**Contrasting behaviours of CO₂, S, H₂O and halogens (F, Cl, Br, I)
in enriched-mantle melts from Pitcairn and Society seamounts**

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Abstract.

In order to improve characterisation of volatiles in the EM1 and EM2 mantle sources, which are interpreted to contain subducted sedimentary or lithospheric components, we report electron microprobe, FTIR and SIMS CO₂, H₂O, S, F and Cl concentrations of variably enriched glasses from Pitcairn and Society seamounts in Polynesia. The analyses complement previously published Cl, Br and I data for some of the same glasses and all the techniques show reasonable agreement of better than 5-9 % for S, Cl and H₂O. The concentrations of H₂O and all the halogens increase as a function of melt evolution with the highest values of 1.6 wt % H₂O, 2100 ppm F, 1500 ppm Cl, 3.7 ppm Br and 80 ppb I in melts with <2 wt % MgO. In contrast, CO₂ and S are strongly influenced by degassing and it is the least evolved melts that preserve the highest CO₂ concentrations that indicate CO₂ oversaturation of some lavas. Comparison of volatile and non-volatile elements of similar compatibility (e.g. H₂O/Ce, Cl/K) as a function of equilibration depth and ⁸⁷Sr/⁸⁶Sr, suggests H₂O and halogens were not significantly degassed from melts equilibrated at >150 bars and most of the variation in H₂O/Ce reflects source variation. Despite their overall enrichment in volatiles, both the Pitcairn and Society EM1 and EM2 sources are depleted in H₂O as well as Cl, Br, and I relative to Ce and K. Slightly different behaviour is suggested for F and a correlation between F/Cl and K/Cl in Pitcairn melts, could be explained by preferential subduction of F relative to Cl into the EM sources. The relative abundances of H₂O, halogens and lithophile elements in melts from different tectonic settings indicate subduction-related H₂O and Cl loss efficiencies are similar at ~90-96%; however, we suggest a lower efficiency for F loss and higher efficiencies for Br and I loss. Nonetheless, dehydrated lithosphere containing 5-10% of its original volatile content is interpreted as the most likely source of volatile enrichment in the Pitcairn and Society mantle sources.

1. Introduction

The geochemistry of seafloor basalts indicates considerable heterogeneity in the Earth's mantle (e.g. Zindler and Hart, 1986; Hofmann, 2003; White, 2010; Stracke, 2012). The magmas produced in intra-plate settings at oceanic islands are commonly enriched in incompatible trace elements, and have more variable Sr, Nd, Pb and He isotope signatures than mid-ocean ridge basalts (MORB) (e.g. Hofmann, 2003; Graham, 2002). Intra-plate Ocean Island Basalts (OIB) characterized by $^3\text{He}/^4\text{He}$ ratios of higher than typical MORB (e.g. Hawaii or Iceland) are thought to sample relatively primitive unprocessed mantle material (e.g. Graham, 2002; Jackson et al., 2010; Kurz et al., 1982; Mukhopadhyay, 2012). In contrast, OIB with low $^3\text{He}/^4\text{He}$ and radiogenic Sr or Pb signatures (e.g. St Helena, Cook-Austral, Canary Islands) are thought to sample recycled sediment and/or lithospheric materials that have been subducted into the mantle over periods of more than two and a half billion years (Cabral et al., 2013; Graham, 2002; Hanyu et al., 2011; Hofmann, 2003; Hofmann and White, 1982; Parai et al., 2009). A recycled origin can explain the radiogenic Pb or Sr signatures and low $^3\text{He}/^4\text{He}$ ratios of OIB that are enriched with incompatible elements, because radiogenic isotopes like ^{87}Sr , ^{206}Pb and ^4He would have high abundances in ancient recycled crustal materials with relatively high concentrations of incompatible trace elements such as Rb, Th and U relative to Sr and He (Hilton and Porcelli, 2013; Hofmann, 2003; Plank and Langmuir, 1998). However, some OIB have high or variable $^3\text{He}/^4\text{He}$ (and primitive Ne isotope signatures) together with radiogenic Sr signatures (e.g. Pitcairn, Society, Samoa) that suggest they sample a combination of both primitive and recycled mantle materials (e.g. Farley et al., 1992; Honda and Woodhead, 2005; Jackson et al., 2007; Staudacher and Allegre, 1989).

The interpretation that enriched OIB sample recycled sedimentary or lithospheric components means OIB can provide important information about long term geochemical

cycling of volatiles and other less-well-constrained elements, that complement the information available from magmas generated in modern arc and back arc settings (e.g. Hofmann, 2003; Stracke, 2012). The fate of volatiles in subduction zones is a subject of ongoing debate (e.g. Dixon et al., 2002; Holland and Ballentine, 2006; Hilton et al., 2002; Ito et al., 1983; Jacobsen and van der Lee, 2006; Kendrick et al., 2011; Parai and Mukhopadhyay, 2012; Rüpke et al., 2004; Wallace, 2005). Sediments and hydrated oceanic lithosphere entering subduction zones have relatively high concentrations of volatile species such as H₂O, halogens, S, CO₂ and atmospheric noble gases (Alt and Honnorez, 1984; Alt and Teagle, 2003; Ito et al., 1983; Staudacher and Allegre, 1988; Kendrick et al., 2011; 2013b). However, volatiles are potentially decoupled from subducting slabs by subduction-related metamorphism and devolatilisation that causes fluid loss (Staudacher and Allegre, 1988; Hilton et al., 2002; Fischer, 2008), and explain the high H₂O/Ce and Cl/K of magmas in arc and back arc settings (e.g. Kent et al., 2002; Sinton et al., 2003; Wallace et al., 2005; Plank et al., 2013). Alternatively, experimental studies have shown that significant water can be stored in nominally anhydrous minerals formed during slab dehydration (e.g. Kohlstedt et al., 1996; Smyth et al., 2006), meaning that a portion of the water entering subduction zones could be cycled deeply into the Earth's mantle (e.g. Jacobsen and van der Lee, 2006).

The fate of water in subduction zones has profound consequences for the geochemical cycles of other trace volatiles and fluid mobile elements. Hydrous minerals are important hosts for halogens and chemically inert noble gases (Jackson et al., 2013; Kendrick et al., 2011). Furthermore, the transport of any fluid mobile element is intrinsically linked to that of water: if significant water is trapped in nominally anhydrous minerals and transported into the deep mantle it implies that this water is unable to advect fluid mobile trace volatiles away from the subducting slab (Kendrick et al., 2011; 2013b).

Submarine glasses from the Pitcairn and Society seamounts of Polynesia are ideal for further evaluating the well-known volatile enrichment of OIB (e.g. Schilling et al., 1980; Jambon and Zimmerman, 1990; Dereulle et al., 1992), because they have extremely variable radiogenic isotopic compositions that extend from enriched compositions that exemplify the so called EM1 and EM2 mantle end-members to an end-member that is close to the MORB mantle or FOZO (Fig 1; Devey et al., 1990; Woodhead and Devey, 1993). Pitcairn is dominated by MORB-like helium with the most primitive neon signatures associated with the EM1 end-member (Fig 5 of Honda and Woodhead, 2005). Nonetheless, the geochemically enriched isotopic signatures of the EM1 and EM2 end-members are usually ascribed to the presence of recycled sediments or lithospheric components in the mantle source (Devey et al., 1990; Hofmann, 2003; Jackson et al., 2007; Woodhead and Devey, 1993). Systematic variations between radiogenic isotope ratios such as $^{87}\text{Sr}/^{86}\text{Sr}$ (or $^{143}\text{Nd}/^{144}\text{Nd}$) and volatile contents could therefore provide new insights into the extent to which recycled sediments contribute to the volatile enrichment of OIB sources or are dehydrated during subduction (e.g. Dixon et al., 2002; Workman et al., 2006).

It has been demonstrated previously that the EM1 and EM2 mantle end-members sampled by the Pitcairn and Society melts are depleted in Cl relative to K (and other trace elements), but that they have Br/Cl and I/Cl ratios similar to the MORB mantle (Kendrick et al., 2012b; Stroncik and Haase, 2004). The current study builds on this information by documenting the H₂O, F, S and CO₂ contents of the Pitcairn and Society melts. This is significant because the CO₂ and S concentrations can provide constraints on magma degassing, and systematic trends between the other volatiles and Cl could potentially provide new information about their relative devolatilisation efficiencies during subduction and subsequent residence of subducted materials in the mantle.

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120 **2. Sampling, methods and standardization**

121 The submarine glasses used in this study have been documented in a number of previous
122 works (e.g. Ackermann et al., 1998; Devey et al., 1990; Honda and Woodhead, 2005;
123 Kendrick et al., 2012b; Woodhead and Devey, 1993). The samples were recovered by
124 dredging active submarine volcanoes in the Pitcairn and Society seamount chains of
125 Polynesia (Fig 2). The samples from the Pitcairn seamounts situated 70-100 km southeast of
126 Pitcairn Island, were recovered during the SO-65 voyage of the German research vessel *F/S*
127 *Sonne* in 1989 (Fig 2; Stoffers et al., 1990). The Society seamount samples were recovered
128 during cruises of the *N.O. Jean Charcot* and *F/S Sonne* vessels from a series of submarine
129 volcanoes southeast of Tahiti during 1983 and 1987, respectively (Fig 2; Cheminee et al.,
130 1989; Stoffers, 1987).

131 The Society glasses derive from the flanks of five different volcanoes and therefore
132 represent the volcanic products of several magma chambers. The majority of Pitcairn glasses
133 derive from the Bounty Volcano, but they encompass distal flank areas of the volcano, have
134 different chemistry, and almost certainly represent different magma batches (Fig 2).
135 Collectively the glasses are considered to represent recent expressions of evolving magma
136 chambers fed by the Pitcairn and Society hotspots (Cheminee et al., 1989; Stoffers, 1987;
137 Stoffers et al., 1990; Devey et al., 2003).

138 Volatiles in 18 Pitcairn and Society glasses selected for this study have been analysed
139 using several complementary techniques: 1) S and Cl were measured along with major
140 elements by Cameca SX-100 electron microprobe at Oregon State University.
141 Complementary trace element analyses were undertaken by laser ablation inductively coupled
142 plasma mass spectrometry at the W.M. Keck Collaboratory for Plasma Spectrometry, Oregon
143 State University. 2) FTIR was used to measure the glass H₂O content at the University of

Oregon; and 3) SIMS measurements of H₂O, CO₂, S, F and Cl were obtained using the Cameca IMS 6F ion microprobe at the Department of Terrestrial Magnetism, Carnegie Institute of Washington. In addition, 4) fourteen of the glasses were previously investigated for Cl, Br and I using the noble gas method (Kendrick et al. 2012b), providing a combined dataset for volatiles in 24 glasses.

Electron microprobe analysis at Oregon State University used an accelerating voltage of 15 keV and current of 30 nA with counting times optimised for measurement of S (30 s) and Cl (100 s), following the approach of Rowe et al. (2009). Precision is estimated at 12 % (2 σ) for Cl based on duplicate analyses of Loihi glass (LO-02-02) that gave 1340 ± 160 ppm Cl compared to ~ 1390 ppm Cl in a previous study (Kent et al., 1999b). Trace element analyses achieved using the NewWave DUV 193 Excimer laser and VG PQ Excell quadrupole ICP-MS followed the techniques reported in Kent et al. (2004). Individual analyses used a spot of between 50-80 μ m diameter and a pulse rate of 4 Hz. The reported concentrations represent the averages of 3-5 measurements made using BCR-2G as the calibration standard and electron microprobe CaO contents. Concentrations determined for BHVO-2G, analysed as an unknown, were within 10% of accepted values. Analogous procedures were used to analyse 5 glasses at the University of Melbourne, for which only Cl, Br and I volatile data were available.

Dissolved H₂O was measured by FTIR using a ThermoNicolet Nexus 670 spectrometer and Continuum microscope at the University of Oregon. Doubly polished wafers of each glass were prepared for analysis, with the thicknesses measured by digital micrometer. Total H₂O concentrations were determined using the OH stretching vibration at 3560 cm⁻¹ and an absorption coefficient of 63 L/mol cm (Dixon et al., 1995). The accuracy of FTIR H₂O measurements on basalt glasses is commonly estimated as $\pm 10\%$ (e.g. Dixon and Clague, 2001). The absorption coefficient for the OH stretching vibration is relatively

constant over a wide range of basaltic to andesitic compositions (Dixon and Clague, 2001; King et al., 2002; Mandeville et al., 2002); however, the choice of absorption coefficient represents an additional uncertainty for evolved alkaline glasses.

SIMS analysis used a focussed primary Cs^+ ion beam (10-15 nA) rastered over a $40 \times 40 \mu\text{m}$ area on the glasses, with a field aperture selected to mask emission from the crater edge and extract ions from only the central $10 \mu\text{m}$ of the sputter crater. The entrance and detector slits were arranged to give sufficient mass resolution (4500) to resolve known volatile interferences, mainly ^{17}O on ^{16}OH , ^{18}OH on ^{19}F , and $^{16}\text{O}_2$ on ^{32}S . Counting times of 10s were employed for ^{12}C and 2s for the remaining isotopes ^{16}OH , ^{19}F , ^{32}S and ^{35}Cl and the normalizing isotope ^{30}Si . The reported concentrations represent the averages of 3-5 individual measurements on each glass, standardized against a suite of 45 basaltic and andesitic glasses for volatile abundances, following methods detailed in Hauri et al. (2002, 2006).

Finally, the concentrations of halogens and K previously reported by Kendrick et al (2012b) were based on irradiation-produced noble gas proxy isotopes measured relative to an air standard, and converted to Cl, Br, I and K via production ratios monitored with mineral standards (Kendrick, 2012). This methodology normally provides very high internal precision of 2-4 % (2σ) for concentration and ratio measurements; however, changes in the Br and I abundances recommended for the scapolite standards (see Kendrick et al., 2013ab), require that the previously reported concentrations are reduced by 20 % for Br and 25 % for I. Revising the Br and I concentrations does not change the conclusions of the previous study, which were based on an internally consistent dataset (Kendrick et al., 2012ab); however, it will facilitate future comparison between laboratories and Br or I measurements made by

different techniques. The basis of the monitor re-calibration is described in detail by Kendrick et al. (2013a).

3. Results

The new electron microprobe, FTIR and SIMS Cl, F, H₂O, CO₂ and S data are reported in Tables 1 and 2 together with selected major and trace elements, key isotopic ratios from previous studies (Devey et al., 1990; Woodhead and Devey, 1993; Honda and Woodhead, 2005; Staudacher and Allegre, 1989) and revised Br and I concentration data from Kendrick et al. (2012b). The full electron microprobe and laser ablation ICPMS datasets, including standard analyses, are available in the electronic supplement.

The most primitive glasses have 6-7 wt. % MgO and 45-49 wt % SiO₂, whereas the most evolved glasses have 1-2 wt % MgO and 55-65 wt % SiO₂ (Fig 3; Tables 1 and 2). The SiO₂, Na₂O and K₂O concentrations of the glasses (Supplementary Data) encompass basanites, alkali basalts, trachy-basalts, trachy-basaltic andesites and trachytes, with the Society glasses recording the most evolved major element compositions (Fig 3)). This large range of melt compositions is a consequence of our sampling strategy, because some of the isotopically most enriched samples represent early-formed highly differentiated melts dredged from small seamounts (Fig 3c; Devey et al., 2003). Note that halogen measurements were conducted on a very small piece of CH DR1 P1-1 glass (e.g. ~0.7 mg; Kendrick et al., 2012b), and while major and trace element data are not available for this glass (Table 2), whole rock data indicate a basanitic composition with 7.8 wt % MgO and 45 wt % SiO₂ similar to the least evolved glasses from Society (Fig 3; Devey et al., 1990).

The different techniques used to measure H₂O, Cl and S yield very similar results indicating the glasses have 0.75 to 1.6 wt. % H₂O; 480 to 2090 ppm F, 200 to 1450 ppm Cl; 250-3700 ppb Br, 21-77 ppb I, 2.3 to 160 ppm CO₂ and 240 to 2500 ppm S (Fig 4; Tables 1 and 2). In general, the highest concentrations of H₂O and halogens occur in the most evolved melts, whereas CO₂ and S have lower concentrations in the more evolved melts (below; Table 1 and 2).

The average discrepancies between the techniques are less than 5-6 % for Cl and S and 9% for H₂O (Fig 4). The discrepancy between SIMS and FTIR H₂O is largest for the more evolved glasses; however, the average discrepancy is similar to the accuracy of these techniques. As a result we believe that our interpretations are not influenced by inter-laboratory biases and standardization summarised in section 2 is not discussed further in this contribution.

In the discussion below we use SIMS data for H₂O, CO₂, S and F; and Br and I concentrations determined by the noble gas method. Chlorine concentrations are based on either the noble gas method, electron microprobe or SIMS data, such that both elements in any ratio have been measured by the same technique. This avoids introducing small biases related the analysis of different sample aliquots.

4. Discussion

Before considering how the volatile content of the Pitcairn and Society melts could be related to subduction-recycling processes, we first evaluate the extent to which volatiles have been modified by shallow level processes occurring during magma residence in the crust or eruption. In addition to fractional crystallisation, two shallow level processes that have the potential to strongly alter the glasses volatile content are degassing and seawater assimilation.

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239 *3.1 Volatile degassing*

240 The Pitcairn and Society glasses included in this study have vesicles ranging from
241 micrometres to millimetres in diameter that are estimated to occupy between ~5 and 30 vol.
242 % of some glasses (Table 3; Ackermund et al., 1998; Aubaud et al., 2005; 2006; Hekinian et
243 al., 1991). Furthermore some of the Society samples were reported to be popping rocks that
244 released the smell of H₂S immediately after dredging (Hekinian et al., 1991), and Ackermund
245 et al. (1998) estimated that sulphides coating the inside surfaces of vesicles in Pitcairn
246 samples 52DS-1 and 57DS-1 accounted for up to ~1 vol. % of the glass. These observations
247 suggest the melts degassed substantial CO₂ and variable quantities of S (Ackermund et al.,
248 1998; Hekinian et al., 1991), as well as limited H₂O, which is present in the vesicles (Aubaud
249 et al., 2005; 2006).

250 Volatile solubility is pressure dependent and solubility models developed from
251 experimental data can be used to calculate equilibrium degassing pressures based on the
252 measured H₂O and CO₂ concentrations (e.g. Dixon et al., 1995; Iacono-Marziano et al.,
253 2012). However, in addition to the pressure effect, CO₂ solubility is strongly dependent on
254 melt composition with CO₂ solubility enhanced by high CaO, K₂O and Na₂O in mafic
255 magmas or the presence of H₂O, and reduced by SiO₂ in more evolved melts (e.g. Dixon et
256 al., 1995; Dixon, 1997; Iacono-Marziano et al., 2012). The solubility of H₂O is less sensitive
257 to composition than CO₂, but H₂O is significantly more soluble in trachytic melts than in
258 rhyolitic magmas (Di Matteo et al., 2004).

259 The SIMS CO₂ and H₂O concentration data have been modelled in Fig 5 using the
260 VolatileCalc program (Newman and Lowenstern, 2002) which is based on the solubility
261 model of Dixon et al., (1995) and Dixon (1997). Newman and Lowenstern (2002) indicated

that VolatileCalc can be used to model mafic compositions in the tholeiite to nephelinite range, including the alkali basalts and basinites relevant to this study (Fig 3). However, the SiO₂ input parameter is limited to the range 40-49 wt. % and the results are questionable for melts with >52 wt % SiO₂ (Newman and Lowenstern, 2002). Despite this limitation, the Pitcairn glasses with SiO₂ of 49.1-55.7 wt % lie close to the equilibrium line in Fig 6b, and taken at face value, the volatile concentrations in these melts appear to have been closely equilibrated to the depth of eruption (Fig 6).

The Society glasses encompass a greater range of compositions than the Pitcairn glasses and the most evolved melts with more than 60 wt % SiO₂ (Fig 3) were modelled as rhyolites rather than basalts in VolatileCalc (Fig 6b). The apparent understaturation of some of the melts could be related to the limitations of the solubility model; however, two of the Society glasses with <49 wt % SiO₂ are indicated to be significantly over-saturated with respect to CO₂ (Fig 6b). A similar degree of oversaturation is also suggested for these glasses by an alternative solubility model developed for alkaline magmas (Table 2; Iacono-Marziano et al., 2012); and in contrast to VolatileCalc this model suggests the Pitcairn glasses could be similarly oversaturated with respect to CO₂ and H₂O (Table 1). Oversaturation of submarine melts with respect to CO₂ is commonly observed on many mid-ocean ridges and is usually interpreted to indicate that although some degassing has occurred, its efficiency was limited by a rate of magma ascent greater than the rate of CO₂ diffusion into vesicles (e.g. Chavrit et al., 2012; Dixon and Stolper, 1995; Pichavant et al., 2013).

The relative importance of degassing is much greater for CO₂ than H₂O or halogens which have relatively high solubilities in silicate melts (Dixon et al., 1995; Dixon 1997; Webster et al., 1999). The two Society samples in this study that were investigated by Aubaud et al. (2005), can be estimated to contain 95-97% of their total CO₂ in vesicles compared to only 10-20 % of their total H₂O (Table 3). However, the significance of these

numbers depends on the relationship between the vesicles and matrix glass: if vesicles were lost from the melt prior to quenching these figures would represent minimums for CO₂ and H₂O degassing, but if the vesicles were derived from a volume of melt larger than the sample, they could overestimate the extent of degassing. We favour the latter interpretation because while matrix CO₂ concentrations show a pronounced decrease toward the more evolved compositions, that is consistent with the expected enhanced degassing of CO₂ in SiO₂-rich melts (Fig 6a), the data in Table 3 would suggest the basanitic sample (CH DR1 P3-4) was degassed more efficiently than the trachytic sample (CH DR4 4-1). Sulphur and Cu show a decrease with melt evolution similar to CO₂ (Fig 6a); however, this is related to a combination of S degassing and crystallisation of sulphide phases, given that sulphides are present in the ground mass as well as within vesicles of the most evolved rocks (Ackermann et al., 1998). In contrast to CO₂ and S, H₂O increases during melt evolution, in a manner that is similar to the halogens and other incompatible elements like K that are not significantly degassed or fractionated by sulphides (Fig 6b).

The extent to which relatively minor H₂O degassing could contribute to the scatter of H₂O concentrations in the MgO concentration plot is unclear, but these data can be explained by mixing depleted mantle and EM magma components in the majority of samples (Fig 6b). Therefore, in order to further isolate the possible effects of H₂O degassing we examine the concentrations of selected volatiles relative to non-volatile lithophile elements of similar compatibility as a function of eruption depth (Fig 7) and ⁸⁷Sr/⁸⁶Sr (Fig 8). The logic is that because element pairs of similar compatibility, like CO₂/Nb, H₂O/Ce, Cl/K and F/Nd, are not strongly modified by crystallisation of common silicate minerals (olivine, pyroxene and plagioclase), variation in these ratios is mainly ascribed to either degassing processes or the source composition. Variations caused by degassing should be revealed by a systematic

relationship to eruption depth, whereas variations related to source composition may be correlated with $^{87}\text{Sr}/^{86}\text{Sr}$.

As would be expected, the CO_2/Nb ratio decreases with decreasing eruption depth, consistent with strong CO_2 degassing (Fig 7a; S/Dy behaves in a similar way and neither ratio is correlated with $^{87}\text{Sr}/^{86}\text{Sr}$). In contrast, the $\text{H}_2\text{O}/\text{Ce}$ ratio varies from 60 to 150 in the majority of samples, but a lower value of 43 suggests H_2O degassing was significant for the shallowest samples (Fig 7b). The glasses have fairly constant F/Nd over the entire range of eruption depth (Fig 7c), and both F/Nd and Cl/K of the Pitcairn samples increase toward shallower depths (albeit with significant scatter), which is the opposite to the trends that would result from degassing (Fig 7d). Notice also that the $\text{H}_2\text{O}/\text{Ce}$ ratio of the Pitcairn samples equilibrated at more than 100 bars show a similar increase toward shallower depth (Fig 7b) and both $\text{H}_2\text{O}/\text{Ce}$ and Cl/K are correlated with $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig 8).

These observations are consistent with previous work indicating that halogens are not significantly degassed from melts erupted in water depths of more than ~500 m (Straub and Layne, 2003; Unni and Schilling, 1978) and the relatively high solubility of H_2O in silicate melts (Dixon et al., 1995; Dixon, 1997; Webster et al., 1999). In the ensuing discussion, and based on the information from Fig 7, we therefore assume that none of the melts have lost halogens through degassing and that melts erupted at pressures of >150 bars have retained H_2O concentrations within ~10% of their original values. The suggested preservation of H_2O concentrations close to pre-degassing values is consistent with the melts either having originally had low CO_2 contents, or more likely that CO_2 degassing occurred predominantly in an open system.

3.2 Seawater assimilation

Previous work has shown submarine magmas can have elevated Cl concentrations, above what can be explained by fractional crystallisation, as a result of assimilating seawater-derived components (e.g. Kendrick et al., 2013a; Kent et al., 1999ab; 2002; le Roux et al., 2006; Michael and Cornell, 1998; Wanless et al., 2011). However, several lines of evidence suggest the Pitcairn and Society melts have not been significantly influenced by assimilation processes.

Firstly, the range of H₂O and Cl concentrations in the melts can be explained by fractional crystallisation and mixing the depleted and enriched magma components (Fig 6b) which are required to explain the range in isotope compositions (Fig 1), and Cl/K does not increase as a function of MgO (Tables 1 and 2; supplementary data Fig S1). The liquid lines of descent in Figs 6b have been calculated with Petrolog3 (Danyushevsky and Plechov, 2011) by progressively crystallising olivine, plagioclase, pyroxene, ilmenite and magnetite and assuming K, H₂O and Cl are all perfectly incompatible. The mineral compositions were evolved during crystallisation according to the mineral models of Arisken et al. (1993), Arisken and Barmina (1999) and Bolikhovskaya et al. (1999). The magma starting compositions at 8 wt % MgO were selected to fit the data and be realistic for MORB and OIB magmas; however, it should be noted that the choice of starting composition and mineral model significantly influences the slope of liquid lines of descent and the models are intended only to be indicative of a melts possible evolution below 4 wt % MgO.

Secondly, it has been demonstrated that in every known case where magmas have assimilated seawater-derived Cl, Cl and H₂O were introduced in high salinity brines, leading to strong correlations between H₂O/Cl, Br/Cl, I/Cl, F/Cl and K/Cl (see Kendrick et al., 2013a for a complete discussion). In contrast, these ratios are not systematically correlated between the Society and Pitcairn glasses, which preserve Br/Cl and I/Cl typical of the mantle (Fig 9; Kendrick et al., 2013a). Note that the H₂O/Cl and F/Cl data in Fig 9c do exhibit a weak

correlation ($r^2 = 0.58$); however, this trend cannot be explained by assimilation of seawater components because $\text{H}_2\text{O}/\text{Cl}$ is not similarly correlated with K/Cl (Fig 9a), and Br/Cl is not correlated with either K/Cl or I/Cl (Fig 9).

Finally, the glasses from both Pitcairn and Society exhibit relationships between $\text{H}_2\text{O}/\text{Ce}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, and Cl/K and $^{87}\text{Sr}/^{86}\text{Sr}$ (Figs 8ac), that would not have been preserved if significant assimilation of seawater-derived components had occurred (seawater $^{87}\text{Sr}/^{86}\text{Sr} = 0.709$; see Fig 9), or if these melts had lost significant H_2O during degassing.

3.3 Volatiles in the Pitcairn and Society EM sources

In the preceding sections we argued Pitcairn and Society melts erupted under water pressures of more than 150 bars preserve H_2O and halogen concentrations of close to their original values. Furthermore, the melts have a limited range of Br/Cl and I/Cl that indicate the behaviours of Br and I are similar to Cl (Figs 8 and 9d; Schilling et al., 1980; Kendrick et al., 2012a; 2013a). In this section we further evaluate variations in the relative concentrations of halogens and H_2O in Pitcairn and Society melts and relate these variations to mixing of depleted and enriched components in the mantle sources (Fig 1).

Despite their high volatile contents, the Pitcairn and Society melts have $\text{H}_2\text{O}/\text{Ce}$, Cl/K , Br/K and I/K ratios, that show marked decreases as a function of mantle enrichment indicated by $^{87}\text{Sr}/^{86}\text{Sr}$ (Figs 8a,c,e and f; Stroncik and Haase, 2004; Kendrick et al., 2012b). It should be noted that similar trends are obtained if $^{143}\text{Nd}/^{144}\text{Nd}$ is used in place of $^{87}\text{Sr}/^{86}\text{Sr}$ or La instead of K; and that sample 45-DS-1, believed to have degassed significant H_2O (Fig 7b), is not shown in these plots. Fluorine is distinguished from the other halogens and H_2O because in contrast to $\text{H}_2\text{O}/\text{Ce}$ and Cl/K , the F/Nd ratios of the Society and Pitcairn melts are

not strongly correlated with $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig 8d). Previous studies have demonstrated comparable depletions of $\text{H}_2\text{O}/\text{Ce}$ in enriched mantle sources sampled by the Shona, Discovery and Azores anomalies of the Atlantic, as well as the Kerguelen and Samoan plumes (Dixon et al., 2002; Wallace, 2002; Workman et al., 2006). The lowest Cl/K were also measured in the enriched source of the Kerguelen plume (Wallace, 2002). In contrast, the Cl/K systematics of the Samoan melts were obscured by seawater assimilation (Workman et al., 2006), but the Samoan melts are characterised by a uniform F/Nd of 22 ± 3 ($n = 88$; 2σ) that does not vary as a function of $^{87}\text{Sr}/^{86}\text{Sr}$ (Workman et al., 2006; cf. Fig 8d).

The characteristically low $\text{H}_2\text{O}/\text{Ce}$, Cl/K , Br/K and I/K ratios of the enriched mantle sources investigated (Fig 8; Dixon et al., 2002; Wallace, 2002; Workman et al., 2006) are consistent with the presence of subducted oceanic lithosphere that was efficiently devolatilised during subduction. Dehydrated lithosphere could generate a strong enrichment in incompatible lithophile elements, whereas its volatiles would have been at least partly lost during subduction (e.g. Dixon et al., 2002; Jambon and Zimmerman, 1990; Workman et al., 2006; Kendrick et al., 2012b). In this scenario, the lack of a strong correlation between F/Nd and $^{87}\text{Sr}/^{86}\text{Sr}$ in the Pitcairn, Society and Samoan melts, which is characteristic of F depletion comparable to the relative depletions of Cl and H_2O (Fig 8d; Workman et al., 2006), could be explained if F was recycled into the enriched mantle sources more efficiently than the heavier halogens and H_2O (Fig 8).

Preferential subduction of F relative to Cl is consistent with the correlation between F/Cl and K/Cl in Pitcairn melts ($r^2 = 0.77$; Fig 10), which cannot be explained by seawater assimilation (section 3.2; Fig 8d). Furthermore, while detailed studies of F behaviour in subduction zones are rare (John et al., 2011; Portnyagin et al., 2007; Straub and Layne, 2003), preferential subduction of F relative to Cl might be expected to result from the higher compatibility of F in mica and amphibole, and the higher solubility of F in the nominally

anhydrous minerals formed during slab dehydration (Bernini et al., 2013; Beyer et al., 2012; Dalou et al., 2012).

3.4 Comparison with other mantle reservoirs

The relative depletion of H₂O, Cl, Br and I in enriched mantle sources (Fig 9) is consistent with the presence of dehydrated subducted sediments or lithospheric components in the EM sources, but it does not constrain the source of volatiles in the enriched-mantle. In order to provide additional inferences on the sources of volatiles in the EM sources, as well as the efficiency of dehydration, we have compiled data for the relative abundances of K, Ce, F, Cl, Br, I, and H₂O in submarine glasses from different tectonic settings (Table 4). The compiled data have been selected to avoid samples obviously influenced by seawater assimilation, which was evaluated using X/Cl plots similar to Fig 8, enabling analyses representative of the mantle to be selected. A striking feature of the compilation is that the EM1 and EM2 mantle reservoirs have H₂O/Cl, Br/Cl and I/Cl ratios that are very similar to MORB, but based on the limited data available MORB has more variable and sometimes higher F/Cl ratios than the EM mantle reservoirs investigated (Table 4).

The similarity between MORB and OIB Br/Cl, I/Cl and H₂O/Cl ratios is partly explained because these elements have similar compatibilities in the mantle and are not easily modified by melting or fractional crystallisation (Kendrick et al., 2012a; Michael, 1995; Dixon et al., 2002). Recent Cl isotope data have suggested Cl in enriched mantle reservoirs may be distinct to that in MORB (John et al., 2010). However, there is no good reason that primordial and recycled volatiles would have similar H₂O/Cl, Br/Cl and I/Cl ratios, so we interpret the relative uniformity of these abundance ratios to indicate that these volatiles either: i) have a dominantly primordial origin in the mantle, and mantle abundance ratios

have not been disturbed by the introduction of recycled materials; or ii) these volatiles have a dominantly recycled origin throughout the mantle, and their relative abundance ratios are controlled by slab processes.

The suggested association of primitive noble gases with recycled materials in the EM1 end-member of the Pitcairn plume (Honda and Woodhead, 2005) implies H₂O, Cl, Br and I could have either a primordial or recycled origin in the Pitcairn melts. However, the lack of a relationship between ³He/⁴He and H₂O/Ce in the Pitcairn samples (Fig 11) and the MORB mantle (Michael, 1995), and the presence of subducted atmospheric noble gases in the convecting mantle (Holland and Ballentine, 2006), is interpreted here to favour a recycled origin for other seawater-derived volatiles like H₂O, Cl, Br, I, throughout most of the mantle.

The low H₂O/Ce (~60-80) and Cl/K (~0.025 (K/Cl = 40)) of the EM sources relative to MORB (H₂O/Ce ~100-300; Cl/K ~0.1-0.05 (K/Cl = 10-20)), can be used together with data from arc-backarc magmas with H₂O/Ce of ~1000-3000 and Cl/K ~1 (Table 4), to estimate the cumulative efficiency of volatile loss during subduction and subsequent residence in the mantle:

$$\% \text{ H}_2\text{O loss} = [(\text{H}_2\text{O}/\text{Ce})_{\text{BABB}} - (\text{H}_2\text{O}/\text{Ce})_{\text{MORB}}] / [(\text{H}_2\text{O}/\text{Ce})_{\text{BABB}} - (\text{H}_2\text{O}/\text{Ce})_{\text{EM}}] \times 100$$

$$\% \text{ Cl loss} = [(\text{Cl}/\text{K})_{\text{BABB}} - (\text{Cl}/\text{K})_{\text{MORB}}] / [(\text{Cl}/\text{K})_{\text{BABB}} - (\text{Cl}/\text{K})_{\text{EM}}] \times 100$$

On this basis, we estimate that both H₂O and Cl are lost from subducted slabs with fairly similar efficiencies of ~90-96 %, a figure that is similar to the H₂O loss efficiency of 92 % previously estimated by comparing sediment and enriched mantle H₂O/Ce ratios (Dixon et al., 2002). The similar efficiencies suggested for H₂O and Cl loss explain why mantle H₂O/Cl varies from only ~10 to ~50 (Table 4), and this ratio does not vary as a function of ⁸⁷Sr/⁸⁶Sr in our samples (Fig 8b).

In comparison to H₂O and the heavy halogens, the mantle F/Cl ratio is more likely to be disturbed by melting and fractional crystallisation, because F is less incompatible than Cl (Bernini et al., 2013; Beyer et al., 2012; Dalou et al., 2012). The available data indicate MORB has typical F/Cl of ~1-10 (Table 4), which overlaps with what has been reported for EM sources (F/Cl of ~1.5-3; Table 4), but probably also reflects melting and fractionation processes. Despite this complexity, many analyses of arc and backarc lavas have F/Cl <1 that are significantly lower than MORB and OIB F/Cl ratios (Table 4), consistent with F being subducted into the mantle preferentially relative to Cl (Straub and Layne, 2003).

Finally, the high Br/Cl and I/Cl ratios of materials entering subduction zones (Kendrick et al., 2013), and the uniquely high I/Cl of backarc basin basalts compared to MORB and OIB (Table 4), requires that I and Br are preferentially lost from subducting slabs relative to Cl in the early part of the subduction cycle (Kendrick et al., 2011; 2013b). Therefore, the total Br and I loss efficiencies during slab dehydration must be more than the F and Cl loss efficiencies (e.g. >90-96%). However, if halogens in the EM reservoirs have a dominantly recycled origin as suggested, the uniformity of H₂O/Cl, Br/Cl and I/Cl in the MORB and OIB mantle (Table 4) imply that subducted H₂O, Cl, Br and I also dominate the MORB inventory of these volatiles. Furthermore after bypassing the arc, H₂O, Cl, Br and I retained in the dehydrated slab (presumably hosted by fluid inclusions, grain boundaries and nominally anhydrous minerals) are not strongly fractionated from each other during melting reactions and mixing into the mantle. As a result, mineral breakdown reactions during subduction may control the abundance ratios of certain volatiles throughout the entire mantle, thus explaining the lack of a strong enrichment of I relative to other halogens in enriched reservoirs inferred to contain subducted sedimentary components (cf. Dereulle et al., 1992).

5. Conclusions

The Pitcairn and Society melts are strongly enriched in trace elements and volatiles relative to typical mid-ocean ridge basalts. However, the most enriched end-members show depletions in most volatiles relative to lithophile elements of similar compatibility, e.g. the most enriched melts have the lowest H₂O/Ce, Cl/K, Br/K and I/K ratios. Comparison of H₂O/Ce and Cl/K of magmas from different tectonic settings suggests H₂O and Cl are lost from subducted slabs with similar efficiencies of ~90-96%.

The relative uniformity of H₂O/Cl, Br/Cl and I/Cl in enriched mantle reservoirs sampled by OIB, and the MORB mantle (Table 4), suggests subducted volatiles have been mixed throughout the entire mantle. Differences between MORB-OIB melts and melts generated in arc and back arc settings imply a higher subduction efficiency for F than Cl (e.g. F loss efficiency of <90%) and lower subduction efficiencies of Br and I (e.g. Br and I loss efficiencies of >90-96%). However, the uniformity of mantle Br/Cl, I/Cl and H₂O/Cl favours a dominantly recycled rather than primordial origin for these volatiles in the mantle.

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Table 1. Sample information and volatile content of Pitcairn glasses

Sample	SO65 45DS-1	SO65 46DS -2	SO65 46DS -7	SO65 48DS-6	SO65 49DS-1	SO65 51DS-1	SO65 51DS-2	SO65 51DS-4	SO65 51DS-9	SO65 52DS-1	SO65 33GTV2	SO65 57DS-1	SO65 57DS-6	SO65 57DS-8
Volcano	Volc. 2	Volc. 2	Volc. 2	Volc. 2	Volc. 2	Volc. 2	Volc. 2	Volc. 2	Volc. 2	Volc. 2	Volc. 2	Volc. 5	Volc. 5	Volc. 5
Dredge depth (m)	490-610	760-770	760-770	1290- 1420	1970- 2080	1610- 1860	1610- 1860	1610- 1860	1610- 1860	2800- 2850	410	2500- 2820	2500- 2820	2500- 2820
Eqm. P –V.Calc (bar)	57	82	82	190	210	180		210	180	340		310	310	
Eqm. P – Alt. (bar)	140	190	120	220	210	190		380	190	600		480	490	
<i>Volatile content</i>														
H ₂ O wt % (SIMS)	0.75	0.83	0.84	1.1	0.83	0.76		1.4	0.79	1.6		1.5	1.5	
H ₂ O wt % (FTIR)	0.81	0.85	0.84	1.1	1.0	0.80		1.6	0.78	1.8		1.5	1.6	
CO ₂ ppm (SIMS)	2.3	7.8	7.1	31	68	58		5.6	55	39		38	39	
S ppm (SIMS)	300	760	770	1240	790	1150		490	1160	510		690	700	
S ppm (EPMA)	260	770	780	1220	810	1150	1400	670	1130	430	510	610	620	650
F ppm (SIMS)	1460	790	800	840	670	480		1160	490	1790		1440	1440	
Cl ppm (SIMS)	910	550	560	470	380	250		890	250	650		540	540	
Cl ppm (EPMA)	930	580	630	530	450	390	280	1000	280	670	680	610	580	560
Cl ppm (NG)*	860	630		500	420		280	860	270	670	660			550
Br ppb (NG)*	3000	2100		1700	1300		870	2500	840	2100	2100			1900
I ppb (NG)*	53	33		38	27		22	58	21	51	37			53
<i>Selected major elements (wt. %)</i>														
MgO	2.9	5.3	5.3	4.7	5.7	5.8	5.6	2.6	5.9	2.1	4.8	2.8	2.8	2.7
SiO ₂	55.6	49.5	49.1	49.2	49.1	50.5	50.4	54.9	51.1	55.3	48.9	55.7	54.8	54.8
<i>Selected trace elements (ppm)</i>														
Ce	174	88	88	92	95	54	71	118	53	193	144	192	184	227
Nb	78	45	45	47	46	26	33	56	25	92	586	75	72	84
Dy	9.7	7.2	7.1	7.3	6.1	5.3	8.1	10	6.0	12	11	14	12	16
Cu	21	48	50	52	62	49		11	49	1.6		5.8	5.7	
Nd	79	48	46	48	45	30	43	64	31	91	78	98	93	117
K	25,500	12,400	12,200	14,000	13,700	7600	7,500	17,800	7200	28,900	14,700	20,400	21,100	23,700
Sm	15	11	10	10	9.0	7.0	10	14	7.4	17	17	20	19	24
La	76	39	39	44	44	22	32	53	24	95	66	90	87	108
(La/Sm) _N	3.2	2.3	2.4	2.7	3.1	2.0	2.0	2.4	2.0	3.5	2.4	2.8	2.9	2.9
<i>Selected isotopes*</i>														
⁸⁷ Sr/ ⁸⁶ Sr	0.70492	0.70423	0.70427	0.70425	0.70501	0.70443	0.70443	0.70393	0.70443	0.70519	0.70410	0.70527	0.70530	0.70528
¹⁴⁴ Nd/ ¹⁴³ Nd	0.51253	0.51269	0.51272	0.51263	0.51250	0.51266	0.51266	0.51281	0.51270	0.51248	0.51271	0.51248	0.51248	0.51246
²⁰⁶ Pb/ ²⁰⁴ Pb	17.74	18.04	18.04	17.85	17.62	17.95	17.94	18.19	17.95	17.45	18.12	17.51	17.51	17.51
³ He/ ⁴ He (R/Ra)	9.1	(9.1)	9.9	7.7	9.3	7.9	7.6	(3.6)	10.6	(1.6)		(4.4)		(6.9)

* Revised Br and I concentrations from Kendrick et al. (2012b). Isotope data from Woodhead and Devey (1993); Honda and Woodhead (2005). Note that samples containing ⁴He of <10⁻⁷ cm³ STP/g (in brackets), include all samples with ³He/⁴He ratios of <7 R/Ra (Ra = the atmospheric ³He/⁴He ratio of 1.39×10⁻⁶), are not considered representative of the parental magma (Honda and Woodhead, 2005). Note equilibrium degassing pressures have been calculated for basaltic melts containing 49 wt % SiO₂ using VolatileCalc (V.Calc.) and an alternative (Alt.) solubility model (Iacono-Marziano et al., 2012).

Table 2. Sample information and volatile content of Society glasses

Cruise/Sample	CH-DR1 P1-1	CH-DR1 P3-4	CH-DR4 4-2	CH-DR4 4-3	CH-DR4 4-1	CH-DR3 3-1	SO47 9DS-1	CH-DR2 2-1	SO47 29DS-1	SO47 81DS-3
Volcano	Mehetia	Mehetia	Rocard	Rocard	Rocard	Teahitia	Teahitia	NW of Teahitia	Moua Pihaa	Cyana
Dredge depth (m)	2500- 2700*2	2500-2700	2500- 3000*2	2500- 3000*2	2500- 3000*2	2100-2600	2360-2800	3000-3500	2200- 2660	2100- 2600
Eqm. P – V.Calc (bar)		310	220*	250*		190	370		370	180*
Eqm. P – Alt. (bar)		310				220	330		380	
<i>Volatile content</i>										
H ₂ O wt % (SIMS)		1.5	1.3	1.3		0.91	0.95		1.4	1.1
H ₂ O wt % (FTIR)		1.6	1.5	1.6		0.84	0.95		1.5	1.4
CO ₂ ppm (SIMS)		75	19	32		100	160		160	17
S ppm (SIMS)		2490	250	280		1020	980		1800	430
S ppm (EPMA)		2200	220	240	190	1030	980	1300	1610	390
F ppm (SIMS)		1450	2010	2090		1050	1100		1860	990
Cl ppm (SIMS)		950	1350	1360		920	580		1410	1240
Cl ppm (EPMA)		1010	1410	1320	1280	1000	630	940	1460	1300
Cl ppm (NG)*	610	1000	1450	1380	1340	960	590	1030	1180	1210
Br ppb (NG)*	1900	2800	3700	3500	3600	3700	1700	2900	3500	3600
I ppb (NG)*	28	46	71	67	70	42	38	77	49	59
<i>Selected major elements (wt. %)</i>										
MgO		5.3	1.4	1.5	1.2	6.9	6.0	6.4	5.2	1.07
SiO ₂		44.9	61.3	60.9	59.8	45.9	48.6	44.3	44.9	65.2
<i>Selected trace elements (ppm)</i>										
Ce		121	247	216	342	94	110	161	139	141
Nb		66	176	154	220	44	50	75	84	89
Dy		6.9	11	9.1	16	5.7	6.8	10	8.4	6.2
Cu		53	0.5	0.4		94	68		15	0.3
Nd		61	149	104	90	50	59	85	69	60
K		16,200	48,300	50,100	48,400	14,100	20,100	17,200	17,900	46,400
Sm		13	18	16	27	10	12	18	14	11
La		53	112	98	162	39	50	74	61	64
(La/Sm) _N	2.7	2.6	3.8	3.8	3.7	2.4	2.6	2.6	2.7	3.8
<i>Selected isotopes*</i>										
⁸⁷ Sr/ ⁸⁶ Sr	0.70466	0.70428	0.70593	0.70587		0.70464	0.70551		0.70371	0.70450
¹⁴⁴ Nd/ ¹⁴³ Nd	0.51276	0.51289	0.51258	0.51265		0.51271	0.51271		0.51293	0.51289
²⁰⁶ Pb/ ²⁰⁴ Pb	19.10	19.10	19.21	19.22		19.13	19.12	19.10	19.22	18.99
³ He/ ⁴ He (R/Ra)		11.1	7.4		7.8					

* Revised Br and I concentrations from Kendrick et al. (2012b). Isotope data from Devey et al. (1990); Staudacher and Allegre (1989), 3He/4He data are reported relative to the Ra, the atmospheric ³He/⁴He ratio of 1.39×10⁻⁶. *2 ‘popping rocks’ (Hekinian et al., 1991). Note equilibrium degassing pressures calculated with VolatileCalc (V.Calc.) assumed basaltic composition with <49 wt % SiO₂ and a rhyolite* compositions for melts with >60 wt % SiO₂. An alternative (Alt.) pressure was calculated for the least evolved melts using the solubility model of Iacono-Marziano et al. (2012).

Table 3. Matrix and vesicle volatile contents

Sample	Matrix (SIMS)		Vesicles (crushing) ¹			% in Vesicles	
	CO ₂ ppm	H ₂ O Wt %	Vol. %	CO ₂ ppm	H ₂ O Wt %	CO ₂	H ₂ O
CH DR1 P3-4	75	1.5	29%	2831	0.41	97%	21%
CH DR4 4-2	19	1.3	8.6%	372	0.15	95%	10%

1 – Data of Aubaud et al. (2005).

Table 4. Representative magma volatile characteristics in different settings¹

	H ₂ O/Ce	H ₂ O/Cl	F/Cl	Br/Cl ×10 ⁻³	I/Cl ×10 ⁻⁵	K/Cl
<i>Mantle-derived melts</i>						
Arc/Back Arc Basin	1000-3000	5-80	0.2-1.5	1-3.2	3-90	~1
Basalts ²						
MORB ³	150-250	10-50	~1-10	2.8-3.2	3-9	10-20
EM1 Pitcairn	80	30-40	1.5-3	2.8	5-9	>40
EM2 Society/Samoa	60	10-20	1.5-3	3.2	4-8	>40

1 – The data are compiled from published analyses of melt inclusions or submarine glasses that have not been affected by degassing or assimilation of seawater-derived components [which would reduce all X/Cl ratios (except Br/Cl) to lower values (Kendrick et al., 2013a)].

2- Manus Basin (Sinton et al., 2003; Kendrick et al., 2012b; Shaw et al., 2012); Kamchatka Arc (Portnyagin et al., 2007); Izu-Bonin Arc (Straub and Layne, 2003); Sunda Arc (Vigouroux et al, 2012); Lau Basin (Hahm et al., 2012).

3 - Jambon et al. (1995); Kendrick et al. (2012a; 2013a); Micheal (1995); Schilling et al. (1978; 1980).

Fig 1

Fig 1. The $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ systematics of the Pitcairn and Society melts included this study (Devey et al., 1990; Honda and Woodhead, 2005). MORB from two previous halogen studies are shown for reference (Kendrick et al., 2013a; 2012a), note that MORB occupy a large part of this diagram with typical $^{87}\text{Sr}/^{86}\text{Sr}$ in the range of 0.7021-0.7035 and $^{206}\text{Pb}/^{204}\text{Pb}$ in the range of 17.5 to 19.5 (see Hofmann, 2003 or Stracke, 2012).

Fig 2

Fig 2. Sketch locality maps showing the approximate positions of dredges undertaken during voyages of the FS Sonne and NO Jean Charcot to the Society and Pitcairn seamounts during the 1980's. Bathymetric data and dredge locations for these localities were reported in Cheminee et al. (1989), Stoffers et al. (1987; 1990) and Devey et al. (1990; 2003). The inset shows the positions of the Society and Pitcairn seamount chains in the South Pacific, with respect to the East Pacific Rise (EPR), Tonga Trench and New Zealand (NZ).

Fig 3

Fig 3. ab) Major element compositions of Pitcairn and Society glasses with classification after Le Bas and Streckeisen (1986). c) SiO₂ versus ⁸⁷Sr/⁸⁶Sr.

Fig 4

Fig 4. Comparison of S, H₂O and Cl measurements by electron microprobe at Oregon State University, FTIR at the University of Oregon, SIMS at the Carnegie Institute and the noble gas method at the University of Melbourne. The 1:1 line and 10% envelopes are shown in each plot together with the average difference between the techniques which is based on best fit data regressions forced through the origin.

Fig 5

Fig 5. a) SIMS CO₂ and H₂O concentrations in Society and Pitcairn melts showing isobars (lines of constant pressure) calculated for a basalt with 49 wt % SiO₂ at 1200 °C using the VolatileCalc program (Newman and Lowenstern, 2002). b) Pressure in bars estimated from the dredging depth and calculated for the H₂O and CO₂ concentrations using VolatileCalc (Table 1 and 2; note that Society samples with >60 wt % SiO₂ were modelled as rhyolite).

Fig 6

Fig 6. Pitcairn and Society glass volatile and incompatible element concentrations as a function of MgO. Column a) CO₂, S and Cu (a chalcophile element); column b) H₂O, Cl and K (a lithophile element with incompatibility similar to Cl and H₂O). Liquid lines of descent calculated with Petrolog3 (Danyushevsky and Plechov, 2011) are shown for fractional crystallisation of hypothetical MORB and enriched-mantle (OIB) components assuming H₂O, Cl and K are excluded from all crystallising phases (see text). Increments of 10% are shown, with melts of ~1 wt % MgO produced by crystallisation of ~80-85% of the original magma. column c) F, Br and I concentrations are governed by similar processes as Cl, but modelled liquid lines of descent are not shown.

Fig 7

Fig 7. Volatile/non-volatile ratios of CO_2/Nb , H_2O/Ce , Cl/K and F/Nd as a function of calculated equilibration depth (see Fig 5b). Melts equilibrated at pressures of more than 150 bars are suggested to have retained their H_2O as well as halogens during degassing.

Fig 8

Fig 8 Volatile/non-volatile ratios of $\text{H}_2\text{O}/\text{Ce}$, Cl/K , F/Nd , Br/K and I/K and the $\text{H}_2\text{O}/\text{Cl}$ ratio as a function of mantle enrichment measured by $^{87}\text{Sr}/^{86}\text{Sr}$. Note that for clarity, the H_2O data are not shown for 45-DS-1 which is indicated to have lost H_2O in Fig 7b. The correlation coefficients in each plot are for the slopes defined by the combined Pitcairn and Society data.

Fig 9

Fig 9. Halogen and H₂O data for the Pitcairn and Society melts. Assimilation of seawater-components such as high salinity brines would produce strong co-variation in Br/Cl, I/Cl, F/Cl, K/Cl and H₂O/Cl which is not observed. High salinity brines are characterised by higher than seawater Br/Cl ratios, whereas altered ocean crust (AOC) is expected to have lower than seawater Br/Cl (Kendrick et al., 2013a). The italicised bold numbers inside the H₂O/Cl axes indicate salinity in wt % salts. Note that the mantle field in d is based on the compiled data of Kendrick et al. (2013a) which show no significant difference between OIB and MORB (see also Schilling et al 1978; 1980).

Fig 10

Fig 10. F/Cl versus K/Cl in Pitcairn and Society melts. K/Cl increases toward the enriched mantle end-member because K is preferentially subducted into the mantle compared to Cl (Fig 9c; (Kendrick et al., 2012b; Stroncik and Haase, 2004). F/Cl is correlated with K/Cl in the Pitcairn melts.

Fig 11

Fig 11. $^3\text{He}/^4\text{He}$ (R/Ra) versus $\text{H}_2\text{O}/\text{Ce}$ for Pitcairn and Society samples containing $>10^{-7} \text{ cm}^3 \text{ STP/g } ^4\text{He}$ (Tables 1 and 2; Staudacher and Allegre, 1989; Honda and Woodhead, 2005). Note that Pitcairn samples have an average $^3\text{He}/^4\text{He}$ of 9 R/Ra that is similar to MORB (Graham, 2002), and that $^3\text{He}/^4\text{He}$ is not correlated with $\text{H}_2\text{O}/\text{Ce}$. The $^3\text{He}/^4\text{He}$ ratios are given relative to the atmospheric value of 1.39×10^{-6} .