Quantifying brine assimilation by submarine magmas: examples from the Galápagos Spreading Centre and Lau Basin

Mark A. Kendrick¹*, Richard Arculus², Pete Burnard³, Masahiko Honda²

1- School of Earth Sciences, University of Melbourne, Victoria 3010, Australia
2- Research Schoo of Earth Sciences, Australian National University, ACT 0200, Australia.
3- CRPG, CNRS, Nancy, France.

*Corresponding Author: mark.kendrick@unimelb.edu.au ; Tel +61 3 8344 6933; Fax +61 3 8344 7761

Geochimica et Cosmochimica Acta – revised 18th August 2013

Words = 6462
Abstract. Volatiles are critically important in controlling the chemical and physical properties of the mantle. However, determining mantle volatile abundances via the preferred proxy of submarine volcanic glass can be hampered by seawater assimilation. This study shows how combined Cl, Br, I, K and H2O abundances can be used to unambiguously constrain the dominant mechanism by which melts assimilate seawater-derived components, and provide an improved method for determining mantle H2O and Cl abundances. We demonstrate that melts from the northwest part of the Lau Basin, the Galápagos Spreading Centre and melts from other locations previously shown to have anomalously high Cl contents, all assimilated excess Cl and H2O from ultra-saline brines with estimated salinities of 55 ± 15 wt. % salts. Assimilation probably occurs at depths of ~3-6 km in the crust when seawater-derived fluids come into direct contact with deep magmas. In addition to their ultra-high salinity, the brines are characterised by K/Cl of <0.2, I/Cl of close to the seawater value (~3×10^-6) and distinctive Br/Cl ratios of 3.7-3.9×10^-3, that are higher than both the seawater value of 3.5×10^-3 and the range of Br/Cl in 43 pristine E-MORB and OIB glasses that are considered representative of diverse mantle reservoirs [Br/Cl_mantle = (2.8 ± 0.6)×10^-3 and I/Cl_mantle = (60 ± 30)×10^-6 (2σ)]. The ultra-saline brines, with characteristically elevated Br/Cl ratios, are produced by a combination of fluid-rock reactions during crustal hydration and hydrothermal boiling. The relative importance of these processes is unknown; however, it is envisaged that a vapour phase will be boiled off when crustal fluids are heated to magmatic temperatures during assimilation. Furthermore, the ultra-high salinity of the residual brine that is assimilated may be partly determined by the relative solubilities of H2O and Cl in basaltic melts. The most contaminated glasses from the Galápagos Spreading Centre and Lau Basin have assimilated ~95 % of their total Cl and 35-40 % of their total H2O, equivalent to the melts assimilating 1000-2000 ppm brine at an early stage of their evolution. Dacite glasses from Galapagos contain even higher concentrations of brine components (e.g. 12,000 ppm), but the H2O and Cl in these melts was probably concentrated by fractional crystallisation after assimilation. The Cl, Br, I and K data presented here confirm the proportion of seawater-derived volatiles assimilated by submarine magmas can vary from zero to nearly 100 %, and that assimilation is closely related to hydrothermal activity. Assimilation of seawater components has previously been recognised as a possible source of atmospheric noble gases in basalt glasses. However, hydrothermal brines have
metal and helium concentrations up to hundreds of times greater than seawater, and brine assimilation could also influence the helium isotope systematics of some submarine glasses.
Introduction

Magmatic volatile components that exsolve into supercritical fluids or gases include H$_2$O, CO$_2$, halogens, S, N and noble gases. The major volatiles exert important controls on the physical properties of mantle minerals, mantle solidus temperatures, melt viscosity and influence the style of volcanic eruptions (e.g. Carroll and Holloway, 1994; Filiberto and Treiman, 2009; Litasov et al., 2006). The trace volatiles, especially iodine and noble gases, are powerful markers that can potentially constrain the distribution of recycled versus primordial volatile components within the Earth’s mantle (Deruelle et al., 1992; Graham, 2002; Hilton and Porcelli, 2003; Kendrick et al., 2012a). The volatile contents of basaltic glasses from different tectonic settings (e.g. mid-ocean ridge, back arc and oceanic island) are therefore of great interest, but relating the measured concentrations of volatiles in basaltic glasses to mantle abundances is challenging.

The least soluble volatiles (CO$_2$ and noble gases) are degassed from erupting lavas and as a result only melt inclusions trapped within deep magma chambers record pre-eruptive CO$_2$ concentrations, and noble gases occur dominantly in CO$_2$ vesicles (Burnard et al., 2002; Graham, 2002; Saal et al., 2002). In contrast, H$_2$O and halogens have much higher solubilities in basaltic melts, and halogens appear to be retained in melts erupted in water depths of greater than ~500 m (Straub and Layne, 2003; Unni and Schilling, 1978). Nonetheless seawater assimilation can be a potentially serious obstacle to determining the primary mantle source characteristic of halogens, H$_2$O and any other volatile that has a high abundance in seawater and a comparatively low abundance in mantle-derived melt (e.g. Fisher, 1997; Graham, 2002; Kent et al., 1999ab; 2002; Michael and Cornell, 1998; Michael and Schilling, 1989; Patterson et al., 1990).

Numerous studies have demonstrated that atmospheric noble gases (Ne, Ar, Kr, Xe) are a distinctive and ubiquitous component within basalt glasses (e.g. Graham, 2002; Hilton...
and Porcelli, 2003). It is likely that some fraction of these atmospheric noble gases are introduced by seawater assimilation processes (e.g. Patterson et al., 1990); however, atmospheric noble gases could also be introduced during sample preparation (Ballentine and Barfod, 2000), or they could be present as a recycled component within the mantle (Bach and Niedermann, 1998; Sarda, 2004).

In contrast to noble gases, assimilation of Cl is associated with seafloor hydrothermal activity and while it has been documented in Hawaii (Coombs et al., 2004; Kent et al., 1999ab) and some fast spreading centres (le Roux et al., 2006), it is uncommon in basalts generated at slow spreading centres (Michael and Cornell, 1998; Michael and Schilling, 1989). Improving constraints on the spatially limited assimilation processes affecting Cl concentrations has implications for the origin of atmospheric noble gases in basalt glasses, and igneous petrology. Assimilation accelerates volatile saturation and triggers exsolution of fluid phases meaning it can cause rapid crystallisation of magmas and critically influence the way oceanic crust accretes (Coogan et al., 2003; Perfit et al., 2003; Soule et al., 2006). Furthermore, it has been proposed that partial melting of seawater-altered oceanic crust contributes to the petrogenesis of silicic mid-ocean ridge lavas such as dacites (Wanless et al., 2010; 2011).

The assimilated components proposed in previous Cl studies have poorly defined but high Cl/H$_2$O ratios that preclude the direct involvement of seawater and favour a role for brines with salinities of ~10-50 wt % salts, or Cl-rich minerals formed by seawater alteration (Kent et al., 1999ab; 2002; le Roux et al., 2006; Michael and Schilling, 1989; Perfit et al., 1999; Wanless et al., 2010; 2011). This study extends the previous analyses to include Br and I in 19 glasses that have assimilated varying proportions of seawater-derived volatiles and sample different parts of the Earth’s mantle. We show how multi-component correlations between Cl, Br, I, K and H$_2$O can be used to rigorously test the nature of
seawater assimilation, and quantify the proportions of seawater-derived halogens and H2O in 
basalt glass. In addition, we refine previous estimates of mantle Br/Cl and I/Cl by re-
examining standardisation (Kendrick et al., 2012ab) thereby providing improved agreement 
with earlier halogen studies (Jambon et al., 1995; Schilling et al., 1978; 1980), and 
demonstrating fairly limited variation of Br/Cl and I/Cl in the Earth’s mantle.

1.1 Samples

Pristine basalt glasses were selected from a range of seafloor settings with varying 
exposure to assimilation processes. Enriched mid-ocean ridge basalt (E-MORB) glasses 
defined as having primitive mantle normalised (La/Sm)_N of >1 were selected from the Mid-
Atlantic Ridge at the Famous location (36° 50’ N) and the popping rock area (13° 50’ N) 
(Bryan et al., 1979; Bougault et al., 1988; Langmuir et al., 1977). These samples were 
expected to preserve pristine mantle halogen signatures because E-MORB have high 
concentrations of incompatible trace elements and assimilation of Cl is asserted to be a minor 
artefact for E-MORB formed at slow spreading ridges (Michael and Cornell, 1998). 
Furthermore, the popping rock sample 2πD43 is famous for its uniquely good preservation of 
mantle noble gas signatures (e.g. Moreira et al., 1998; Mukhopadhyay, 2012), which suggest 
it is very unlikely to have assimilated significant seawater-derived H2O or Cl during 
emplacement (cf. Ballentine and Barfod, 2000; Burnard et al., 1997; Moreira et al., 1998; 
Sarda, 2004; Staudacher et al., 1989; Trieloff et al., 2003).

Samples expected to show the effects of seawater contamination comprise: basalt and 
dacite glasses recovered from 0° 50’ N from the Galápagos Spreading Centre during Alvin 
dive 1652, that investigated an area of crust exhibiting particularly extensive hydrothermal 
alteration (Embley et al., 1988); and N-MORB samples from the southern Juan de Fuca
Ridge where there is also significant hydrothermal activity (45-46° N; Smith et al., 1994). Additional N-MORB, which are defined as having \((\text{La}/\text{Sm})_N\) of <1, were available for locations on the East Pacific Rise (12° 46’ N; Hekinian et al., 1983) and Mid-Atlantic Ridge (30-32° N; Bougault and Treuil, 1980). The Galápagos glasses recovered during Alvin dive 1652 are pristine but have been shown to exhibit traces of seawater assimilation (Michael and Cornell, 1998; Perfit et al., 1999). N-MORB samples were selected from the other locations because their generally low Cl content renders them more susceptible to seawater assimilation than Cl-rich E-MORB (Michael and Cornell, 1998), although the high \(^{40}\text{Ar}/^{36}\text{Ar}\) ratio of sample CH98-DR11 (>25,000) suggests minimal assimilation in this case (Marty and Humbert, 1997).

As a contrast to the variably enriched MORB samples, five glasses were selected from the northwest Lau Basin (14-16° S; Lupton et al., 2009), primarily because of their high \(^3\text{He}/^4\text{He}\) ratios of 12-28 Ra (where Ra is the atmospheric \(^3\text{He}/^4\text{He}\) ratio of \(1.4 \times 10^{-6}\)) and neon isotope signatures that are typical of primitive mantle sampled by some ocean island basalts (OIB; Lupton et al., 2009; 2012). Despite the unusual \(^3\text{He}/^4\text{He}\) signatures, the trace element abundances of these glasses are fairly typical of MORB \([(\text{La}/\text{Sm})_N]\) of 0.4-1.2], and they lack evidence for slab-derived subduction components (Lytle et al., 2012). These glasses were however of additional interest because the effects of seawater assimilation have been previously documented elsewhere in the Lau Basin (Kent et al., 2002).

2. Methods and halogen standardisation

The majority of samples included in this study were characterised using a range of techniques during the 1970’s and 80’s, and re-analysed at the University of Melbourne using a Cameca SX-50 electron microprobe for major elements and laser ablation system coupled
to an Agilent 7700x inductively-coupled plasma mass spectrometer (ICP-MS) for trace elements (supplementary information). In contrast, ICP-MS was used to analyse trace elements in solutions formed by dissolving 50 mg sized aliquots of the Famous samples. Chlorine measurements by electron microprobe had a detection limit of ~85 ppm and were standardised using Durango apatite (0.41 wt % Cl) and scapolite (1.43 wt % Cl; supplementary information).

Simultaneous Cl, Br, I and K measurements were achieved via the noble gas method (Kendrick, 2012). Samples of ~10-30 mg comprising pristine glass chips (0.2-1 mm in size) were wrapped in Al-foil, placed in an irradiation canister, and irradiated in position 5c of the McMaster Nuclear Reactor, Canada (irradiations UM#44: 42 hrs on 27/02/2011 received $10^{19}$ neutrons cm$^{-2}$; thermal/fast = 2.7; and UM#48: 30 hrs on 15/12/2011 received $8 \times 10^{18}$ neutrons cm$^{-2}$; thermal/fast = 2.7). Irradiation-produced noble gas proxy isotopes ($^{38}$ArCl, $^{80}$KrBr, $^{128}$XeI and $^{39}$ArK) were then extracted from the samples by furnace heating and measured on the MAP-215 noble gas mass spectrometer at the University of Melbourne. It was found that gas released from 10 mg sized samples at 300 °C was at the blank level, and the majority of samples were therefore preheated to 300 °C before extraction of halogen-derived noble gas isotopes in a single 1500 °C step of 20 minutes duration. Small blank corrections amounted to <1% of the sample gas and the abundances of noble gas proxy isotopes ($^{38}$ArCl, $^{80}$KrBr, $^{128}$XeI and $^{39}$ArK), determined by comparison to an air standard, were converted to Cl, Br, I and K on the basis of production ratios monitored with Hb3Gr and scapolite halogen standards (Fig 1; Kendrick, 2012).

The noble gas method has significant advantages over radiochemical neutron activation analyses used in previous Br and I studies of basalt glass (Deruelle et al., 1992; Jambon et al., 1995; Schilling et al., 1978; Schilling et al., 1980): 1.) chemical separation of halogens is not required which avoids the possibility of fractionating halogen abundance.
ratios during extraction; 2.) very high sensitivity and low detection limits mean it can be applied to small samples and it is therefore easier to obtain high purity glass separates; and 3.) it has very high internal precision of ~2-4% (2σ), compared to ~20-40% (2σ) in previous studies (Deruelle et al., 1992; Jambon et al., 1995; Schilling et al., 1978; 1980; Unni and Schilling, 1977). Nonetheless, the external precision (or accuracy) of the method is dependent on the availability of well characterised halogen standards and some refinements to the Br and I abundances in the scapolite standards used by Kendrick et al. (2012ab) have proven necessary (Kendrick et al., 2013).

The Br/Cl and I/Cl ratios now recommended for the standards (Fig 1) are considered superior to the original values (Kendrick, 2012) because they are independent of the Bjurböle meteorite standard, and they provide improved agreement with other techniques (Table S5; supplementary information; Hammerli et al., 2013). Adoption of the new standard values (Fig 1) means revising previously reported Br and I abundances (Kendrick et al., 2012ab) downwards by 20 % for Br and 25 % for I. This change enables a fairer comparison of Br/Cl ratios for basalt glasses obtained by the noble gas method and reported by Jambon et al. (1995) and Schilling et al. (1978, 1980) (see below). However, it does not alter the conclusions of the earlier studies that were based on internally consistent data sets (Kendrick et al., 2012ab). A full description of the monitor re-calibration is available in the electronic supplement.

3. Results

The electron microprobe and noble gas method gave similar K and Cl concentrations (Fig 2). The basalt glasses contain 32-1560 ppm Cl, 0.1-5.9 ppm Br and 1.6-41 ppb I, compared to maxima of 3,900 ppm Cl, 14 ppm Br and 28 ppb I in the dacite glasses from the Galápagos
Spreading Centre (Table 1). As in previous studies, halogens have higher concentrations in the more evolved samples, but each sample group has constant Br/Cl, I/Cl and K/Cl ratios over a range of MgO (Table 1; Fig 3).

The E-MORB samples from the Mid-Atlantic Ridge (2πD43 and Famous locations) yield Br/Cl of $(2.6 \pm 0.1) \times 10^{-3}$ that are indistinguishable from the revised value obtained for Macquarie Island E-MORB (Fig 4; Table 1; Kendrick et al., 2012b). The Atlantic E-MORB have I/Cl of $(50 \pm 10) \times 10^{-6}$ that are slightly less variable than those obtained for Pacific E-MORB from Macquarie Island ($(60 \pm 30) \times 10^{-6}$; Fig 4). In contrast, K/Cl varies from values of 10-12 for the Famous and Macquarie E-MORB to a distinctly higher value of $18 \pm 1$ for 2πD43 (Fig 4 and Table 1; 2σ uncertainties).

In comparison to the E-MORB glasses, the N-MORB glasses exhibit much greater scatter in K/Cl, Br/Cl and I/Cl (Fig 4). The five glasses from the northwest part of the Lau Basin, with high $^3$He/$^4$He ratios of 12-28 Ra (Lupton et al., 2009), define a linear array in the Br/Cl versus I/Cl, and Br/Cl versus K/Cl plots (Fig 4) but these parameters are not correlated with $^3$He/$^4$He (Table 1). One end-member has a composition very similar to E-MORB and the second end-member has a composition similar to glasses from the Galápagos Spreading Centre that are enriched in Br/Cl relative to seawater and have very low K/Cl of $\sim 1$ (Fig 4).

4. Discussion

4.1 Inter-laboratory comparison

The K and Cl concentrations of basalt glasses determined using the noble gas method and electron microprobe are in good agreement with the majority of data scattering within 10% of the 1:1 line (Fig 2). The K and Cl concentrations determined here are also similar to those reported for glasses with the same dredge numbers in previous studies, although
discrepancies of 10-20% exist in some cases (cf. Jambon et al., 1995; Michael and Cornell, 1998; Perfit et al., 1999).

The Br/Cl ratios reported for the 19 MORB glasses in this study (Table 1), and the revised values for Macquarie Island MORB (Kendrick et al., 2012b), and Society and Pitcairn glasses (Kendrick et al., 2012a), overlap the ranges of Br/Cl reported by Schilling et al. (1978; 1980) and Jambon et al. (1995) (Fig 5). Sample CL-DR01 yielded a Br/Cl ratio of $(3.3 \pm 0.1) \times 10^{-3}$ in this study, that is approximately half the outlying value of $6.3 \times 10^{-3}$ reported by Jambon et al. (1995). Furthermore, sample CH98-DR11 yielded a Br/Cl ratio of $(3.0 \pm 0.1) \times 10^{-3}$ in this study (Table 1) that is indistinguishable from the ratio of $3.2 \times 10^{-3}$ in Jambon et al. (1995), suggesting the data from these laboratories are broadly comparable at the quoted levels of uncertainty (Fig 5).

The 19 MORB glasses in this study (Table 1), and the revised values for 36 glasses from Pitcairn, Society and Macquarie Island (excluding 3 outliers; Fig 4) have a mean I/Cl ratio of $(60 \pm 30) \times 10^{-6}$ (2σ; Kendrick et al., 2012ab). In comparison, the I/Cl ratios obtained by combining the 14 MORB glasses analysed by Deruelle et al. (1992) and Jambon et al. (1995) extend from $20 \times 10^{-6}$ to a much higher value of $\sim 10^{-4}$ (Fig 5b). The highest values are similar to the outlying values obtained for the Macquarie Island samples, which are attributed to palagonite contamination (Fig 5b; Kendrick et al., 2012b), and iodine could have been over-estimated in some of the MORB samples analysed by Dereulle et al. (1992) if the large samples required for radiochemical neutron activation analysis included palagonite contaminants. Very minor palagonite contamination is a potentially serious artefact in iodine analyses because based on the maximum reported concentration of $\sim 1$ wt % organic C in palagonite (Kruber et al., 2008; McLoughlin et al., 2011), and typical I/C ratios of organic matter (Kennedy and Elderfield, 1987), palagonite could contain up to a $\sim 1000$ times more I than pristine MORB glass (Table 1).
4.2 The Br/Cl, I/Cl and K/Cl of uncontaminated mantle melts

The E-MORB glasses from Macquarie Island in the SW Pacific (excluding 3 outliers; Fig 4) and the samples from the Famous and popping rock locations on the Mid Atlantic Ridge all have very similar Br/Cl and I/Cl ratios that define clusters rather than mixing trends in Fig 4 and tight groups in Fig 5. The lack of visible mixing trends in these data implies the halogens were sourced from mantle reservoirs with similar Br/Cl and I/Cl ratios (e.g. the grey box in Fig 4a), and the melts did not assimilate seawater-derived halogens. The mantle origin of halogens in the Macquarie Island and Famous melts is further supported by correlations between the concentration of Cl and other trace elements (e.g. La, U, Ba and Nb) that have low concentrations in seawater (e.g. Kamenetsky and Eggins, 2012; Kendrick et al., 2012b; Michael and Cornell, 1998).

There are still insufficient data to define realistic ranges of Br/Cl and I/Cl in basalt glasses that have not been contaminated by seawater-derived components. The E-MORB glasses from Macquarie Island, Famous and Popping Rock locations all have very similar Br/Cl of (2.7 ± 0.2)×10⁻³ (Fig 4). However, if we include ocean island basalt (OIB) glasses from the Pitcairn and Society seamounts, which also appear to be free of seawater contaminants (Kendrick et al., 2012a), we define typical ‘mantle’ values of (2.8 ± 0.6)×10⁻³ for Br/Cl and (60 ± 30)×10⁻⁶ for I/Cl (Fig 5). These data show the halogen abundance ratios are surprisingly uniform with 2σ variations of only ~20 % for Br/Cl and ~50 % for I/Cl in a number of MORB and OIB reservoirs. In comparison, this limited sample set has K/Cl varying from 10 to 40, with a mean of 18 ± 19, demonstrating mantle Br/Cl and I/Cl are much less variable than mantle K/Cl.
If the entire mantle has been processed to some degree, the relative degrees variation in mantle Br/Cl (~20 %), I/Cl (~50 %) and K/Cl (>100 %) could reflect the geochemical similarities of these elements during subduction recycling (e.g. John et al., 2011; Kendrick et al., 2011; 2012a; 2013; Stroncik and Haase, 2004). Previous studies have shown Cl, Br, I and K all have similar compatibilities in silicate melts with MgO of ~1-27 wt %, suggesting their relative abundance ratios are fairly conservative during normal degrees of partial melting and fractional crystallisation (Fig 3; Kendrick et al., 2012ab; Schilling et al., 1980).

4.3 Assimilation of seawater-derived brines

In contrast to uncontaminated MORB samples that form clusters in Figure 4, the 5 glasses selected from the northwest part of the Lau Basin define binary mixing arrays between Br/Cl, I/Cl, K/Cl and H$_2$O/Cl (Figs 4 and 6; SIMS H$_2$O data are from Lytle et al. (2012)). These mixing arrays have correlation coefficients of ~0.99, and low MSWD values that demonstrate very high qualities of fit (Fig 6), and similar mixing trends are obtained for a much larger data set of previously published K/Cl, F/Cl and H$_2$O/Cl data (Fig 7ab; Lytle et al., 2012). The mixing lines in Figures 6 and 7 are interpreted to extend from a mantle end-member with K/Cl of 20 ± 10 (Fig 7a) and Br/Cl and I/Cl very similar to E-MORB (Fig 6) to a second assimilated end-member that has Br/Cl, I/Cl, K/Cl and H$_2$O/Cl very similar to the Galápagos glasses (Fig 6).

The high Br/Cl ratios of the assimilated components identified from the mixing trends in Figs 6a and 6b are most easily explained if the melts from the Lau Basin, as well as the Galápagos Spreading Centre, assimilated high salinity brines, and these data do not favour alternative mechanisms of assimilating seawater-derived components (Fig 6). Assimilation of alteration minerals such as amphibole (or salt) is not favoured because these minerals are...
characterised by low Br/Cl ratios of $<0.4 \times 10^{-3}$ (Fontes and Matray, 1993; Holser, 1979; Kendrick, 2012). As in previous studies, the H$_2$O/Cl ratio of the assimilated components are much lower than seawater or any possible low salinity vapour-phase (Figs 6d and 7ab; Kent et al., 1999ab; 2002; Michael and Schilling, 1989; Le Roux et al., 2006; Perfit et al., 1999; Wanless et al., 2011). Three of the glasses have measured H$_2$O/Cl of 2.0-2.5 (Lytle et al., 2012) and the H$_2$O/Cl intercepts obtained from the various regressions in Figures 6d, 7a and 7b are all 1.6 or lower. These data can be reasonably interpreted to indicate a brine salinity of more than 40 wt. % salts (Table 2), and a salinity of 55 ± 15 wt % salts is adopted for the calculations in section 4.4.

Plotting H$_2$O, K and Cl data from previous studies in which assimilation of seawater components has been investigated (Coombs et al., 2004; Le Roux et al., 2006; Kent et al., 1999ab; 2002; Wanless et al., 2011), yields mixing trends that are very similar to those in Figures 6d and 7a (Fig 8). These data distributions strongly suggest that brines are the dominant assimilant in all the oceanic settings investigated, and furthermore that in these settings the brines have a very restricted range of ultra-high salinities (e.g. 55 ± 15 wt. % salts; Fig 8). The low H$_2$O/Cl ratios of the assimilated components are shown very clearly in our three element plots that use Cl as the denominator, because the data converge on the assimilant (e.g. Figs 6, 7 and 8). In contrast, variability in mantle Cl/K, H$_2$O/K or H$_2$O/Nb ratios mean the uniform nature of the assimilant is masked in plots that use K or Nb as the denominator (e.g. Le Roux et al., 2006; Kent et al., 1999ab; 2002; Wanless et al., 2011).

4.4 Quantity and depth of brine assimilation

The proportion of halogens assimilated by the melts included in this study can be precisely quantified using the binary mixing models presented in Figures 6 and 7. The
proportion of assimilated Cl can be estimated from any X/Cl ratio that has characteristic
values in the mantle and brine (equation 1).

\[
\% \text{ assimilated Cl} = \left[ \frac{X/\text{Cl}_{\text{brine}} - X/\text{Cl}_{\text{glass}}}{X/\text{Cl}_{\text{brine}} - X/\text{Cl}_{\text{mantle}}} \right] \times 100
\]  

The proportion of assimilated Cl can then be converted to a Cl concentration, and because the
brine salinity is constrained as 55 ± 15 wt. % (Table 2), the concentration of H2O assimilated
can also be calculated (e.g. Table 3).

Brine assimilation is quantified for five selected samples in Table 3. In each case, we
assume the brine has K/Cl of 0.02-0.2 which is a reasonable estimate for a complex solution
comprising Na+, K⁺, Ca²⁺, Mg²⁺ and Fe³⁺ salts (e.g. Vanko, 1988). The Br/Cl ratio of the
brine is within uncertainty of the intercepts in Figures 6a and 6b, and appears to be slightly
higher for the Lau Basin samples ((3.9 ± 0.1) ×10⁻³) than the Galápagos Spreading Centre
((3.7 ± 0.1) ×10⁻³) or Juan de Fuca samples ((3.6 ± 0.2) ×10⁻³). The Lau Basin glasses show
significant spread in all chemical parameters meaning the mantle end-member can be
reasonably estimated to have K/Cl of 20 ± 10 (Fig 7a) and Br/Cl similar to E-MORB ((2.7 ±
0.2 × 10⁻³; Figs 6a and b). In contrast, the Galapagos samples all have very low K/Cl (Fig
6d; Michael and Cornell; 1998; Perfit et al., 1999) and in this case we use two conservative
estimates for mantle K/Cl (12 ± 10 and 30 ± 20) and Br/Cl of (2.8 ± 0.6) × 10⁻³ which is
based on a wide selection of uncontaminated MORB and OIB samples (section 4.2; Table 3).
The different methods of calculation adopted in Table 3 give an indication of the
uncertainties: each method gives statistically indistinguishable results for the degree of brine
assimilation but the levels of precision vary (Table 3). Brine assimilation in the Juan de Fuca
samples is poorly resolved (Table 3), but the most contaminated samples from the Lau Basin
and all of the Galapagos Spreading Centre samples are indicated to have assimilated ~95 %
of their total Cl and 35-40 % of their total H₂O (Table 3). Future studies can use calculations
analogous to these to make reliable corrections for assimilated H$_2$O and Cl with quantifiable uncertainty.

The Galápagos Spreading Centre samples with MgO of 1.6 to 6.9 wt % all have indistinguishable Br/Cl (Fig 3) and I/Cl (Table 1), indicating they have assimilated similar proportions of their total Cl (Fig 6). If brine assimilation occurred at an early stage of melt evolution, when the melts had MgO concentrations $>$6.9 wt %, the maximum concentration of $\sim$12,000 ppm brine components calculated for dacite 1652-5 (Table 3) could result from fractional crystallisation (Fig 3). In contrast, melts with $\sim$7 wt. % MgO from both Lau and Galápagos (NLD 49-1 and 1652-10) are estimated to have assimilated 1000 to 2000 ppm of brine (Table 3), which based on densities of $\sim$1.4 g cm$^{-3}$ for the brine and 2.9 g cm$^{-3}$ for the melt, would be equivalent to $\sim$2-4 cm$^3$ of brine being assimilated per litre of melt. Note that the amount of brine assimilated would be less if assimilation occurred at an even earlier stage of melt evolution when the melts had $>$7 wt. % MgO.

A final constraint relevant to the interpreted assimilation mechanisms is the depth at which assimilation occurs. Carbon dioxide and H$_2$O concentrations reported for melts from the northwest part of the Lau Basin range from 2 to 240 ppm CO$_2$ and 0.2 to 1.3 wt % H$_2$O, indicating CO$_2$ + H$_2$O saturation pressures of $\sim$150 to 600 bars (Lytle et al., 2012). In comparison, most of the samples were dredged from depths of only 1800 to 2400 m equivalent to a pressure of $<$250 bars (Fig 7c; Lytle et al., 2012). These data indicate some of the Lau samples with low K/Cl ratios, that assimilated up to 2000 ppm brine, were over-saturated with respect to volatiles on the seafloor (Fig 7c), suggesting that brine assimilation must have occurred at a higher pressure in the subsurface. If the melt assimilated the brine under hydrostatic conditions, the implied depth of assimilation is more 3 km beneath the seafloor (Fig 7c). Similar depths of assimilation, of up to 5 km beneath the seafloor, are
indicated by CO$_2$ and H$_2$O concentration data for glasses from the East Pacific Rise (le Roux et al., 2006) and Hawaii (Coombs et al., 2004).

4.5 Brine generation and assimilation mechanisms

Seafloor hydrothermal vents commonly expel seawater-derived fluids with temperatures of ~250-420 °C and salinities ranging from ~0.1 to 8 wt. % salts (e.g. Campbell and Edmond, 1989; Coumou et al., 2009; Fontaine et al., 2007; You et al., 1994); however, fluid inclusions with much higher salinities of 30-50 wt % salts are common in deeper parts of the hydrothermal system (e.g. Kelley et al., 1992; 1993; Lécuyer et al., 1999; Nehlig, 1991; Vanko, 1988; Vanko et al. 2004). The available data suggest a portion of these brines is sometimes assimilated by deep seated magmas intruding layers 2b and 3 of the crust (Figs 6 to 8; sections 4.3-4.4). In this section, we briefly outline how crustal brines with high Br/Cl ratios (Fig 6) might be generated and why the assimilated brines have a very limited range of salinity (e.g. 55 ± 15 wt. % salts; Figs 7 and 8).

Firstly, the average salinity of seawater-derived fluids in the oceanic crust is increased by preferential incorporation of OH$^-$, relative to Cl$, into hydrous alteration minerals such as clays, chlorite, talc, epidote, mica, amphiboles (e.g. Ito and Anderson, 1983; Palmer, 1992; Vanko, 1986). At suitably low water-rock ratios this mechanism (alone) can produce ultra-saline brines and Cl-rich amphiboles with 1-4 wt. % Cl (e.g. Markl and Bucher, 1998; Vanko, 1986; 1988). Given the size of the amphibole anion site limits the ability of Cl$^-$ to substitute for OH$^-$ (Volfinger et al., 1985), and because Br$^-$ is larger than Cl$, it is likely that amphiboles have lower Br/Cl ratios than coexisting brines (e.g. Svensen et al., 2001); however, the magnitude of the Br/Cl fractionation between brine and amphibole at the relevant pressure and temperature conditions is unknown. Therefore it is possible that fluid-rock interactions
and hydration of the oceanic crust (alone) could generate fluids with the salinity (55 ± 15 wt. % salts) and Br/Cl ratio of the assimilated brine (Figs 6 and 7). Alternatively, much higher Br/Cl ratios ranging from \( \sim 4 \times 10^{-3} \) up to \( 30 \times 10^{-3} \) in eclogite fluid inclusions with salinities of 22-40 wt. % salt have previously been ascribed to this mechanism (Svensen et al., 2001).

Seawater-derived fluids can undergo phase separation (or hydrothermal boiling) at multiple levels within the oceanic crust (Bischoff and Pitzer, 1985; Bischoff and Rosenbauer, 1989; Coumou et al., 2009). Adiabatic decompression produces low salinity vapours and conjugate brines with up to 8 wt % salts close to the seafloor (e.g. Bischoff and Pitzer, 1985; Coumou et al., 2009; Lécuyer et al., 1999). However, phase separation could occur at deeper crustal levels in response to switches from lithostatic to hydrostatic pressure or heating (e.g. Lécuyer et al., 1999; Vanko, 1988; Vanko et al., 2004). Brines infiltrating the cracking front surrounding magma chambers in layer 3 of the crust, and brines that come into direct contact with deep-seated magmas via deeply penetrating faults, will be rapidly heated to magmatic temperatures (e.g. \( 1100-1200 \, ^{\circ}C \); Bischoff and Rosenbauer, 1989). The resulting superheated fluids will boil, with the vapour phase lost to the upper part of the hydrothermal system and dense residual brines potentially retained in a lower layer of the crust (Fig 9; Bischoff and Rosenbauer, 1989; Fontaine and Wilcock, 2006) and/or assimilated by the magma (e.g. Figs 6, 7 and 8). It is possible that in this situation, the relative solubilities of \( \text{H}_2\text{O}, \text{Cl} \) and \( \text{Br} \) in basaltic melts could limit the salinity (and Br/Cl) of the brine that can be assimilated; e.g. the melt may become saturated with respect to \( \text{H}_2\text{O} \) but remain under-saturated with respect to Cl (cf. Dixon et al., 1995; Webster et al., 1999).

The relative behaviour of Br and Cl during phase separation is not well constrained and may vary depending on pressure and temperature conditions (e.g. Berndt and Seyfried, 1990; 1997; Liebscher et al., 2006; Foustoukos and Seyfried, 2007). In many cases vent fluids with variable salinity preserve seawater Br/Cl ratios (Campbell and Edmond, 1989;
You et al., 1994), consistent with experimental data that indicate no significant fractionation of Br/Cl between brines and vapours (e.g. Berndt and Seyfried, 1990; 1997). In this case, or if Br is preferentially partitioned into the vapour (e.g. Foustoukos and Seyfried, 2007), fractionation of Br/Cl during crustal hydration combined with phase separation could explain the high Br/Cl ratios of the assimilated brines (Fig 6). However, low salinity vapours from 9-10° N on the East Pacific Rise have lower than seawater Br/Cl ratios (Oosting and Von Damm, 1996), which is consistent with experimental data that favour preferential partitioning of Br, relative to Cl, into dense brines (Liebscher et al., 2006). Therefore it is also possible that under the relevant pressure-temperature conditions, boiling off a low Br/Cl vapour phase in an open system, could account for the inferred high salinity and high Br/Cl ratio of the assimilated brine (Figs 6 and 7).

Finally, it has been suggested that further fractionation of vent fluid Br/Cl ratios could result from precipitation of halite (e.g. Berndt and Seyfried, 1997; Foustoukos and Seyfried, 2007). This mechanism is unlikely to contribute to the Br/Cl signature of brines assimilated at >400 bars (Figs 6 and 7) however, because at this pressure precipitation of halite is only possible during cooling (e.g. Bodnar and Vityk, 1994). In contrast, brines at depths of >3km would be heated from amphibolite facies temperatures of 500-700 °C (e.g. Vanko, 1988) to magmatic temperatures of ~1100-1200 °C during assimilation (Fig 9).

4.6 Implications for petrology and geochemistry

The Br/Cl ratios of brines assimilated in the northwest part of the Lau Basin, and the Galápagos Spreading Centre, are well defined by the binary mixing model in Figure 6. Although a small number of samples have been analysed for Br (5 from Lau and 3 from Galápagos; Fig 6), these data suggest the assimilated brines had fairly uniform Br/Cl ratios
that were slightly different in the two locations (Fig 6). The implied uniformity of the brines
Br/Cl (Fig 6), and the fairly uniform H$_2$O/Cl ratios of assimilated components elsewhere
(Figs 6, 7 and 8), strongly suggest that brines are efficiently segregated from OH- and Cl-
having alteration minerals before assimilation. Assimilation of OH- and Cl-bearing
alteration minerals together with brines cannot explain the mixing arrays in Figures 6, 7 and
8, because brines mixed together with alteration minerals would have very variable Br/Cl,
I/Cl, K/Cl and H$_2$O/Cl ratios. Nonetheless the wall rocks adjacent to active magma chambers
at temperatures of 1100-1200 °C will have been efficiently dehydrated and are likely to have
very low H$_2$O and Cl contents. It is therefore plausible that some dehydrated wall-rock is
assimilated together with the brines, and this may help reconcile the halogen data that require
brine assimilation (and no significant assimilation of altered oceanic crust) with previously
reported O-isotope data that are more easily explained by wall rock assimilation (e.g. Perfit et
al., 1999; Wanless et al., 2011).

Hydrothermal brines can have ppm concentrations of elements such as Ba, Sr, Cu and
Pb (Coombs et al., 2004; Hardardottir et al., 2009; Schmidt et al., 2007). However, these
elements usually have equivalent or higher concentrations in mantle melts (e.g. Lytle et al.,
2012), meaning assimilation of a few hundred ppm of brine (e.g. Table 3) is unlikely to
perturb the mantle signatures of these elements in magmatic glasses. Similarly, it seems
unlikely that assimilation of a few hundred ppm of brine would greatly influence the O-
isotope signature of a mantle melt, unless dehydrated wall rock is assimilated with the brine
(above). In contrast, brine assimilation could potentially alter the mantle signatures of H-
isotopes, B and noble gases which all have relatively high concentrations in seawater
compared to the mantle (Kent et al., 1999ab). The noble gases are particularly interesting
because they are expected to be strongly partitioned into the vapour phase during phase
separation (Kennedy, 1988), and the extent to which brine assimilation influences noble gases
may therefore depend strongly on the role of phase separation in generating the brine (section 4.5).

Recently published data for melts from the northwest part of the Lau Basin (Hahm et al., 2012; Lupton et al., 2012; Lytle et al., 2012), show that melts best preserving high mantle-like H₂O/Cl ratios, appear to exhibit slightly more variation in \( ^3\text{He}/^4\text{He} \) than the melts most influenced by brine assimilation (Fig 10a), and the melts with high mantle-like H₂O/Cl ratios also preserve the highest most mantle-like \( ^{20}\text{Ne}/^{22}\text{Ne} \) ratios (Fig 10b). These data allow the possibility that brine assimilation has influenced both the \( ^3\text{He}/^4\text{He} \) ratio and \( ^{20}\text{Ne}/^{22}\text{Ne} \) ratio of the Lau Basin melts. We briefly explore the feasibility of this suggestion and explore its significance to demonstrate how noble gases might be combined with H₂O and halogen data in future studies.

Brine assimilation could potentially influence the He isotope systematics of the melts because even after phase separation, hydrothermal brines with negligible atmospheric helium are enriched in mantle-derived (± radiogenic) helium sourced from oceanic crust by hundreds of times relative to seawater helium concentrations (Kennedy, 1988). Correlations between \( ^4\text{He}/^{40}\text{Ar}^* \) and \( ^{36}\text{Ar}/^{40}\text{Ar}^* \) in some basalt glasses have previously been interpreted as indicating some helium is assimilated together with atmospheric contaminants (Fisher, 1997). Brines circulated through very young oceanic crust will acquire helium with a \( ^3\text{He}/^4\text{He} \) ratio of close to the mantle average, whereas brines circulated through older crust will be relatively enriched in radiogenic \( ^4\text{He} \). As a result, brine assimilation could have a subtle effect on the \( ^3\text{He}/^4\text{He} \) ratios of basalt glasses, by either shifting melt \( ^3\text{He}/^4\text{He} \) ratios toward the crustal average (e.g. Fig 10a), or perturbing the \( ^3\text{He}/^4\text{He} \) ratios to lower values (Graham, 2002).

In contrast to He, seawater has relatively high concentrations of atmospheric Ne, Ar, Kr and Xe compared to the mantle (Ozima and Podosek, 2002), and seawater-derived brines
as well as altered oceanic lithosphere are dominated by atmospheric Ne, Ar, Kr and Xe isotope signatures (Kennedy, 1988; Kendrick et al., 2011; 2013; Staudacher and Allegre, 1988). If the proposed mixing trends in Fig 10b are ascribed to brine assimilation alone (and not late stage air contamination; e.g. Ballentine and Barfod, 2000), the convex shape of the trends suggests that the mantle signatures of heavy noble gases (Ne, Ar, Kr, Xe) are overprinted by brine assimilation more easily than mantle H₂O/Cl (or halogen) signatures. Furthermore, based on the Ne and Cl concentrations of the glasses investigated (Hahm et al., 2012; Lytle et al., 2012; Lupton et al., 2012), the curvature of the proposed mixing trends (Fig 10b) suggests the brines had Ne/Cl ratios broadly similar to seawater (within a factor of 5-10) and higher than the mantle. This would be possible if: atmospheric noble gases were acquired from lithological reservoirs in the sub-surface; or phase separation was a minor process in generating the brines’ salinity (cf. section 4.5).

Collection of further noble gas data combined with H₂O and Cl are required to better evaluate the extent to which noble gas isotope ratios are correlated with variations in H₂O/Cl (cf. Fig 10). This is important because noble gas versus H₂O/Cl plots can be used to provide new inferences on the sources of atmospheric noble gases and address long standing uncertainties in the origin of atmospheric noble gases in pristine glasses (e.g. Patterson et al., 1990; Ballentine and Barfod, 2000). If the correlations proposed in Figure 10 are substantiated, and modern air contamination during sample preparation is shown to be a minor artefact (cf. Ballentine and Barfod, 2000), the noble gas data would provide powerful constraints on the alternative brine generation and assimilation mechanisms outlined in section 4.5.

5. Summary and Conclusions
Submarine lavas exhibit limited variation in Br/Cl and I/Cl with average and 2 standard deviation values of \([2.8 \pm 0.6 \times 10^{-3}]\) and \([(60 \pm 30) \times 10^{-6}]\), respectively, in 43 MORB and OIB samples shown to be free of significant seawater contamination (based on correlations between Cl and other trace elements or isotopes). These ratios are invariant with respect to MgO and considered representative of the mantle sources.

Assuming the entire mantle has been processed to some degree, the relative degrees of variation in MORB and OIB Br/Cl (~20 %), I/Cl (~50 %) and K/Cl (>100 %), could reflect the behaviour of these elements during subduction. These elements do not appear to be fractionated during the degrees of partial melting and fractional crystallisation required to generate silicate melts with MgO of 1-27 wt %.

Assimilation of seawater-derived halogens can be recognised from mixing lines generated in Br/Cl, I/Cl, F/Cl, K/Cl and H\(_2\)O/Cl plots (Figs 6, 7 and 8). The H\(_2\)O/Cl and Br/Cl data do not favour the direct involvement of seawater, low salinity vapour phases or crustal alteration minerals in the assimilation process. Rather they demonstrate melts from the Lau Basin, Galápagos Spreading Centre and all other locations with anomalously Cl-rich glasses previously investigated, assimilated brines with salinities of 55 ± 15 wt. % salts (Figs 7 and 8).

The high salinity and elevated Br/Cl signature of the brines are generated by a combination of fluid-rock interaction, with preferential incorporation of OH\(^-\rangle Cl^\rangle Br^-\) into hydrous minerals, and phase separation. The relative importance of these processes is unknown, but open system boiling of hydrothermal fluids during, or immediately prior to, assimilation is likely to generate extremely saline brines, and the relative solubilities of Cl, Br and H\(_2\)O in basalt melts may further limit the salinity and Br/Cl ratios of the brines that can be assimilated.
Mixing models allow the proportion of seawater-derived H$_2$O and Cl introduced by brine assimilation to be precisely quantified. The melts from the Lau Basin and Galápagos Spreading Centre assimilated up to 35-40 % of their total H$_2$O and 95 % of their total Cl. Similar calculations can be used to reliably correct measured H$_2$O and Cl abundances for assimilation enabling improved estimates of mantle H$_2$O and Cl.

The widespread assimilation of seawater-derived brines, rather than seawater, implies assimilation could potentially influence the helium isotope systematics of some mantle melts. Plotting elemental or isotopic ratios, such as $^3$He/$^4$He, as a function of H$_2$O/Cl is an effective method for assessing the extent to which the ratio is influenced by brine assimilation (e.g. Fig 10).

Acknowledgements

Stanislav Szczepanski is thanked for technical assistance in the University of Melbourne noble gas laboratory. Dr Mark Kendrick was the recipient of an Australian Research Council QEII Fellowship (project number DP 0879451). Some of the samples analysed here were provided to RJA by Charles Langmuir and Michael Perfit, 35 years ago, some came from CRPG core shed, others were collected during the SS07/07 voyage of Australia’s Marine National Facility (RV Southern Surveyor): the Facility’s staff, captain and crew, are thanked for their efficient operation of that voyage. I am indebted to Dr John Bennett and Attila Stopic (ANSTO) for undertaking neutron activation analyses and answering numerous queries about neutron fluences and K$_0$ standardisation (supplementary information). Michael Perfit, Michelle Coombs and an anonymous reviewer are gratefully acknowledged for constructive comments that improved this manuscript.
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Table 1. Basalt Glass total fusion halogen data (2σ analytical uncertainty)

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<th>Sample name</th>
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<th>(La/Sm)$_N$</th>
<th>$^{3}$He/$^{4}$He R/Ra</th>
<th>Mass (mg)</th>
<th>Cl (ppm)</th>
<th>Br (ppb)</th>
<th>I (ppb)</th>
<th>K (wt.%)</th>
<th>Br/Cl (wt. ×10$^{-3}$)</th>
<th>I/Cl (wt. ×10$^{-6}$)</th>
<th>K/Cl (wt. ×10$^{-6}$)</th>
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<td>8.2-8.5</td>
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<td>0.8</td>
<td>8.1 ± 0.2</td>
<td>28.9</td>
<td>92</td>
<td>309</td>
<td>3.7</td>
<td>0.10</td>
<td>3.34 ± 0.09</td>
<td>40 ± 2</td>
<td>10.9 ± 0.8</td>
</tr>
<tr>
<td><strong>North west Lau Basin (14-16 S°)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>NLD 20-1</td>
<td>9.1</td>
<td>1.2</td>
<td>18.6</td>
<td>24.0</td>
<td>163</td>
<td>549</td>
<td>4.2</td>
<td>0.11</td>
<td>3.36 ± 0.09</td>
<td>26 ± 2</td>
<td>6.6 ± 0.4</td>
</tr>
<tr>
<td>NLD 39-1</td>
<td>12.0</td>
<td>18.1</td>
<td>1,560</td>
<td>5,900</td>
<td>15</td>
<td>0.23</td>
<td>3.79 ± 0.07</td>
<td>9.4 ± 0.4</td>
<td>1.5 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NLD 49-1</td>
<td>7.0</td>
<td>0.5</td>
<td>20.8</td>
<td>16.5</td>
<td>635</td>
<td>2,420</td>
<td>5.1</td>
<td>0.06</td>
<td>3.81 ± 0.07</td>
<td>8.0 ± 1.0</td>
<td>0.9 ± 0.1</td>
</tr>
<tr>
<td>NLD 13-1</td>
<td>8.6</td>
<td>0.7</td>
<td>28.1</td>
<td>14.0</td>
<td>67</td>
<td>210</td>
<td>2.4</td>
<td>0.07</td>
<td>3.12 ± 0.07</td>
<td>36 ± 3</td>
<td>10.2 ± 0.7</td>
</tr>
<tr>
<td>NLD 48-1</td>
<td>8.4</td>
<td>0.4</td>
<td>15.9</td>
<td>15.9</td>
<td>340</td>
<td>1,290</td>
<td>4.0</td>
<td>0.03</td>
<td>3.78 ± 0.09</td>
<td>12 ± 1</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>Mac. Is. E-MORB</td>
<td>5.9-8.8</td>
<td>0.9-4.9</td>
<td>7.1-8.3</td>
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<tr>
<td>Seawater</td>
<td>19,400</td>
<td>65,877</td>
<td>58</td>
<td>0.038</td>
<td>3.5</td>
<td>3.1</td>
<td>0.02</td>
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</tbody>
</table>

Additional major and trace element data are available in the electronic supplement. Italicised values for MgO, La/Sm and $^{3}$He/$^{4}$He are published values (Langmuir et al., 1977; Lupton et al., 2009; Lytle et al., 2012; Marty and Zimmermann, 1999; Moreira et al., 1998; Nishio et al., 1998). Macquarie Island data are revised according to the revised Br/Cl and I/Cl ratios of the scapolite standards (Fig 1; Kendrick et al., 2013). Note that $^{3}$He/$^{4}$He ratios are reported as R/Ra where Ra is the atmospheric $^{3}$He/$^{4}$He ratio of 1.39×10$^{-6}$. E-MORB form a continuum with N-MORB are defined here as having primitive mantle normalised La/Sm [(La/Sm)$_N$] of > 1 (Hofmann, 2003).
### Table 2. Estimated brine salinity

<table>
<thead>
<tr>
<th>H$_2$O/Cl</th>
<th>Wt. % Salts$^1$</th>
<th>Wt.% NaCl eq.</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Northwest part of the Lau Basin</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;2.5</td>
<td>&gt;42</td>
<td>&gt;37</td>
<td>Min. meas. H$_2$O/Cl (Lytle et al., 2012)</td>
</tr>
<tr>
<td>&lt;2.0</td>
<td>&gt;48</td>
<td>&gt;42</td>
<td></td>
</tr>
<tr>
<td>0.7 ± 0.5</td>
<td>60-90</td>
<td>55-90</td>
<td>Fig 6d</td>
</tr>
<tr>
<td>0.6$^{+1.6}_{-1.3}$</td>
<td>&gt;45</td>
<td>&gt;40</td>
<td>Fig 7a; NWL data</td>
</tr>
<tr>
<td>1.6$^{+1.4}_{-1.0}$</td>
<td>38-75</td>
<td>33-70</td>
<td>Fig 7a; all data</td>
</tr>
<tr>
<td>−0.0$^{+0.8}_{-1.0}$</td>
<td>&gt;70</td>
<td>&gt;64</td>
<td>Fig 7b; NWL data</td>
</tr>
<tr>
<td>−1.0$^{+0.8}_{-0.8}$</td>
<td></td>
<td></td>
<td>Fig 7b; all data</td>
</tr>
</tbody>
</table>

$^1$ – Wt. % salts calculated assuming the composition of seawater salt with a Cl weight fraction of 0.55.
Table 3. Quantification of brine assimilation in selected samples (2σ uncertainties)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured Cl ppm</th>
<th>Measured H₂O wt. %²</th>
<th>Assim. Cl %</th>
<th>Calculated Assim Cl ppm</th>
<th>Assim. brine ppm</th>
<th>Assim. H₂O %</th>
<th>Basis of calculation¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lau Basin</strong></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>NLD 49-1</td>
<td>635</td>
<td>0.25</td>
<td>96 ± 2</td>
<td>610 ± 10</td>
<td>2000 ± 600</td>
<td>36 ± 8</td>
<td>K-1</td>
</tr>
<tr>
<td></td>
<td>92 ± 12</td>
<td>580 ± 80</td>
<td></td>
<td>1900 ± 600</td>
<td>35 ± 15</td>
<td></td>
<td>Br-1</td>
</tr>
<tr>
<td>NLD 13-1</td>
<td>67</td>
<td>0.25</td>
<td>49 ± 26</td>
<td>33 ± 17</td>
<td>110 ± 60</td>
<td>2 ± 1</td>
<td>K-1</td>
</tr>
<tr>
<td></td>
<td>33 ± 17</td>
<td>22 ± 11</td>
<td></td>
<td>70 ± 40</td>
<td>1.7 ± 0.4</td>
<td></td>
<td>Br-1</td>
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<tr>
<td><strong>Galápagos Spreading Centre</strong></td>
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<td></td>
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</tr>
<tr>
<td>Alv 1652-10</td>
<td>340</td>
<td>0.26</td>
<td>87 ± 11</td>
<td>300 ± 40</td>
<td>980 ± 290</td>
<td>17 ± 4</td>
<td>K-2</td>
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<tr>
<td></td>
<td>95 ± 3</td>
<td>320 ± 10</td>
<td></td>
<td>1100 ± 300</td>
<td>18 ± 4</td>
<td></td>
<td>K-3</td>
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<td></td>
<td>89 ± 17</td>
<td>300 ± 60</td>
<td></td>
<td>1000 ± 300</td>
<td>18 ± 8</td>
<td></td>
<td>Br-2</td>
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<tr>
<td>Alv 1652-5</td>
<td>3,870</td>
<td>1.38</td>
<td>94 ± 5</td>
<td>3600 ± 200</td>
<td>12000 ± 3000</td>
<td>39 ± 8</td>
<td>K-2</td>
</tr>
<tr>
<td></td>
<td>89 ± 17</td>
<td>3400 ± 700</td>
<td></td>
<td>11000 ± 4000</td>
<td>37 ± 16</td>
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<td>Br-2</td>
</tr>
<tr>
<td><strong>Juan de Fuca</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alv 2269-2</td>
<td>154</td>
<td></td>
<td>40 ± 50</td>
<td>60 ± 80</td>
<td>190 ± 280</td>
<td></td>
<td>K-2</td>
</tr>
<tr>
<td></td>
<td>50 ± 50</td>
<td>80 ± 80</td>
<td></td>
<td>260 ± 260</td>
<td></td>
<td></td>
<td>Br-2</td>
</tr>
</tbody>
</table>

1- Sample K/Cl and Br/Cl are given in Table 1. All brines are assumed to have K/Cl of 0.1 ± 0.09 and 55 ± 15 wt. % salts (comprising 0.55 Cl by mass). Brine Br/Cl (estimated from Fig 6a) are (3.9 ± 0.1)×10⁻³ for Lau; (3.7 ± 0.1)×10⁻³ for Galápagos; and (3.6 ± 0.2)×10⁻³ for Juan de Fuca. Mantle K/Cl values are: 20 ± 10 (K-1); 12 ± 10 (K-2); or 30 ± 20 (K-3). Mantle Br/Cl values are: (2.7 ± 0.2)×10⁻³ (Br-1) or (2.8 ± 0.6)×10⁻³ (Br-2).

2- Water concentrations from Lytle et al. (2012) and Perfit et al. (1999).
Fig 1. Scapolite standards used to monitor the production of $^{38}$Ar$_{Cl}$, $^{80}$Kr$_{Br}$, and $^{128}$Xe$_{I}$ in 7 irradiations have good reproducibility (Kendrick, 2012). The absolute Br/Cl and I/Cl ratios recommended for the monitors have been revised using a combination of techniques described in the supplementary information (Kendrick et al., 2013). Analyses 1-119 were undertaken by laser microanalysis (Kendrick, 2012), but the more recent analyses have been undertaken by fusing scapolites in a resistance furnace, enabling improved measurement of iodine in samples SP/BB2 (supplementary information).
Fig 2 (Kendrick et al., 2013)

Fig 2. K and Cl concentrations of glasses determined from irradiation produced $^{39}\text{Ar}_K$ and $^{38}\text{Ar}_Cl$ using the noble gas method and electron microprobe data show good agreement. The 1:1 reference line and a 10% envelope are shown for reference.
Fig 3. The Cl concentration and Br/Cl of magmatic glasses versus MgO (note the break in scale on the x-axis). The most evolved glasses have the highest Cl concentrations but the constancy of Br/Cl within any sample group over a range of MgO indicates Br/Cl is not fractionated as a function of partial melting or fractional crystallisation (see also (Kendrick et al., 2012a).
Fig 4. Halogen and K three element plots for the samples in this study: a) Br/Cl versus I/Cl, and b) Br/Cl versus K/Cl. The composition of seawater is shown as a star in both panels. The grey box in ‘a’ highlights the mean and 2 standard deviation values of Br/Cl and I/Cl ratios measured in E-MORB from Macquarie Island, Famous and popping rock locations. These samples are free of seawater contaminants (text) but the outlying I/Cl ratios are ascribed to palagonite contamination (see Fig 5b). The range of mantle K/Cl is poorly defined and the grey box is ‘open’ to higher K/Cl in part ‘b’.
Fig 5. Br/Cl and I/Cl data obtained for basalt glasses using the noble gas method (this study; Kendrick et al., 2012a; Kendrick et al., 2012b) and radiochemical neutron activation analyses in previous studies (Deruelle et al., 1992; Jambon et al., 1995; Schilling et al., 1978; Schilling et al., 1980). The noble gas data are assigned 2σ uncertainties of 5% for Br/Cl and 10% for I/Cl that reflect the reproducibility of these parameters in the most uniform standard (Fig 1). The RNAA Br/Cl data is assigned a 2σ uncertainty of 20% (Unni and Schilling, 1977), but uncertainties of 10-40%, based on the I measurement are shown for I/Cl (Deruelle et al., 1992). E-MORB has strikingly uniform Br/Cl and I/Cl; the highest I/Cl ratios are attributed to palagonite contamination that affect different aliquots of a single sample (47979; highlighted in dark grey box) to different extents (see text).
Fig 6 (Kendrick et al., 2013)

Fig 6. Halogen, H₂O and K systematics of samples contaminated by seawater-derived components (H₂O data are from Perfit et al. (1999) and Lytle et al. (2012). The composition of seawater is shown as a star in each panel. An interpreted mixing line is shown through samples from the northwest part of the Lau Basin (NW Lau Spreading Centre and Rochambeau Riffs) with statistics defining the quality of fit (statistical regressions were performed using Microsoft Excel and the Isoplot program (Ludwig, 2009)). Note that brine salinities are shown in italicised bold labels on the H₂O/Cl axis in part d. The H₂O/Cl of the brine (e.g. salinity) depends on the K/Cl of the brine and is estimated as 55 ± 15 wt. % salts (see text and Table 2).
Fig 7. Recently published ion-microprobe data for melts from the northwest part of the Lau Basin (Lytle et al., 2012): H$_2$O/Cl versus a) K/Cl and b) F/Cl showing the trends identified in Fig 6 are regionally significant. The regression uncertainties are 2$\sigma$ and were obtained using 'robust regressions' in the Isoplot program (Ludwig, 2003). In each case regressions are shown for all data and data from the North West Lau Spreading Centre (NWL) only. Note than Altered Ocean Crust (A.O.C.) has higher H$_2$O/Cl than unaltered rocks and low K/Cl (Ito et al., 1983; Sano et al., 2008). c) saturation pressure calculated from H$_2$O and CO$_2$ concentrations reported in Lytle et al (2012) using the VolatileCalc program (Newman and Lowenstern, 2002).
Fig 8. Chlorine, $\text{H}_2\text{O}$ and $\text{K}$ data for samples investigated in previous studies (log scale; Coombs et al., 2004; Kent et al., 1999ab; 2002; Le Roux et al., 2006; Wanless et al., 2011). Altered ocean crust (AOC) has variable composition but is estimated to have higher $\text{H}_2\text{O}/\text{Cl}$ than unaltered rocks (and in most cases seawater) and $\text{K/Cl}$ of 0.3-2 (Ito et al. 1983; Sano et al., 2009); seawater and brines with salinities of 5, 10, 20, 30 and 50 wt % salts are shown for reference. The data are all interpreted as lying on mixing lines between mantle reservoirs with $\text{K/Cl}$ of ~7-30 and $\text{H}_2\text{O}/\text{Cl}$ of 10-60; and an ultra-saline brine with $\text{H}_2\text{O}/\text{Cl}$ of <1.6. As originally identified by Michael and Schilling (1989), assimilation of altered ocean crust cannot explain $\text{Cl}$ over enrichment.
Fig 9. Conceptual model for brine circulation at a spreading centre modified after Bischoff and Rosenbauer (1989). Seawater is drawn into the crust where it begins to hydrate the crust and is heated. Preferential incorporation of $\text{OH}^+ > \text{Cl}^- > \text{Br}^-$ into hydrous minerals increases the salinity and $\text{Br}/\text{Cl}$ of the fluids. Fluids coming into direct contact with magmas via a ‘cracking front’ or deeply penetrating faults are super-heated with vapours boiled off and brines either retained in the deep crust or assimilated by the magma. Long term trapping of brine is demonstrated by the prevalence of low salinity vent fluids (e.g. Endeavour Field, Juan de Fuca Ridge; Seyfried et al., 2003), and the high $\text{Br}/\text{Cl}$ of brine-contaminated melts (Figs 4 and 6). Fluid inclusions (F.I.) in quartz veins associated with Cl-rich amphibole in greenschist and amphibolite facies gabbros have salinities of ~50 wt % salt and trapping temperatures of 600-700 °C (Vanko, 1986; 1988). W/R denotes water/rock.
Fig 10. Noble gas versus H₂O/Cl plots used to assess the possible role of brine assimilation in altering noble gas signatures. The mean $^{3}$He/$^{4}$He ratio of 15.4 R/Ra is shown as a dashed line in part a. The $r$-values in part b define the curvature of the proposed mixing trends where $r = (^{22}\text{Ne}/\text{Cl})_{\text{brine}}/(^{22}\text{Ne}/\text{Cl})_{\text{mantle}}$ (Langmuir et al., 1978).