that are substantially greater than typical for mantle amphibole and phlogopite ($\text{Cl}/\text{H}_2\text{O}_{\text{Slab}}$ and $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ ratios for these are generally ≤ 0.02 and 0.05 [4,15]). Apatite is also unlikely to be the primary chlorine host, as lava samples with the strongest fluid signature have $\text{Cl}/\text{P}_2\text{O}_5$ ratios (e.g. VFR 1.1, MTJ 0.76, Mariana Trough 0.38) considerably greater than the maximum $\text{Cl}/\text{P}_2\text{O}_5$ ratio in apatite (~ 0.1 for chlorapatite). From this we suggest that another chlorine-rich phase, possibly a free fluid, also exists in the mantle wedge source regions of many back-arc and arc magmas.

The estimated slab fluid $\text{Cl}/\text{H}_2\text{O}_{\text{Slab}}$ and $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ ratios in back-arc glasses correlate with proximity to the arc front (see insets in Fig. 6A,B), suggesting a progressive decrease in chlorine enrichment in the slab fluid component with increasing distance from the arc front. Although data from other (uncontaminated) back-arc suites

are required to confirm this trend, it is unlikely that it relates simply to variations in composition of the slab itself, as slab fluids typically appear to be dominated by material derived from dehydrated oceanic crust [41,60] – which on a global scale we expect to be relatively uniform in composition – and not from recycled sediment. Two plausible explanations for this correlation are progressive changes in composition of fluid released from the slab, and/or fractionation of the slab fluid component during progressive transport and equilibration within the mantle wedge [51,58]. The composition of fluids released from the downgoing slab will be strongly influenced by pressure–temperature conditions, breakdown reactions and the mineralogy of residual phases. However, the high chlorine contents found in many eclogite fluid inclusions [6–8] relative to our estimates of the compositions of the slab fluids that participate in magmatism suggest that slab dehydration at relatively shallow levels preferentially removes chlorine relative to water. If this is the case then the trend to lower slab fluid chlorine contents with increasing distance from the arc front may simply represent the continuation of this process. The $\text{Cl}/\text{H}_2\text{O}_{\text{Slab}}$ and $\text{Cl}/\text{K}_2\text{O}_{\text{Slab}}$ ratios for Scotia Sea glasses (those furthest from the arc front) also overlap the compositions of mantle amphibole and phlogopite, suggesting that the relation between chlorine enrichment and arc-front distance could, at least in part, reflect the presence and absence of an additional chlorine-rich phase.

Finally, our data also provide an estimate of the flux of chlorine from the slab to the back-arc in the VFR. Bach et al. [41] suggested that tectonic erosion and crustal growth rates in the adjacent Tonga arc are roughly equal, and if this is the case then chlorine flux along the VFR should be representative of that from the subducting slab to the supra-subduction zone environment. The measured $\text{Cl}/\text{H}_2\text{O}$ and $\text{Cl}/\text{K}_2\text{O}$ ratios in VFR lavas with $\text{MgO} > 6$ wt% (combined with previously estimated H_2O and K_2O fluxes [41]) equate to a total chlorine flux of 224–1120 kg/m/yr into the VFR back-arc crust. If this derives from a 5 km thick subducted ocean crustal section and all chlorine within the slab is lost during de-

volatilization [41], the calculated chlorine flux requires ~ 0.01 – 0.05 wt% average crustal chlorine composition, similar to other estimates of the bulk chlorine content of the oceanic crust (e.g. < 0.05 [34]). If, as suggested by Philippot et al. [10] $\sim 70\%$ of subducted chlorine remains in the subducted slab, then the required average crustal chlorine concentration required is ~ 0.03 – 0.16 wt%.

5. Conclusion

Matrix glasses from submarine-erupted Lau Basin lavas show large ranges in both chlorine concentration and the ratios of chlorine to other incompatible elements. Fractionated lavas have the highest overall chlorine contents, although primitive glasses with MgO > 6 wt% still have chlorine abundances that range from 0.008 to 0.08 wt%.

Chlorine enrichment in back-arc magmas results from two different processes. Glasses from the CLSC and ELSC are enriched in chlorine relative to other incompatible elements but exhibit minimal slab fluid signatures. We suggest that this, as well as similar chlorine enrichment in back-arc lava suites from the Woodlark and North Fiji basins, is the result of assimilation of chlorine-rich, seawater-derived material by back-arc magmas during magma storage and transport in the oceanic crust. Our data also suggest that chlorine assimilation occurs during bulk assimilation of altered oceanic crust material (although this material must also contain significantly higher chlorine concentrations than typical altered oceanic crust), rather than via selective assimilation of chlorine-rich brines or minerals.

In addition, chlorine is a major component in the slab fluids that contribute to many arc and back-arc magmas, as chlorine enrichment (relative to K_2O , H_2O and TiO_2) in glasses from the VFR and MTJ, as well as from the Mariana Trough and Scotia Sea and several arc lava melt inclusions suites, is associated with addition of other slab-derived fluid components. From this we suggest that chlorine is present at weight percent concentrations in the slab fluids that participate in

arc and back-arc magmatism and plays an important role regulating fluid-mediated mass transfer into and within the mantle wedge. The estimated Cl/ H_2O and Cl/ K_2O ratios of the slab fluid component also appear to correlate with the proximity to the arc front. Progressive dehydration of the slab, as well as re-equilibration and transport within the mantle wedge, may influence the overall degree of chlorine enrichment of the mantle source. In addition, the degree of chlorine enrichment observed in many back-arc lavas appears too great to be explained by melting of amphibole, phlogopite or apatite within the mantle source and suggests that chlorine may reside in another phase, possibly a chlorine-rich fluid, within the mantle wedge.

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