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The halogen (F, Cl, Br, I) and H₂O systematics of Samoan lavas: assimilated-seawater, EM2 and high-^{3}He/^{4}He components

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Abstract. The Samoan mantle plume samples two or more mantle components including: an extreme EM2 composition with $^{87}Sr/^{86}Sr$ >0.720, and a primitive component with high $^{3}He/^{4}He$. The high $^{87}Sr/^{86}Sr$ melts have a unique potential to constrain the composition of the EM2 mantle end-member that is commonly attributed to subduction recycling. However, a previous study of H_2O, CO_2, S, F and Cl in Samoan glasses was hampered by the presence of unresolved assimilated sea water. The current study builds on the earlier work by extending the volatile database to include the trace halogens Br and I, and reporting new volatile data for additional glasses with $^{87}Sr/^{86}Sr$ up to 0.7125 and $^{3}He/^{4}He$ of up to 15 Ra (Ra is the atmospheric $^{3}He/^{4}He$ ratio of 1.39×10^{-6}).

The selected glasses with MgO of 4.0 to 6.5 wt. % have CO_2 concentrations of 4 to 200 ppm that reflect degassing of CO_2 on the seafloor. In contrast, the glasses contain 0.7-1.9 wt. % H_2O, 880-1870 ppm F, 470-1700 ppm Cl, 1.8-6.9 ppm Br, 18-130 ppb I and 0.6-1.5 wt. % K. Correlations between the concentrations of these elements suggest the melts retain H_2O concentrations close to pre-degassing values and demonstrate the melts have been variably affected by assimilation of seawater-derived brines. The brines are indicated to have had salinities of 55 ± 15 wt. % salt, F/Cl ratios close to seawater (e.g. <0.0001), Br/Cl ratios ~40 % higher than seawater, and I/Cl ratios ten times the seawater value. It is calculated the melts assimilated brine fractions of 0 to 0.45 wt. %, which contributed up to ~30 % of the total H_2O and up to ~70% of the total Cl in the melts.

After accounting for the effects of brine assimilation, the Samoan melts are suggested to have a fairly constant magmatic Cl/K of 0.05 ± 0.2, which is lower than the median MORB value. Assimilation-corrected H_2O/Ce values are not correlated with $^{87}Sr/^{86}Sr$, but the sample with the highest $^{87}Sr/^{86}Sr$ of 0.7125 has an assimilation-corrected H_2O/Ce of 83 ± 3, that is significantly lower than typical MORB values of 150-300. These data confirm that the Samoan EM2 source is depleted in H_2O, and perhaps Cl, relative to lithophile elements of similar compatibility.

The glasses deemed free of seawater components, including the least enriched sample with $^{3}He/^{4}He$ of 15 Ra and the most enriched sample with $^{87}Sr/^{86}Sr$ of 0.7125, have indistinguishable Br/Cl and I/Cl that are within the narrow range determined for EM1 and EM2 glasses from Pitcairn and Society and mid-ocean ridge basalts (e.g. Br/Cl = 0.0028 ± 0.0006; I/Cl = 0.00006 ± 0.00003; 2σ). The uniformity of mantle Br/Cl and I/Cl could be explained if halogens are not significantly subducted into the mantle. However, an alternative possibility is that the subduction zone 'filter' controls the abundance ratios of halogens recycled into the mantle, and recycled halogens with associated H_2O, have been circulated throughout the mantle.

1. Introduction

The enriched trace element and isotope signatures of Oceanic Island Basalts (OIB) that sample the EM1, EM2 and HIMU mantle reservoirs are commonly attributed to the involvement of recycled sediments and/or altered oceanic crust/lithospheric materials introduced by subduction-recycling (e.g. Eiler et al., 2000; Hofmann and White, 1982; Hofmann, 2003; Jackson et al., 2007; White and Hofmann, 1982; Weaver, 1991; Workman et al., 2008; Zindler and Hart, 1986). OIB melts commonly have high concentrations of H_2O and other volatiles compared to MORB (e.g. Moore, 1970; Schilling et al., 1980); however, it is unclear if the high volatile content of EM1 and EM2 melts can be explained by subduction recycling. EM1 and EM2 melts are typically depleted in H_2O relative to trace elements of similar compatibility (e.g. Ce, La) that are inferred to have a recycled origin (e.g. Dixon and Clague, 2001; Dixon et al., 2002; Wallace, 2002; Workman et al., 2006; Kendrick et al., 2014a). Furthermore, a high proportion of seawater-derived volatiles (e.g. H_2O, Cl, noble gases) entering subduction zones are lost as slab fluids into the sub-arc mantle, and the extent to which these volatiles can be subducted into the deeper mantle is unclear (Hilton et al., 2002; Ito et al., 1983; Parai and Mukhopadhyay, 2012; Rüpke et al., 2004). The relative abundances of magmatic volatiles and trace elements in OIB melts that sample deeply recycled components can therefore provide a better understanding of global volatile recycling processes (Dixon et al., 2002; Wallace, 2002; Workman et al., 2006), with implications for the relative importance of subducted versus primordial volatile components in the Earth's mantle (cf. Holland and Ballentine, 2006; Mukhopadhyay, 2012; Staudacher and Allègre, 1988).

Samoan OIB are of particular interest for constraining the composition of the EM2 mantle end-member because they record the strongest $^{87}Sr/^{86}Sr$ enrichment of any known mantle component (>0.720; Jackson et al., 2007; 2009). Furthermore, submarine glasses

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86 which are required for measuring the magmas volatile contents have been recovered with

87 $^{87}Sr/^{86}Sr$ up to 0.7125, compared to a maxima of 0.706 in EM2 glasses from the Society

88 seamounts (Fig 1; Devey et al., 1990). The Samoan glasses can be used to place potentially

89 unique constraints on the volatile characteristics of the EM2 end-member, provided the

90 geochemical complexity in melts is sufficiently well understood. Current data indicate that

91 isotopic variation in Samoan melts result from mixing an EM2 component with a primitive

92 component characterised by lower $^{87}Sr/^{86}Sr$ and high $^{3}He/^{4}He$ (e.g. Fig 1; Farley et al., 1992;

93 Jackson et al., 2007). However, additional mantle components could also be present, and a

94 previous study of volatiles (CO_2, H_2O, S, F and Cl) in Samoan lavas was hampered by the

95 unresolved presence of assimilated seawater (Workman et al., 2006).

96 The aim of the current study is to further elucidate the origins of halogens and water

97 in Samoan melts. This is achieved by analysing the scarcest halogens Br and I, in addition to

98 Cl and F, and extending the volatile database to include the most enriched glasses now

99 available (Jackson et al., 2007). The new data are of particular interest because iodine is an

100 essential element for life that has a high abundance in organic-rich marine sediments and has

101 previously been suggested as a possible marker for subducted sedimentary components in the

102 mantle (Deruelle et al. 1992). We have already shown that the enriched mantle reservoirs

103 sampled by the Society and Pitcairn seamounts have MORB-like I/Cl (Kendrick et al., 2012a;

104 2014a); however, we deemed the current study necessary to test if the more strongly enriched

105 Samoan melts with exceptionally high $^{87}Sr/^{86}Sr$ (Fig 1) might be characterised by more

106 elevated I/Cl ratios. In addition, multi-element correlations between F, Cl, Br, I, H_2O and

107 incompatible trace elements such as K enable us to rigorously evaluate possible seawater

108 assimilation processes (Kendrick et al., 2013a). We demonstrate that Samoan melts

109 assimilated variable amounts of high salinity brine(s), and we use a quantitative mixing

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110   model to correct the measured H_2O and Cl abundances for assimilation, thus providing

111   improved constraints on mantle-derived H_2O and Cl in all of the samples investigated.

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2. Samples and methodology

114   The samples selected for the current study include: i) nineteen pristine glasses from

115   Samoan volcanoes in the SW Pacific, including fourteen samples previously characterised by

116   Workman et al. (2006); ii) palagonite separated from a Samoan glass, and iii) two pristine

117   glasses from Baffin Bay, Canada.

118   The Samoan glasses were all dredged from water depths of between 780 and 4400m.

119   The majority of samples were recovered during the 1999 AVON2/3 cruise of *RV Melville*

120   from the Vailulu'u, Malumalu and Ta'u volcanoes at the eastern end of the Samoan chain

121   (Fig 2; Workman et al., 2004; 2006). The Vailulu'u volcano represents the current

122   expression of the Samoan hotspot and U-series and ^{40}Ar-^{39}Ar dating indicate the samples

123   from Vailulu'u, Malumalu and Ta'u have ages of between ~100 yrs and ~0.3 Ma

124   (McDougall, 2010; Hart et al., 2000; Sims et al., 2008; Workman et al., 2006). Additional

125   samples recovered during the AVON2/3 cruise and the 2005 ALIA cruise of *RV Kilo Moana*

126   (Jackson et al., 2007; Koppers et al., 2008; 2011), were selected from the more westerly Muli

127   and Taumatau volcanos for this study. Sample 128-21 recovered from Taumatau, at the

128   western termination of the Samoan chain, has an age of 4.8 Ma (Fig 2; Koppers et al., 2008),

129   and the highest $^{87}Sr/^{86}Sr$ of any glass yet recovered from Samoa (Jackson et al., 2007).

130   The palagonite alteration separated from the surface of ALIA-104-04 glass was

131   analysed to test if significant halogens are incorporated into altered glass and therefore if

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132   undetected alteration of magmatic glasses could significantly influence our results (cf.

133   Kendrick et al., 2012b; 2013a).

134   The Baffin Bay glasses which sample the proto-Icelandic plume, are ~60 Ma and

135   were selected from coastal outcrops, their eruption depths are unknown but pillow textures

136   suggest subaqueous conditions (Jackson et al., 2010; Robillard et al., 1992; Kent et al., 2004).

137   These glasses are related to the picrites that preserve the highest measured terrestrial $^3He/^4He$

138   ratio of ~50 Ra in olivine phenocrysts (Starkey et al., 2009; Stuart et al., 2003). They have

139   primitive Pb isotope signatures and primitive $^3He/^4He$ up to 24 Ra, that are probably lower

140   than the picrites because of their low He concentrations and radiogenic ingrowth of ^4He over

141   the ~60 Ma since eruption (discussion in Jackson et al., 2010). These samples were selected

142   to test if high $^3He/^4He$ glasses from Baffin Bay and Samoa have similar and unique Br/Cl and

143   I/Cl ratios characteristic of high $^3He/^4He$ reservoirs within Earth's mantle (see also Kendrick

144   et al., 2013a).

145   Analyses undertaken for this study include: i) Cl, Br, I and K measurements on all

146   Samoan and Baffin samples conducted using the noble gas method utilising irradiation-

147   produced noble gas proxy isotopes ($^{38}Ar_{Cl}$, $^{80}Kr_{Br}$, $^{128}Xe_I$ and $^{39}Ar_K$; Kendrick, 2012).

148   Pristine glass fragments (0.4-2 mm in size) were hand-picked under a binocular microscope

149   and cleaned using distilled water and acetone. 10-30 mg of each sample was then irradiated

150   in either position 5c of the McMaster nuclear reactor, Canada (irradiation UM#48; 15th

151   December 2011; 42 hours; total neutron fluence of 1.2×10^{19} neutrons cm^{-2}; thermal/fast =

152   2.7); or in the Central Thimble facility of the USGS Triga reactor, Denver, USA (irradiation

153   UM#53; 28th November 2012; 80 hours; total neutron fluence of 6.4×10^{18} neutrons cm^{-2};

154   thermal/fast = 0.8).

Irradiation produced noble gas proxy isotopes were extracted from the samples by heating in an ultra-high vacuum tantalum resistance furnace. Palagonite was analysed in 20 minute heating steps at temperatures of 300 °C and 1500 °C, because up to 50% of the halogen-derived noble gases in palagonite are released at 300 °C. In comparison, noble gases are only released from glasses at >500 °C (Kendrick et al., 2012a) and the glasses were preheated to 300 °C before being fused in single 20 minute heating step at 1500 °C. The extracted gases were purified by standard gettering procedures and analysed with the MAP-215 noble gas mass spectrometer at the University of Melbourne (see Kendrick, 2012 or Kendrick et al., 2013a for details).

Noble gas proxy isotopes were converted to Cl, Br, I, K and Ca abundances on the basis of $^{38}Ar_{Cl}$/Cl, $^{80}Kr_{Br}$/Br, $^{128}Xe_I$/I, $^{39}Ar_K$/K and $^{37}Ar_{Ca}$/Ca production ratios monitored with the Hb3gr ^{40}Ar-^{39}Ar flux monitor (1072 Ma; Roddick, 1983) and three scapolite standards (Kendrick, 2012; Kendrick et al., 2013a). The reported concentrations were cross-checked with electron microprobe Cl, K and Ca determinations undertaken at the University of Melbourne (see Table S1; Kendrick et al., 2014a). Halogen concentration and ratio measurements have internal precision as high as 1-2% (2σ; Table S1). However, standardisation limits 2σ reproducibility between irradiations to the 5% level for Br and 10 % for I (Fig S2), and the external precision is estimated at 10% for all elements (see Kendrick, 2012 and Kendrick et al., 2013a for detailed discussion).

SIMS measurements of H_2O, CO_2, S, F and Cl in three new samples (77-09, 104-04 and 128-21) were undertaken at the Department of Terrestrial Magnetism, Carnegie Institute of Washington, using a Cameca IMS 6F ion microprobe, following procedures comparable to those of Workman et al. (2006). Several glasses from dredges 71, 77, 78, 79, 104 and 128 were analysed by electron microprobe and laser ablation inductively coupled plasma mass

179 spectrometry at the University of Melbourne. The operating conditions of the Cameca SX-50

180 electron microprobe included an accelerating voltage of 15 keV, current of 30 nA and 20 sec

181 counting times, which gave a detection limit of 260 ppm for Cl.   The Agilent 7700x ICP-MS

182 is coupled to a 193 nm excimer laser. The glasses were analysed using a beam diameter of

183 ~80 μm and BHVO2G as the calibration standard: BCR2G, analysed as an unknown, gave

184 reproducible results close to recommended values (Table S1). Typical analytical conditions

185 have been described in detail elsewhere (Woodhead et al., 2007).

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3. Results

188 The new volatile, trace and major element data for Samoan and Baffin glasses are

189 summarised together with representative data from the literature in Table 1 and presented

190 with the standard data in the electronic supplement (Table S1; Fig S2).

> **Commented [MK1]:** Standard data for BCR2G are in Table 1, halogen standards are shown in Fig S2

191 The Samoan glasses represent alkali basalts and trachy-basalts, they contain 45.2 to

192 48.2 wt. % SiO_2, 3.4 to 6.1 wt. % total alkalis ($Na_2O + K_2O$), and 6.5 to 4.0 wt. % MgO. The

193 Baffin glasses are basalts with ~49 wt. % SiO_2, ~2.2 wt. % alkalis ($Na_2O + K_2O$), and ~8.5 wt.

194 % MgO (Table S1; Kent et al., 2004; Workman et al. 2006).

195 The Samoan glasses have 4 to 200 ppm CO_2 but are strongly enriched in incompatible

196 trace elements with 0.6 to 1.7 wt. % K. They have water concentrations of 0.67-1.9 wt. %

197 H_2O, and halogen concentrations of 490-1790 ppm Cl, 1.9-7.2 ppm Br, 19-130 ppb I and

198 900-1900 ppm F (Fig 3; Table 1).   In contrast, the Baffin glasses have much lower

199 concentrations of incompatible trace elements and volatiles with ~0.1 wt. % K, 70-80 ppm

200 Cl, 130-240 ppb Br and 3-6 ppb I (Fig 3; Table 1). The low halogen content of the Baffin

201 glasses is unlikely to be explained by degassing because the Cl concentrations are at the

upper end of the range determined for melt inclusions in related samples (Maisonneuve, 2012) and the glasses have normal K/Cl ratios of 13-20 (Cl/K = 0.05-0.08) that do not suggest Cl loss.

The concentrations of Cl, Br and I vary over more than two orders of magnitude between the Baffin and Samoan samples (Fig 3). The majority of samples have I/Cl within the range of $[60 \pm 30] \times 10^{-6}$ that is typical of OIB and MORB glasses (Fig 3c; see Kendrick et al., 2013a). In contrast, the Samoan samples with the highest Cl concentrations have unusually high Br/Cl ratios of up to 4.3×10^{-3}; these values exceed the range of $[2.8 \pm 0.6] \times 10^{-3}$ (2σ) defined by 55 MORB and OIB glasses from other locations analysed by the same technique (Kendrick et al., 2013a), and 45 glasses analysed in other laboratories (Jambon et al., 1995; Schilling et al., 1980), that are collectively considered typical of the mantle (Fig 3b). The highest K/Cl of 18 (Cl/K = 0.06) determined for the Samoan samples is fairly typical of mantle values defined by a global database of 566 submarine glasses (Fig S3; Michael and Cornell, 1998; Kendrick et al., 2012b), but the samples with the highest Cl concentrations have low K/Cl of 5.7 (Cl/K = 0.17) and the lowest measured F/Cl of 0.5 (Figs 3ad).

The palagonite separated from sample 104-04 has concentrations of 35 ppm Cl, 200 ppb Br, 85 ppb I and 0.09 wt. % K, which indicate that it is depleted in Cl, Br and K by ~7-30 times, and enriched in I by ~5 times, compared to pristine glass from this sample (Table 1). As a result, the palagonite has an I/Cl ratio of 2400×10^{-6} that is 140 times greater than the unaltered glass (Table S1). The high concentration of I in palagonite confirms that the I/Cl ratio of a glass separate could be influenced by the presence of undetected palagonite contaminants, or incipient alteration (Kendrick et al., 2013a); however, it is important to note that minor contamination is unlikely to significantly influence the Br/Cl or K/Cl ratios.

Commented [MK2]: This section makes it clearer than the basis for 'mantle' halogen ratios is 55 MORB and OIB glasses

Consistent with many more from Jambon and Schilling – but thesestudies had different standards.

Commented [MK3]: Thispaper included a compilation of published K/Cl data

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The purity of our glass separates was tested by performing duplicate analyses of glass separated from samples 76-08 and 78-01, that were both strongly affected by palagonite alteration of the rims. Similar results were obtained for 76-08-a and 76-08-b (Tables 1 and S1), confirming efficient removal of contaminating material and demonstrating that the iodine data are reliable for the majority of samples that were more easily prepared as high purity glass separates (Table 1). In contrast, duplicates of 78-01 gave significantly different results for I/Cl, which confirms the sensitivity of this measurement to minor contamination. In this case 78-01-a with an I/Cl ratio of 90×10^{-6} is considered most representative of the melt (Table 1), and the higher I/Cl of 270×10^{-6} obtained for 78-01-b is ascribed to contamination and has been omitted from the figures for clarity (Table 1).

4. Discussion

The H_2O and halogen content of the Samoan glasses is partly controlled by the mantle source; however, before evaluating the volatile systematics of the source we must first determine the extent to which these volatiles have been modified by shallow level processes including fractional crystallisation, degassing and seawater assimilation.

4.1 Magma degassing and assimilation of seawater components

The Samoan glasses have vesicularities of 1 to 30 vol. % and low CO_2 concentrations of 4-230 ppm that provide evidence for degassing (see Fig 4; Table 1; Workman et al., 2006). The combined H_2O and CO_2 data indicate that many of the melts were in equilibrium with a H_2O-rich vapour phase (shown by the isopleths in Fig 4a). However, the glasses are suggested to preserve water concentrations close to their pre-degassing values because: i) very little H_2O is lost during open system degassing (Fig 4a); and ii) the equilibrium vapour phase in samples 68-03 and 73-03 (erupted at the shallowest depths of ~1000 m, with

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250   vesicularities of 5-20 vol. %), is calculated to contain only 0.01-0.05 wt % H_2O, thus

251   demonstrating that the low water content of these samples (0.7 wt. %; Fig 4) cannot be

252   explained by closed system degassing (Workman et al., 2006; this study). Complex multi-

253   stage degassing scenarios are possible; however, we demonstrate below that the majority of

254   Samoan melts were more strongly influenced by H_2O added through assimilation processes

255   than by H_2O lost during degassing.

256   In the absence of significant H_2O degassing, the concentration of H_2O, as well as

257   incompatible trace elements such as K and Cl, are expected to vary in the Samoan melts as a

258   result of partial melting, mixing isotopically distinct components in the mantle source, and

259   subsequent fractional crystallisation (Fig 5). The liquid lines of descent (LLD) in Fig 5 were

260   modelled with Petrolog3 (Danyushevsky and Plechov, 2011) by progressively removing

261   olivine, pyroxene, plagioclase, ilmenite and magnetite, assuming K, Cl and H_2O are all

262   perfectly incompatible (Fig 5). The Samoan volcanoes sample multiple magma batches and

263   the concentrations of K, H_2O and Cl in the mantle end-members are not known. However, it

264   is significant that, in contrast to K and H_2O, Cl does not follow the expected broad trend

265   toward higher concentrations in the more evolved melts (Fig 5). The lack of a relationship

266   between Cl and MgO, together with the low K/Cl of Cl-rich glasses (Fig 2a and 4; K/Cl of

267   <10 or Cl/K of >0.1), could be explained if some of the melts assimilated seawater-derived Cl

268   (e.g. Coombs et al., 2004; Kendrick et al., 2013a; Kent et al., 1999; 2002; le Roux et al.,

269   2006; Michael and Cornell, 1998; Michael and Schilling, 1989).

270   Possible assimilation processes are evaluated in Fig 6 by examining F, Cl, Br, I, H_2O

271   and K co-variation in three element diagrams that use Cl as a common denominator. This

272   method of plotting the data is advantageous for this purpose because mixing trends are

273   revealed as straight lines (Fig 6). The binary mixing trends in Fig 6 are interpreted to result

Commented [MK5]: This caveat is added to address reviewer 1 comments – we have not fitted a curve to the data the LLD are to illustrate melt evolution which applies regardless of batch.

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274 from mixing mantle-derived halogens and halogens introduced by an assimilated brine

275 because:

276   i)   Extrapolation of the data suggests that one end-member has the

277 characteristics of a brine including: 1) low H_2O/Cl that indicates a high

278 salinity; 2) low K/Cl of <0.2 that is required to maintain charge balance in a

279 Cl^- dominated, Na^+, Ca^{++}, Fe^{++}, K^+ brine; and 3) low F/Cl ratio that would

280 result from the low solubility of F in a seawater-derived Ca- (± P-) bearing

281 aqueous solution (Fig 6; Seyfried and Ding, 1995). In contrast, the second

282 end-member has K/Cl, H_2O/Cl, Br/Cl and I/Cl ratios similar to those defined

283 as representative of the mantle in several previous studies of submarine

284 MORB and OIB glasses (Jambon et al., 1995; Schilling et al., 1978, 1980;

285 Michael and Cornell, 1998; Kendrick et al., 2012ab; 2013a; 2014a).

286   ii)   The variations in Br/Cl, K/Cl, F/Cl and H_2O/Cl are not correlated with

287 $^{87}Sr/^{86}Sr$ (or $^3He/^4He$), which is the expected result of assimilating brines

288 with very high concentrations of Cl, and low concentrations of Sr, relative to

289 the melts (Kendrick et al., 2013a). In contrast, correlations between K/Cl

290 and $^{87}Sr/^{86}Sr$, or Br/Cl and $^{87}Sr/^{86}Sr$, might be expected if the variation was

291 intrinsic to the mantle or related to subduction recycling (e.g. Stroncik and

292 Haase, 2004; Kendrick et al., 2012a; 2014a).

293   iii)   Similar mixing trends have been observed in MORB previously and are

294 therefore unrelated to subduction but can be explained by brine assimilation

295 (Kendrick et al., 2013a).

296   iv)   The samples closest to the suggested brine end-member come from the

297 Vailulu'u volcano which is the most hydrothermally active of the Samoan

Commented [MK6]: This section is organised differently, the brine characteristics are listed prominently.

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298   volcanos investigated (Staudigel et al., 2004), and therefore a likely location

299   for magmas to assimilate hydrothermal brines.

300   v)   The lack of a correlation between Cl and MgO provides independent

301   evidence that the melts have assimilated seawater-derived Cl in some form

302   (Fig 5).

Commented [MK7]: This is important supporting evidence assimilation has occurred.

303   The good fit of the mixing model to halogen data for glasses from 5 different

304   volcanoes that erupted from ~100 yrs to 5 Ma is extremely significant (Fig 6). It suggests

305   that over the last 5 Ma, all the Samoan volcanoes have had sources characterised by similar

306   Br/Cl, I/Cl, F/Cl, H_2O/Cl and K/Cl ratios and that the magmas have been affected by

307   remarkably uniform assimilation processes (section 4.1.1).   This observation is consistent

308   with the uniformly high salinity of brines (55 ± 15 wt. % salts) assimilated by magmas

309   exhibiting anomalously high Cl concentrations at other mid-ocean ridge and oceanic island

310   settings investigated for Cl assimilation processes (see Fig 8 of Kendrick et al., 2013a; data of

311   Coombs et al., 2004; Kent et al., 1999; 2002; le Roux et al., 2006; Wanless et al., 2011). As a

312   point of comparison, assimilation of Cl at both Samoan and Hawaiin volcanoes appears to be

313   related to location (Dixon and Clague, 2001), and in contrast to some previous studies, there

314   is no evidence that the most evolved melts have assimilated the highest proportion of Cl (Fig

315   5; cf. Wanless et al., 2011).

316

317   *4.1.1 Brine characteristics and origin*

318   Hydrothermal vent fluids typically have K/Cl of <0.05 and F/Cl of <0.0001 that are

319   close to the seawater values of 0.02 and 0.00007, respectively (Li and Schoonmaker, 2003;

Commented [MK8]: Data for vents are summarised

320   Mottl et al., 2011). As already mentioned, a low K/Cl ratio is required to maintain charge

321   balance in a seawater-derived Na-Ca brine (Vanko, 1988), and a low F/Cl ratio is expected

because of fluorine's uptake by minerals and low solubility in aqueous fluids (e.g. Frohlich et al., 1983; Seyfried and Ding, 1995). The salinity of vent fluids is variable, and typically in the range 1-8 wt. % salts (Oosting and von Damm, 1996; Fontaine et al., 2007), but much higher salinity fluids with up to 60 wt. % salt are preserved in fluid inclusions from deeper greenschist-amphibolite facies environments in the oceanic crust (Vanko, 1986; 1988; Kelley et al., 1993). Therefore, the uniformly high salinity of the brines (55 ± 15 wt % salt) assimilated by magmas from several different Samoan volcanoes (Fig 6), and other seafloor locations (see Kendrick et al., 2013a data of Wanless et al. 2011, Coombs et al., 2004; Kent et al, 1999; 2002; Le Roux et al., 2006), suggests that: i) assimilation may be restricted to high salinity brines by the relative solubilities of Cl and H_2O in silicate melts; and ii) assimilation is more likely to occur at depths of >2-3 km in the crust rather than on the seafloor (see also Coombs et al., 2004; Kendrick et al., 2013a; le Roux et al., 2006).

The Br/Cl and I/Cl ratios of the melts do not fit the binary mixing model in Fig 6 as well as the K/Cl, F/Cl and H_2O/Cl ratios. This is not explained by analytical uncertainty which is at the 2-8 % level (2σ) for both Br/Cl and I/Cl (Table S1). Palagonite contamination (or incipient alteration of the glasses) has the potential to influence the glasses' I/Cl ratios; however, the low concentrations of Cl and Br in palagonite indicate that its presence would have a negligible effect on Br/Cl ratios (section 3; Table 1). Therefore we suggest that the quality of fit for both Br/Cl and I/Cl in our mixing model (Fig 6) is influenced by variation of these ratios in the assimilated brines. This is possible because whereas K/Cl, F/Cl and H_2O/Cl are all fixed by requirements of solubility and charge balance, Br and I are highly soluble trace constituents. As a result the Br/Cl and I/Cl ratios of brines behave as essentially free variables. The mixing model indicates that, on average, the Samoan melts assimilated brines with Br/Cl of ~0.005, that were about 40 % higher than seawater, and I/Cl ratios that were on average about ten times seawater (Fig 6c,d and e).

A previous study of magmatic glasses demonstrated that, as in Samoa, brines assimilated by melts from the Galapagos Spreading Centre and the NW part of the Lau Basin had Br/Cl ratios 10's of percent higher than seawater (Kendrick et al., 2013a). However, in contrast to Samoa, these glasses preserved I/Cl ratios closer to the seawater value (Kendrick et al., 2013a). The data available for vent fluids demonstrate that fluid interaction with I-rich organic matter present in marine sediments elevates the I/Cl ratios, and to a lesser extent Br/Cl ratios, of some vent fluids above seawater values (Campbell and Edmund, 1989; You et al., 1994; Kawagucci et al., 2011). The majority of vent fluids preserve seawater-like Br/Cl (e.g. von Damm et al., 1997; Seyfried et al., 2003); however, lower than seawater Br/Cl ratios are known from condensed vapour phases (~1 wt % salt) emitted at 9-10° N on the East Pacific Rise (Oosting and von Damm, 1996).

It is concluded that the elevated I/Cl ratios inferred for the Samoan brines are consistent with a fluid history involving interaction with sediments. A number of processes may have contributed to the elevated Br/Cl ratios of the brines including fluid interaction with sediments, and partitioning of $H_2O{>}Cl{>}Br$ into hydrous alteration minerals such as amphibole (Fig 6; Kendrick et al., 2013a). It remains unclear if high salinity brines formed by phase separation under specific conditions might also be enriched in Br/Cl relative to the vapour phase (Oosting and von Damm, 1996; Berndt and Seyfried, 1997; von Damm et al., 1997; Liebscher et al., 2006; Foustoukos and Seyfried, 2007). However, sub-critical seawater would boil when heated to magmatic temperatures during assimilation, with the likely result that vapour phases would be preferentially vented on the seafloor, and the dense residual brines would be preferentially assimilated by the magma (Fig 6; Kendrick et al., 2013a) and/or retained in the lower crust (e.g. Bischoff and Rosenbauer, 1989).

If brine assimilation occurred at depths of >2 km beneath the seafloor as suggested, then the preservation of the mixing trends in Fig 6 is consistent with the suggestion that very

15

372   little H_2O was lost during degassing of CO_2 from these melts (Fig 4a; Table 1). Sample 128-

373   21 with only 4 ppm CO_2 (Fig 4a), lies on the mixing lines in Figs 6b and 6d, suggesting

374   minimal H_2O loss occurred (Fig 4a). The Vailulu'u samples show scatter in H_2O/Cl;

375   however, the samples recovered from ~1000 m in dredges 70 and 73 (Table 1) include both

376   the lowest and highest H_2O/Cl ratios, suggesting the scatter is unrelated to degassing (Fig 6a).

377   The preservation of the mixing trends also suggests ratios of incompatible elements (e.g.

378   Br/Cl, I/Cl, F/Cl, H_2O/Cl) were not significantly altered by fractional crystallisation of the

379   Samoan magmas after assimilation (Fig 6).

380

381   *4.2 Samoan mantle source characteristics*

382   The mixing model in Fig 6 enables the amount of H_2O and Cl introduced into the

383   Samoan magmas by brine assimilation to be quantified. The calculations can be undertaken

384   using any ratio that differs between the mantle and brine and 10% increments of the total Cl

385   are shown on each of the mixing lines in Fig 6 with the associated uncertainties summarised

386   for individual samples in Table 1. The Br/Cl data are important because this ratio exhibits

387   limited variation in the mantle (0.0028 ± 0.0006 (2σ); Kendrick et al., 2013a; 2014a),

388   suggesting the least contaminated Samoan samples with Br/Cl of 0.0029 lie close to the

389   mantle end-member (Fig 6). In comparison, the Br/Cl of the brine obtained from the

390   regression of data in Fig 6c (0.0046 ± 0.004; 2σ), is about twice the mantle value. In contrast,

391   hydrothermal fluids have F/Cl of <<0.01 (Seyfried and Ding, 1995; Li and Schoonmaker,

392   2003), which is many times lower than the maximum F/Cl of 2.3 measured in a Samoan

393   glass (Fig 6a). As a result, mixing calculations based the F/Cl ratio, using conservative

394   estimates for the brine (0.01000 ± 0.00999) and mantle (2.4 ± 0.5) end-members (Fig 6a),

395 give results that are more precise but indistinguishable from similar calculations undertaken

396 with the Br/Cl data (cf. samples 76-08-a and 76-08-b in Table 1).

397 The mixing calculations indicate that sample 75-10 with the highest measured F/Cl

398 ratio assimilated between zero and 26% of its total Cl, and the other T'au samples from

399 dredges 74 and 75 probably also assimilated very little Cl (Table 1). In comparison, samples

400 68-03, 71-02, 71-11, 71-13, 71-22 and 76-11 are estimated to have assimilated about 70% of

401 their total Cl (Table 1). The quantitative mixing model developed here indicates that water

402 assimilation is more significant than was previously recognised on a qualitative basis (cf.

403 Workman et al., 2006). However, the proportion of the H_2O assimilated by the T'au magmas

404 is close to zero and probably accounts for a maximum of 20-30 % of the total H_2O in samples

405 68-03 and 73-03 (Table 1). In absolute terms, the T'au melts are estimated to have

406 assimilated up to a few hundred parts per million of brine and sample 71-02 is estimated to

407 have assimilated 0.45 ± 13 wt. % brine (Table 1). Based on reasonable estimates for the

408 densities of brine (1.3-1.4 g cm^3) and melt (2.6-2.7 g cm^3), this is equivalent to a maximum of

409 8 or 9 cm^3 of brine being assimilated by a litre of magma (Fig 6; Table 1).

410 The assimilation-corrected H_2O/Ce and Cl/K ratios of Samoan melts are plotted

411 together with the measured F/Nd ratio, which is not influenced by brine assimilation, as a

412 function of $^{87}Sr/^{86}Sr$ in Fig 7. Note that each ratio represents an element pair of similar

413 compatibility, and that Cl/K is used in preference to K/Cl to enable comparison of

414 volatile/lithophile pairs expressed in the same format (whereas K/Cl provides a common

415 denominator in Fig 6). The MORB mantle has H_2O/Ce of 150-300 (e.g. Michael, 1995) and

416 F/Nd of 20 ± 6 (Workman et al., 2006), but as a result of unresolved seawater assimilation, its

417 Cl/K is less well defined (Michael and Cornell, 1998): we adopt a Cl/K of 0.05-0.1 that

418 encompasses the median value of previous MORB analyses (0.08 ± 0.01), but it should be

419 noted that MORB can have much lower Cl/K values (see Fig S3).

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420   The assimilation-correction reduces the measured H_2O/Ce ratio by 0-30 %, which has

421   a minor impact on the interpretation of the H_2O data (Fig 7a; Table 1; Workman et al., 2006).

422   In contrast, the assimilation correction has a profound effect on the Cl/K data reducing

423   measured Cl/K ratios from maxima of 0.17-0.18 to assimilation-corrected values of ~0.05

424   (Figs 7b; Table 1). The mean assimilation-corrected Cl/K of 0.05 ± 0.02 (2σ) is controlled by

425   the binary mixing model used to correct the data (Fig 6), and the scatter of the data around

426   the mean corrected Cl/K value therefore reflects the fit quality of the model (Fig 6).   The

427   modelling indicates that most of the variation in Cl/K (or K/Cl) measured in Samoan glasses

428   results from brine assimilation (Fig 6); however, the fit quality means that minor systematic

429   variation in the Cl/K of the Samoan source is not precluded (Fig 7b).

430   In general, the model indicates the Samoan source has lower H_2O/Ce and Cl/K than

431   median MORB, but F/Nd at the high end of the MORB range (Fig 7).   Therefore, despite

432   their overall trace element and volatile enrichment, the Samoan, Society and Pitcairn EM

433   magmas are all depleted in H_2O and Cl, but not F, compared to median MORB and lithophile

434   elements of similar compatibility (Kendrick et al., 2014a).   A relative depletion of Cl as well

435   as H_2O may therefore be a characteristic of EM reservoirs (Fig 7; Dixon et al., 2002, Wallace,

436   2002; Stroncik and Haase, 2004; Kendrick et al., 2014a).   However, pooling the data from

437   Society, Pitcairn and Samoa which extends to the highest [87]Sr/[86]Sr (Fig 1), suggests that the

438   H_2O/Ce and Cl/K ratios are not strongly correlated with [87]Sr/[86]Sr (Fig 7; cf. Workman et al.,

439   2006), and/or that part of the Samoan source probably has higher H_2O/Ce and Cl/K at any

440   given [87]Sr/[86]Sr than either the Pitcairn or Society sources (Fig 7).

441   Finally, the five Samoan glasses least affected by brine assimilation (samples 74-02;

442   75-02; 75-10; 77-09 and 128-21) include sample 128-21 with the highest [87]Sr/[86]Sr of 0.7125,

443   and sample 75-02 with a [3]He/[4]He of 15 R/Ra (Table 1) that represent the EM2 and primitive

444   components of the Samoan plume, respectively (Fig 1; Jackson et al., 2007).   The Br/Cl and

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I/Cl ratios of these samples are similar to the Baffin Bay sample with ^{3}He/^{4}He of 24 R/Ra (Table 1) and other MORB and OIB samples, suggesting that all these mantle reservoirs have Br/Cl and I/Cl ratios similar to the MORB range (Fig 8; Kendrick et al., 2013a; 2014a). This conclusion is further supported by the mixing systematics of Br/Cl and I/Cl in glasses with ^{3}He/^{4}He of 16-28 Ra from the NW part of the Lau Basin (Kendrick et al., 2013a).

4.3 Implications for the global volatile cycling

> **Commented [MK9]:** This section has been simplified and is more circumspect

The apparent uniformity of Br/Cl and I/Cl in the Earth's mantle (Fig 8; I/Cl = 0.00006 ± 0.00003) reflects the similar compatibilities of these elements in the mantle (e.g. Schilling et al., 1980; Balcone-Boissard et al., 2010; Kendrick et al., 2012b), and is in stark contrast to the behaviour of these elements in Earth's surface reservoirs and subduction zones. The Br/Cl ratio varies by more than an order of magnitude in the surface reservoir and I/Cl is even more variable (e.g. Holser, 1979; Muramatsu and Wedepohl, 1998; Kendrick et al., 2013b). Seawater has an I/Cl ratio of 0.000003 that is ~10,000 times lower than the maximum values of ~0.03 found in some organic-rich marine sediments, sedimentary marine pore fluids and serpentinites (Kendrick et al., 2013b; John et al., 2011; Muramatsu and Wedepohl, 1998; Muramatsu et al., 2001; Snyder et al., 2005).

The uniformly low I/Cl of the mantle (0.00006 ± 0.00003) compared to the maximum of ~0.03 in sedimentary rocks and serpentinites, could be simply explained if halogens are not significantly recycled into the mantle, and halogens have a dominantly primordial origin in the mantle (Schilling et al., 1978). However, it is increasingly recognised that a significant portion of the volatiles entering subduction zones could be deeply subducted into the mantle (e.g. Jacobsen and van der Lee, 2006; Walter et al., 2011). Furthermore, the non-radiogenic noble gas isotopes in the mantle are now believed to have a dominantly subducted atmospheric origin (cf. Porcelli and Wasserburg, 1995; Sarda et al., 1999; Sarda 2004;

19

469 Trieloff et a., 2000; Holland and Ballentine, 2006), implying that subduction of other

470 seawater-derived volatiles is likely.

471   Estimated rates of Cl subduction in sediments, altered ocean crust and serpentinites

472 are more poorly defined than Cl outputs through volcanism and it is unclear from the existing

473 data if there is a net flow of Cl into the mantle, or a net flow of Cl out of the mantle, at the

474 present day (cf. Table 2; Schilling et al., 1978; Ito et al., 1983; Sharp and Barnes, 2004; Sano

475 et al., 2008; Barnes and Cisneros, 2012). The scenario in Table 2 demonstrates that contrary

476 to early assumptions, net subduction of Cl is possible, if Cl and other volatiles are

477 inefficiently lost through magmatic arcs. In this scenario, we envisage that deeply subducted

478 Cl would be stored in cold deep reservoirs within the slab, such as serpentinites, that can be

479 subducted beyond magmatic arcs (Schmidt and Poli, 1998; Green II et al., 2010). The

480 subducted Cl would then be incrementally lost into mantle reservoirs beyond the arc, with

481 perhaps ~1-10 % of the initial Cl concentrated with other trace elements in the EM source

482 (Kendrick et al. 2014b). This figure is comparable to the proportion of subducted H_2O

483 estimated to reach the EM source (Dixon et al., 2002). Higher efficiencies of Cl loss through

484 the arc are of course possible, if balanced by significant reductions in the input flux, or

485 increases in the arc magma Cl flux (cf. Table 2). However, the net flow of Cl is more likely

486 to have been into the mantle, in the past, if primordial heavy halogens (like noble gases), had

487 very low abundances as a result of catastrophic outgassing early in Earth's history (Tolstikhin

488 et al., 2014), or if volatiles were introduced to Earth in a late veneer post-dating accretion of

489 the mantle (Wänke, 1981; Deruelle et al., 1992; Javoy, 1997; Bonifacie et al., 2008; Holland

490 et al., 2009).

491   The relative uniformity of mantle Br/Cl and I/Cl (Fig 8) can be reconciled with

492 significant Cl subduction in the following ways: one possibility is that the subduction of Cl in

493 sedimentary rocks and serpentinites with high I/Cl is balanced by subduction of altered ocean

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crust, which has an unknown halogen signature but could include much lower I/Cl. Alternatively, if the altered ocean crust has Br/Cl and I/Cl overlapping the MORB range subduction of altered ocean crust could dominate the Cl subduction budget (cf. Table 2; Kendrick et al., 2014b). A second possibility is that halogens present in sediments and serpentinites with initially high I/Cl might be fractionated during subduction such that I is preferentially lost in fluids, and the minerals, fluid inclusions and grain boundaries hosting halogens in deeper slab environments acquire MORB-like Br/Cl and I/Cl ratios (cf. Kendrick et al., 2011). A combination of these processes seems plausible because studies of eclogite facies serpentinites have shown that Cl is preferentially subducted to greater depths than Br or I (Kendrick, et al., 2011; John et al., 2011). Furthermore, halogens in subduction related fluids have I/Cl ratios that decrease across the arc from maximum values of ~0.01 in the forearc, to ~0.001 in the arc and to lower MORB-like ratios of <0.0001 in some backarc basins (Kendrick et al., 2013b; 2014b). The alternative possibility that halogens were not subducted into the sources of the investigated back arc basin basalts (BABB) with MORB-like Br/Cl and I/Cl, is not favoured by the elevated Cl/K and H_2O/Ce ratios of these BABB, that demonstrate up to 90 % of their total Cl is related to subduction (Kendrick et al., 2014b).

Commented [MK10]: Eclogite facies rocks are mentioned

5. Summary and conclusions

Submarine glasses from Samoa contain halogens derived from the mantle and introduced by assimilation of high salinity brines (e.g. 55 ± 15 wt % salts), with F/Cl of close to seawater, Br/Cl of ~0.005 that is ~40% higher than seawater, and I/Cl of ten times the seawater value. Quantitative corrections for brine assimilation show 0-70 % of the total Cl and 0-30 % of the total H_2O in the Samoan melts investigated was introduced by brines accounting for up to 0.45 % of the melt mass. The preservation of the mixing trends in melts that have

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experienced some degassing favours the dominance of open system degassing with minimal H$_2$O loss.

Assimilation-corrected data confirm that, despite an overall volatile enrichment, the Samoan EM2 end-member with Cl/K of 0.05 ± 0.02 (2σ) and H$_2$O/Ce of 83 ± 3 is modestly depleted in Cl relative to K as well as H$_2$O relative to Ce, compared to median MORB. Furthermore, the samples least affected by brine assimilation, with ^{87}Sr/^{86}Sr of 0.7045-0.7125, have indistinguishable Br/Cl and I/Cl, within the MORB range that is currently estimated as $(2.8 ± 0.6) \times 10^{-3}$ for Br/Cl and $(60 ± 30) \times 10^{-6}$ for I/Cl (2σ; Kendrick et al., 2013a). The uniformity of mantle Br/Cl and I/Cl can be explained if the subduction zone 'filter' controls the relative abundances of Cl, Br and I in deeply subducted slabs and recycled halogens have been circulated throughout the entire mantle. Differences in the Cl/K and H$_2$O/Ce of different mantle components then reflect the efficiency and timing of slab dehydration.

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Acknowledgements

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Table 1. Summary of measured and assimilation-corrected volatile data for Samoan and Baffin samples

Volcano/Location	*Vailulu'u*								*Ta'u*			*Malumalu*
Sample number	68-03	70-01	71-02	71-11	71-13	71-22	73-03	73-12	74-02	75-02	75-10	76-03
Depth (bars)	100-60	150-70	440-400	440-400	440-400	440-400	100-80	100-80	250-190	270-190	270-190	280-200
Selected volatiles[1]												
CO_2 ppm	*23*	*7*	*179*	*150*	*150*	*200*	*13*	*12*	*46*	*21*	*35*	*52*
H_2O wt %	*0.67*	*1.0*	*1.2*	*1.3*	*1.1*	*1.2*	*0.71*	*0.81*	*1.4*	*1.5*	*1.2*	*1.3*
F ppm	*930*	*920*	*900*	*920*	*880*	*1030*	*1000*	*980*	*1870*	*1370*	*1230*	*1180*
Cl ppm	1570	1010	1790	1610	1520	1530	1600	1360	870	720	650	1610
Br ppb	6290	3830	7230	5480	6510	6580	6600	5420	2480	2120	1890	5630
I ppb	59	47	82	56	74	71	75	59	41	46	40	72
Selected major and trace elements												
MgO wt %	*6.0*	*6.3*	6.5	*6.2*	*6.2*	*5.5*	*5.9*	*6.0*	*4.0*	*4.9*	*5.2*	*5.5*
K wt %	0.98	0.81	1.06	0.99	0.97	0.84	1.30	1.07	1.37	1.13	1.07	1.56
Ce ppm	*91*	*72*	*96*	*88*	*86*	*90*	*97*	*109*	*161*	*112*	*110*	*123*
Assimilation-correction model (2σ uncertainties)[2]												
F/Cl *s	0.61 ± 0.7	1.0 ± 0.1	0.60 ± 0.07	0.61 ± 0.07	0.64 ± 0.07	0.61 ± 0.07	0.91 ± 0.10	0.89 ± 0.10	1.9 ± 0.2	1.9 ± 0.2	2.3 ± 0.3	1.1 ± 0.1
Br/Cl ×10⁻³												
Cl_{assim} ppm	1170 ± 90	590 ± 100	1350 ± 110	1210 ± 100	1120 ± 100	1150 ± 90	1000 ± 140	860 ± 120	180 ± 160	160 ± 130	20 ± 150	870 ± 180
Cl_{mantle} ppm	390 ± 90	420 ± 100	450 ± 110	400 ± 100	400 ± 100	380 ± 90	600 ± 140	500 ± 120	690 ± 160	560 ± 130	630 ± 150	740 ± 180
H_2O_{assim} wt. %	0.17 ± 0.08	0.09 ± 0.04	0.20 ± 0.09	0.18 ± 0.08	0.17 ± 0.08	0.17 ± 0.07	0.15 ± 0.07	0.13 ± 0.06	0.03 ± 0.03	0.02 ± 0.02	0.00 ± 0.02	0.13 ± 0.06
H_2O_{mantle} wt. %	0.50 ± 0.08	0.91 ± 0.04	0.98 ± 0.09	1.12 ± 0.08	0.93 ± 0.08	1.03 ± 0.08	0.56 ± 0.07	0.68 ± 0.06	1.37 ± 0.03	1.48 ± 0.02	1.20 ± 0.02	1.17 ± 0.06
Brine wt. %	0.39 ± 0.11	0.19 ± 0.06	0.45 ± 0.13	0.40 ± 0.11	0.37 ± 0.11	0.38 ± 0.11	0.33 ± 0.10	0.28 ± 0.09	0.06 ± 0.06	0.05 ± 0.05	0.01 ± 0.05	0.29 ± 0.10
% assim. Cl	75 ± 6	59 ± 10	75 ± 6	75 ± 6	74 ± 6	75 ± 6	62 ± 9	63 ± 9	21 ± 19	22 ± 18	3 ± 23	54 ± 11
% assim H_2O	26 ± 11	9 ± 4	17 ± 7	14 ± 6	15 ± 7	14 ± 6	21 ± 9	16 ± 7	2 ± 2	2 ± 1	0 ± 2	10 ± 5
$Cl/K_{measured}$	0.16	0.12	0.17	0.16	0.16	0.18	0.12	0.13	0.06	0.06	0.06	0.10
$Cl/K_{corrected}$	0.04 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	0.06 ± 0.01	0.05 ± 0.01
$H_2O/Ce_{measured}$	74	139	123	148	128	133	73	74	87	134	109	106
$H_2O/Ce_{corrected}$	55 ± 8	127 ± 6	102 ± 9	127 ± 9	109 ± 9	114 ± 8	58 ± 7	63 ± 5	85 ± 2	132 ± 2	109 ± 2	95 ± 5
Selected isotopes[1]												
⁸⁷Sr/⁸⁶Sr	*0.70540*	*0.70537*	*0.70594*	*0.70539*		*0.70547*	*0.70562*	*0.70665*		*0.70452*	*0.70453*	*0.70641*
³He/⁴He (R/Ra)	*10.0*		*9.5*	*9.9*		*9.6*				*15.1*		

1 – CO_2, H_2O and F data by SIMS, Cl, Br and I data by the noble gas method (see Table S1 for the full dataset). Legacy data are shown in bold italics are from Workman et al. (2004; 2006); Jackson et al.(2007; 2010); Kent et al. (2004); the ³He/⁴He ratios measured by crushing are reported as R/Ra where Ra is the atmospheric ³He/⁴He value of 1.39×10⁻⁶.

2 - The model parameters are derived from the measured H_2O, F, Cl and Br together with the following formula:
% assim Cl = $(X/Cl_{meas}-X/Cl_{mantle})/(X/Cl_{brine}-X/Cl_{mantle})×100$, where X = Br or F; Br/Cl_{Mantle} = (2.8 ± 0.6)×10⁻³ (Kendrick et al., 2013a); Br/Cl_{brine} = (4.6 ± 0.4)×10⁻³(Fig 6c); F/Cl_{Mantle} = 2.4 ± 0.5; and F/Cl_{brine} = 0.01 ± 0.00999. H_2O_{assim} = Cl_{assim}/brine salinity/0.55, where brine salinity = 55 ± 15 wt. % salts and salts have seawater composition with 55 wt. % Cl.

Table 1. Continued

Volcano/Location	Malumalu						Muli			Taumatau	Baffin Bay	
Sample number	76-08-a	76-08-b	76-11	77-09	78-01-a	78-01-b	79-04	104-04 glass	104-04 palagonite	128-21	100-24	100-21
Depth (bars)	280-200	280-200	280-200	360-290	230-220	230-220	350-280	250	250	260	Submarine	Submarine
Selected volatiles[1]												
CO_2 ppm	*37*	*As for a*	*59*	108	nd	nd	nd	77	nd	4	nd	nd
H_2O wt %	*1.2*	*As for a*	*1.2*	1.9	nd	nd	nd	1.7	nd	1.2	nd	nd
F ppm	*1240*	*As for a*	*1230*	1600	nd	nd	nd	1030	nd	1270	nd	nd
Cl ppm	1370	1420	1620	1070	960	490	1060	1090	35	1050	79	67
Br ppb	4890	5200	6220	3550	3470	1920	2010	3810	200	3000	240	130
I ppb	69	62	67	70	83	133	29	19	85	93	6	3
Selected major and trace elements												
MgO wt %	*5.6*	*As for a*	*4.9*	5.0	4.7	As for a	4.2	6.2	nd	6.0	*8.4*	*8.6*
K wt %	1.34	1.39	1.40	1.49	1.73	0.92	1.61	0.62	0.09	1.60	0.10	0.14
Ce ppm	*116*	*As for a*	*120*	144	186	As for a	324	91	nd	135	*13*	*12*
Assimilation-correction model (2σ uncertainties)[2]												
F/Cl	0.89 ± 0.10		0.76 ± 0.08	1.7 ± 0.2				0.99 ± 0.11		1.5 ± 0.2		
Br/Cl×10^{-3}		3.7 ± 0.1			3.6 ± 0.1	3.9 ± 0.3	1.90 ± 0.05				2.99 ± 0.05	1.92 ± 0.04
Cl_{assim} ppm	870 ± 120	690 ± 440	1110 ± 120	320 ± 180	440 ± 300	300 ± 160		640 ± 110		380 ± 160	8 ± 30	
Cl_{mantle} ppm	500 ± 120	730 ± 440	510 ± 120	750 ± 180	510 ± 300	190 ± 160		450 ± 110		670 ± 160	70 ± 30	
H_2O_{assim} wt. %	0.13 ± 0.06	0.10 ± 0.08	0.17 ± 0.07	0.05 ± 0.03	0.07 ± 0.05	0.04 ± 0.03		0.10 ± 0.04		0.06 ± 0.03	<0.01	
H_2O_{mantle} wt. %	1.07 ± 0.06	1.10 ± 0.08	1.03 ± 0.07	1.85 ± 0.03				1.60 ± 0.04		1.14 ± 0.03		
Brine wt. %	0.29 ± 0.09	0.23 ± 0.16	0.37 ± 0.11	0.11 ± 0.07	0.15 ± 0.11	0.10 ± 0.06		0.21 ± 0.07		0.13 ± 0.06	0.00 ± 0.00	
% assim. Cl	63 ± 9	48 ± 31	69 ± 7	30 ± 17	46 ± 32	61 ± 32		59 ± 10		36 ± 15		
% assim H_2O	11 ± 5	9 ± 7	14 ± 6	3 ± 2				6 ± 3		5 ± 3		
$Cl/K_{measured}$	0.10	0.10	0.12	0.07	0.06	0.05		0.17		0.07	0.08	
$Cl/K_{corrected}$	0.04 ± 0.01	0.05 ± 0.03	0.04 ± 0.01	0.05 ± 0.01	0.03 ± 0.02	0.02 ± 0.02		0.07 ± 0.02		0.04 ± 0.01	0.07 ± 0.03	
$H_2O/Ce_{measured}$	103	103	100	132				186		89		
$H_2O/Ce_{corrected}$	92 ± 5	95 ± 7	86 ± 6	129 ± 2				176 ± 5		83 ± 3		
Selected isotopes[1]												
$^{87}Sr/^{86}Sr$	*0.70637*	*As for a*	*0.70720*	*0.70726*	*0.70890*	*As for a*	*0.70490*	*0.70483*		*0.71250*	*0.70322*	*0.70381*
$^3He/^4He$ (R/Ra)				*10.6*	*8.1*	*As for a*		*15.3*			*23.8*	*9.0*

Table 2. A possible Cl budget favouring net Cl subduction

	Thickness km	Rock 10^9 kg a^{-1}	Cl [2]ppm	Cl 10^9 kg a^{-1}
Input[1]				
Sediments	0.5	4	600	2
Altered Ocean Crust (AOC)	6	52	150	8
Serpentinite (20 %)	3	4	1200	5
40 % lost during arc magmatism*, supply to arcs (R)[3] =				*6*
Net input to deeper mantle =				***9***
Output				
Mid-ocean ridge (MORB)	~6	48	100	5
Oceanic Island (OIB)	-	4	300	1
Volcanic Arc (M + R)[3]	-	6	1200	7
Output from mantle through arc (M) =				*1*
Net output from mantle =				**7**

Notes: 1) AOC (kg) = MORB + OIB (kg); (cf. Schilling et al., 1978; Ito et al., 1983); serpentinites and sediments (kg) are scaled to AOC based on relative thicknesses; 2) Cl concentrations assume AOC>MORB; Ito et al. 1983; Sharp and Barnes, 2004; Bonifacie et al., 2008; Sano et al., 2008; Barnes and Cisneros, 2012; Kendrick et al., 2013b; 3) Recycled (R) output through volcanic arc is related to input and Cl loss efficiency.

Fig 1. Kendrick et al. (2014)
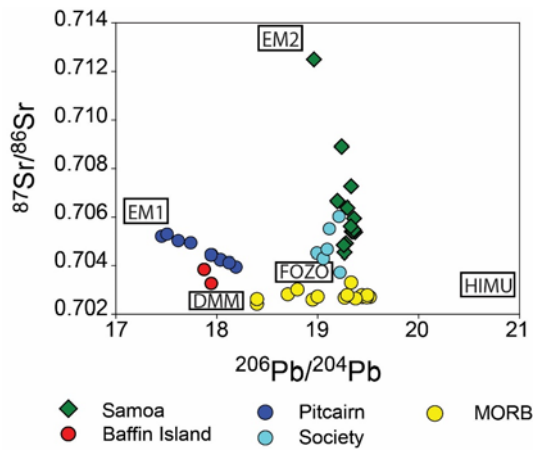
Fig 1. $^{87}Sr/^{86}Sr$ versus $^{206}Pb/^{204}Pb$ data for the Samoan and Baffin glasses used in this study and glasses used in previous halogen studies (Kendrick et al., 2012ab; 2013a, 2014a).   The mantle components are: EM1= enriched mantle 1; EM2 = enriched mantle 2; Himu = high U/Pb; Fozo = focus zone; and DMM = depleted MORB mantle (e.g. Hofmann, 2003). Helium data are shown in Fig S1.
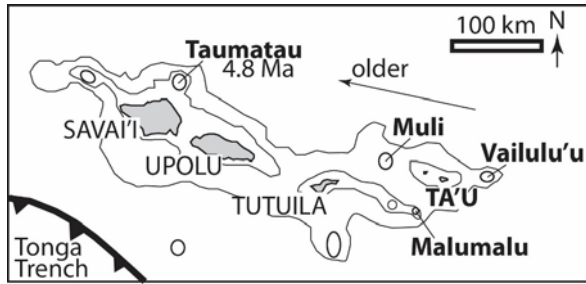
Fig 2. Kendrick et al. (2014)

Fig 2. Sketch locality map of the Samoan Islands showing the volcanoes from which submarine glasses were selected for this study in bold. Emergent Islands are shaded grey and have uppercase labels, whereas seamounts have lower case labels. Vailulu'u is the youngest volcano in the Samoan chain, ages increase westward to a maximum of 4.8 Ma for sample 128-21 dredged from Taumatau (Koppers et al., 2008).

Fig 3 (Kendrick et al., 2014)
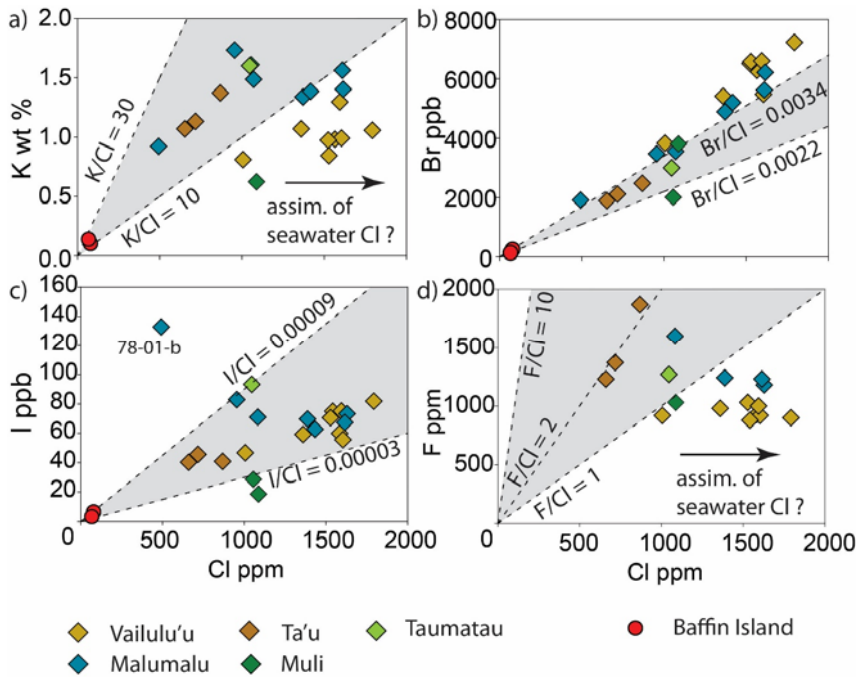
Fig 3. K and halogen concentration plots: a) K versus Cl; b) Br versus Cl; c) I versus Cl; and d) F versus Cl. Note that slopes of K/Cl, Br/Cl and I/Cl given for reference encompass values typical of the mantle (shaded areas; see Kendrick et al., 2012b; 2013a). The mantle range of F/Cl is not well known but it extends up to at least 7 (e.g. Le Roux et al., 2006).

Fig 4. Kendrick et al. (2014)
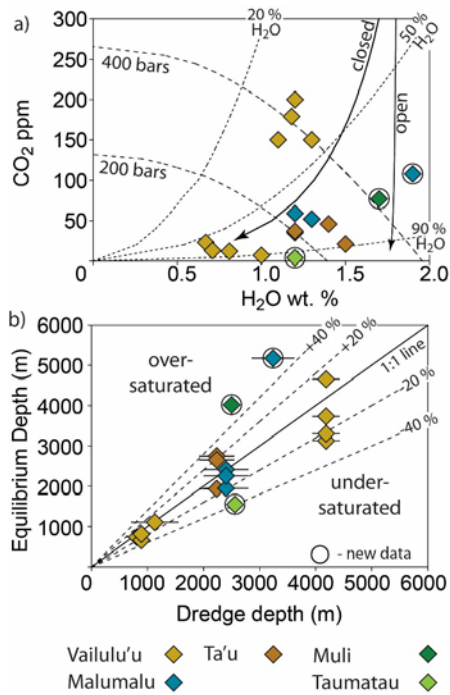
Fig 4. The volatile content of Samoan glasses: a) H₂O wt % versus CO₂ ppm; and b) dredge depth versus equilibration depth in metres (1 bar = 10 metres) calculated using the VolatileCalc solubility model (Newman and Lowenstern, 2002). The isobars (200 and 400 bars), isopleths of vapours comprising 20, 50 and 90 mol % H₂O and examples of open and closed system degassing paths were calculated for a basalt melt with 48wt % SiO₂ at 1200 °C. The sample equilibration depths are based on the measured H₂O, CO₂, SiO₂ and a temperature of 1200 °C. Most of the data are from Workman et al. (2006) with the new data for samples 77-09, 104-04 and 128-21 identified by circles.
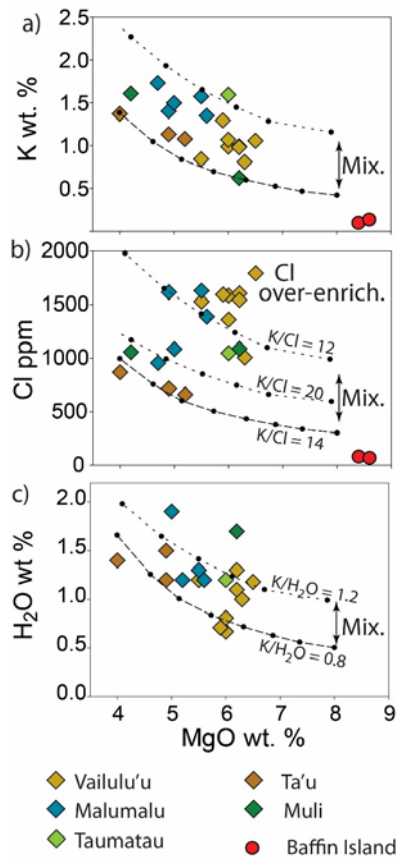
Fig 5. K, Cl and H₂O versus MgO concentration plots: a) K versus MgO; b) Cl versus MgO, and c) H₂O versus MgO. Liquid lines of descent showing the progress of fractional crystallisation in 10% increments are shown for variably enriched melts (dotted and dashed lines). The initial K concentrations were chosen so that the LLD bracket the data; the initial Cl and H₂O concentrations then depend on the K/Cl and K/H₂O ratios of the melts given in b and c.
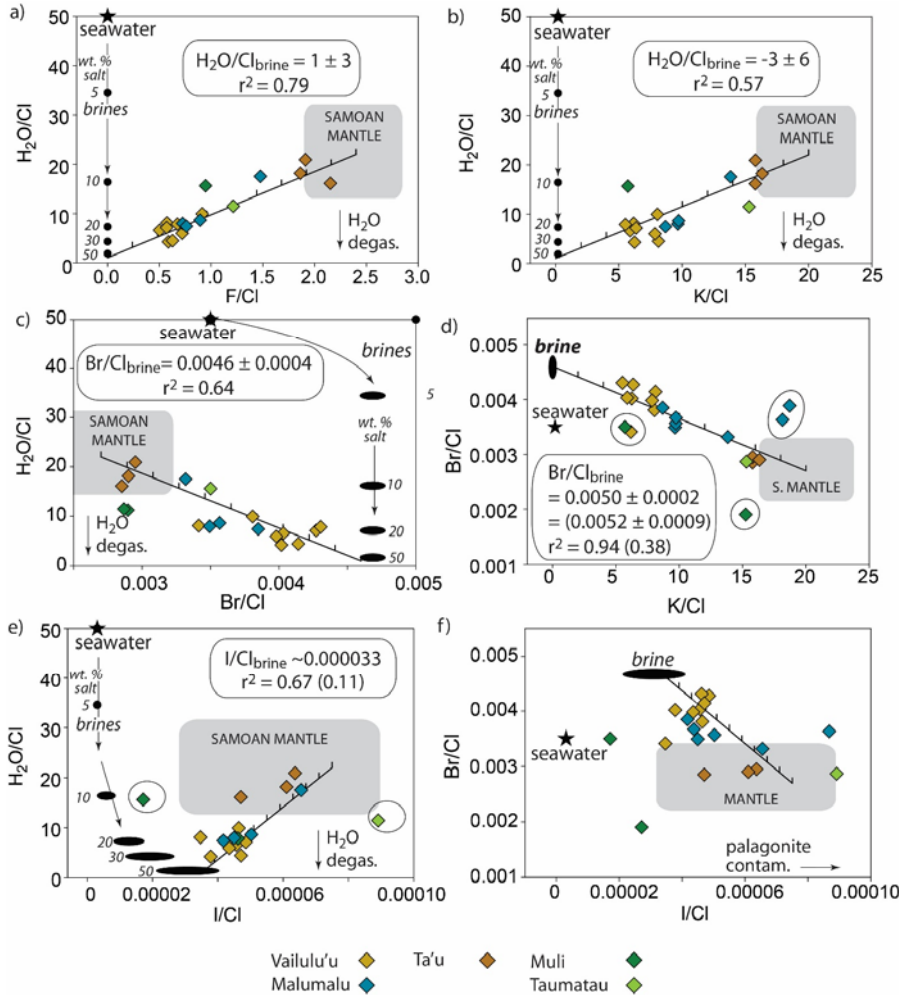
Fig 6. Kendrick et al. (2014)

Fig 6. Mixing systematics of F, Cl, Br, I, H₂O and K in Samoan glasses: a) F/Cl versus H₂O/Cl; b) K/Cl versus H₂O/Cl; c) Br/Cl versus H₂O/Cl; d) K/Cl versus Br/Cl; e) I/Cl versus H₂O/Cl; and f) I/Cl versus Br/Cl. The composition of seawater, brines with 5, 10, 20, 30 and 50 wt. % salt and a field suggested to be representative of the Samoan mantle are shown for reference. The composition of the brine end-member obtained with model 2 regressions in Isoplot (Ludwig, 2009) shows 2σ uncertainties. Note that parts d and e show data for selective regressions that exclude the circled data points, and data for non-selective regressions in parentheses. Note that the mixing lines show 10% increments of total Cl between the mantle and brine end-members.
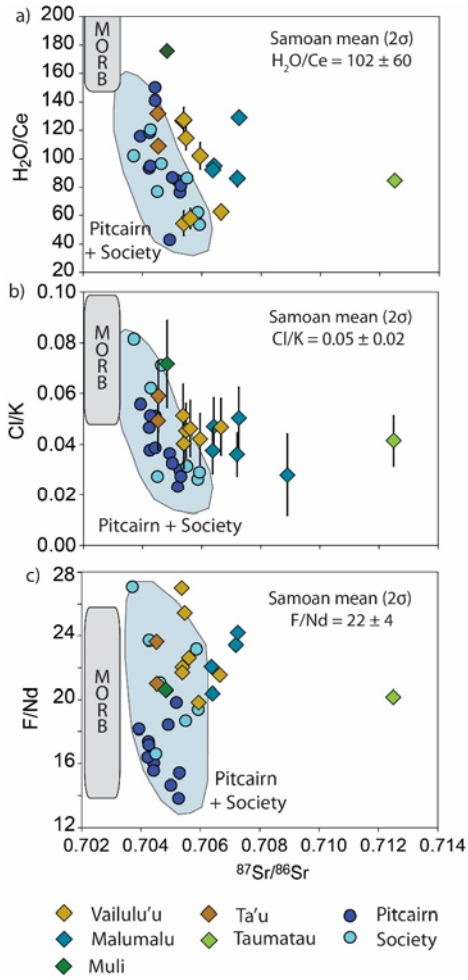
Fig 7. Kendrick et al. (2014)

Fig 7. Assimilation-corrected H$_2$O/Ce (a) and Cl/K (b), and the measured F/Nd (c)of Samoan melts as a function of ^{87}Sr/^{86}Sr. Uncertainty introduced by the assimilation correction controlled by the model fit in Fig 6 is shown in parts a and b (see Table 1). Data for Society and Pitcairn glasses (Kendrick et al., 2014a), and MORB fields are shown for reference.
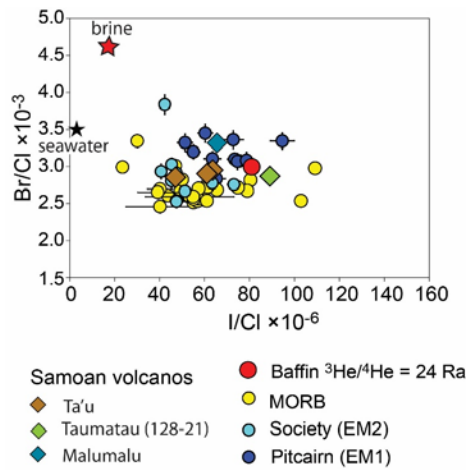
Fig 8. Kendrick et al. (2014)

Fig 8. The Br/Cl versus I/Cl systematics of the five Samoan glasses least affected by brine assimilation and a high $^3He/^4He$ Baffin Bay glass, showing mantle has limited variation in Br/Cl and I/Cl that is not related to $^{87}Sr/^{86}Sr$ or $^3He/^4He$. Data for glasses from Society and Pitcairn (Kendrick et al., 2014a), various MORB glasses (Kendrick et al., 2013a), seawater and the brine used in our mixing model (Fig 6), are shown for reference.