Volatile and Trace Elements in Basaltic Glasses from Samoa: Implications for Water Distribution in the Mantle

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ABSTRACT

We report volatile (H_2O, CO_2, F, S, Cl) and trace element data for submarine alkalic basalt glasses from the three youngest Samoan volcanoes, Ta'u, Malumalu and Vailulu'u. Most samples are visibly sulfide saturated, so have likely lost some S during fractionation. Cl/K ratios (0.04 – 0.15) extend to higher values than pristine MORBs, but are suspected to be partly due to source differences since Cl/K roughly varies as a function of $^{87}Sr/^{86}Sr$. There are no resolvable differences in the relative enrichment of F among sources, and compatibility of F during mantle melting is established to be nearly identical to Nd. Shallow degassing has affected CO_2 in all samples, and H_2O only in the most shallowly erupted samples from Vailulu'u. Absolute water contents are high for Samoa (0.63 – 1.50 wt%), but relative enrichment of water compared to equally incompatible trace elements (Ce, La) is low and falls entirely below normal MORB values. H_2O/Ce (58 – 157) and H_2O/La (120 – 350) correlate inversely with $^{87}Sr/^{86}Sr$ compositions (0.7045 – 0.7089). This leads us to believe that, because of very fast diffusion of hydrogen in mantle minerals, recycled lithospheric material with high initial water and trace element content will lose water to the drier ambient mantle during storage within the inner Earth. The net result is the counter-intuitive appearance of greater dehydration with greater mantle enrichment. We expect that subducted slabs will experience a two-stage dehydration history, first within subduction zones and then in the ambient mantle during long-term convective mixing.

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INTRODUCTION

It is now well established that the distribution of water in Earth's mantle strongly determines the locations and extents of mantle melting (Asimow and Langmuir, 2003; Asimow et al., 2004) along with mantle rheology (Hirth and Kohlstedt, 1996; 2003). However, before we come to a geochemical understanding of water abundances in the mantle, it is necessary to interpret water and other volatile element concentrations in derivative mantle melts. Key issues to understanding primary volatile contents in melts and hence mantle sources are 1) extent of degassing upon eruption, 2) degree of melting and 3) relative enrichment of volatile elements compared to lithophile elements. Volatile element such as hydrogen, carbon, fluorine, sulfur and chlorine are, by nature, decoupled from lithophile elements at or near the Earth's surface. Due to this phenomenon, these elements provide a possible fingerprint of processes that are not actively recorded by the standard suite of incompatible trace elements (e.g. Sr, Rb, U, Th, and the rare earth elements) and may be indicators of the origins of mantle heterogeneities.

Lavas from the Samoan islands and seamounts have unique geochemical characteristics compared to other ocean island basalts (OIBs) as well as mid-ocean ridge basalts (MORBs), including extreme $^{87}Sr/^{86}Sr$ (up to 0.7089), low $^{143}Nd/^{144}Nd$ (down to 0.5125), and highly trace element enriched lavas (Wright and White, 1986; Farley et al., 1992; Workman et al., 2004). These characteristics define the Enriched Mantle 2 reservoir (EM2; Zindler and Hart, 1986). EM2 has classically been interpreted as oceanic crust and terrigeneous sediment that had been recycled back to the mantle through subduction zones (e.g. Weaver, 1991). Upon closer inspection, the standard recycling model of ocean crust/sediment fails as an explanation for producing EM2, due to smooth trace element patterns, low $^{187}Os/^{188}Os$ ratios, incorrect Pb isotope compositions, and high $^{3}He/^{4}He$ ($>8R_A$) in Samoan lavas (Workman et al., 2004). Instead, the origin of EM2 has been modeled with the ancient formation of metasomatised, oceanic mantle lithosphere, followed by storage in the deep mantle and return to the surface in the Samoan plume. Although Samoa is strongly EM2 in character, other mantle reservoirs, such as HIMU (high $^{238}U/^{204}Pb$ mantle; Zindler and Hart, 1986) and PHEM (**P**rimitive **He**lium **M**antle; Farley et al., 1992), are thought to contribute to the Samoan lavas, and hence in one location there is extreme compositional heterogeneity.

Here we report a study of volatile element concentrations in Samoan lavas in order to assess their relative enrichment compared to other trace element and isotope signatures, and to use them as potential clues to the origin of compositional variations in the mantle. We find that water enrichment (identified by H_2O/Ce and H_2O/La ratios) in EM2 lavas has an inverse relationship to lithophile element enrichment (e.g. high Rb/Sr and $^{87}Sr/^{86}Sr$ ratios). The metasomatic model for the formation of EM2 (Workman et al., 2004) would not result in fractionation of water from the lithophile elements, so cannot directly account for the low relative abundance of water compared to other trace elements in "enriched" lavas.

However, the fast diffusion of water through mantle minerals (Mackwell and Kohlstedt, 1990; Wang et al., 1996; Woods et al., 2000; Stalder and Skogby, 2003) provides a very effective means of losing water from EM2 to a water-poor ambient mantle during the long-term (~2.5 Ga) storage of EM2 – to the point of there being very similar bulk water contents (<100 ppm) in EM2 and the Depleted MORB Mantle (DMM). This finding leads credence to the idea that enriched mantle plumes are indeed "hot-spots" (Morgan, 1971; Sleep, 1990; Campbell and Griffiths, 1990) and not "wet-spots" (Schilling, et al., 1980; Green and Falloon, 1998).

2. BACKGROUND

2.1. Geological and Geochemical Setting

The Samoan islands and seamounts are centered on 14°S latitude, stretch from 169-177.5°W longitude (fig. 1), and rest on the outer rim of the geophysical "superplume" of the South Pacific (Su et al., 1994). Seismic tomography images from beneath Samoa show a slow velocity anomaly extending into the lowermost mantle (Montelli et al., 2003), supporting a deep origin for upwelling mantle material feeding the Samoan hotspot. The tectonic setting of Samoa is complicated by having the northern termination of the Tonga Trench only 100 km to the south of the island chain. Hart et al. (2004a) have given a synthesis of the regional tectonic history and how plume-trench interaction has influenced the distribution of Samoan volcanism, specifically the *en-echelon* topographic ridges seen in Figure 1. Hart et al. (2004a) also established, from K-Ar dating and isotope geochemistry of seamounts extending to the west of Savaii, that the Samoan plume has been active for at least 25 million years, producing a 1700 km long volcanic chain.

The easternmost, leading-edge Samoan volcano is the seamount, Vailulu'u (fig. 1); it rises from a 5000 m deep seafloor to a summit depth of 590 m and rests 45 km east of its nearest neighbor, Ta'u Island (Hart et al., 2000). Vailulu'u has been shown to be both volcanically and hydrothermally very active (Hart et al., 2000; Hart et al., 2003; Staudigel et al., 2004; Konter et al., 2004). The power output from Vailuluu's summit crater is estimated to be 610-760 MW, the equivalent of 20-100 Mid-Ocean Ridge black smokers; Mn export is estimated at 240-300 kg/day, or the equivalent of about 10 black smokers (Staudigel et al., 2004; Hart et al., 2003). High ^{3}He anomalies exist in the water column above Vailulu'u, showing that at least this volatile element is actively degassing from upwelling magmas (Staudigel et al., 2004). We suspect that the hydrothermal circulation of seawater and degassing of magmas observed at Vailulu'u is representative of all the Samoan volcanoes at this stage of growth.

One goal of this study is to understand volatile enrichments/depletions as a function of mantle source composition. Each of the three Samoan volcanoes of this study has a distinct and well-characterized geochemical signature, discussed in detail by Workman et al. (2004). In summary, Malumalu displays the most extreme EM2 signature yet documented from ocean island basalts, with ^{87}Sr/^{86}Sr up to 0.7089 and extreme trace element enrichment. Ta'u shows some of the least enriched lavas from Samoa, with Sr-Nd-Pb isotopic values that are close to the mantle component PHEM (**P**rimitive **He**lium **M**antle of Farley et al. [1992]; ^{87}Sr/^{86}Sr = 0.7045); for Ta'u this corresponds to ^{3}He/^{4}He up to 18 R$_{A}$ and a lesser degree of trace element enrichment. Vailulu'u lavas are of intermediate enrichment and are thought to contain a small component of HIMU mantle, giving Vailulu'u the highest ^{206}Pb/^{204}Pb (19.4) in all of Samoa.

2.2. Samples and Volcano ages

Glass samples from the three youngest Samoan volcanoes, Vailulu'u, Malumalu, and Ta'u, have been taken from glassy rims of pillow basalts dredged during the 1999 AVON2/3 cruise aboard the R/V Melville. In this paper, we report data on samples obtained from 11 dredges ranging from 780 to 4170 meters deep – 6 from Vailulu'u, 2 from Ta'u and 3 from Malumalu (see Table 1). All Ta'u and Malumalu dredges are from a similar depth of 2300 – 3600 meters, whereas the shallowest and deepest dredges are from Vailulu'u.

All samples have some vesicles, most with less than 10% by volume and none over about 30%, indicating that these samples have experienced volatile exsolution during eruption. All dredges except 72 (Vailulu'u) and 75 (Ta'u) have sulfides present in nearly every sample (see Table 1); these occur as 10-50 μm spheres and are visible under reflected light in the glass chips that were analyzed. Micro-phenocryts of olivine, spinel, and clinopyroxene are common within the glasses. In a few of the olivine phenocrysts, melt inclusions have been fortuitously exposed, so were analyzed for their volatile contents to compare with volatile abundances in the matrix glass; however, the melt inclusions have not yet been properly studied for major elements and mineral-melt equilibration.

U-series data have been collected for lavas from each Vailulu'u and Malumalu dredge (Sims and Hart, 2004), including the following samples studied here: 63-13, 70-01, 71-02, 71-09, 72-02, 73-01, 73-03, 73-12, 76-01, 78-01. All the above samples show ^{230}Th/^{238}U excesses and are interpreted to be from lava flows that are less than 300 thousand years old. The ^{230}Th/^{238}U excesses shown from Malumalu are similar to those on Vailulu'u, suggesting that Malumalu is not significantly older than Vailulu'u. Two samples from Vailulu'u (63-13 and 70-09) show ^{210}Pb disequilibria and are interpreted to be less than 100 years old (Hart et al., 2000).

The oldest K-Ar age from Tau Island is 0.3 Ma (McDougall, 1985). The youngest volcanic series on Tau (Faleasao) is probably younger than 37,000 years, based on ^{14}C ages of coral inclusions in these volcanics (Hart, unpublished). Additionally, there was an underwater eruption just west of Tau in 1866 (see description in Keating, 1992).

3. ANALYTICAL TECHNIQUES

Multiple glass chips from the quenched rims of dredged pillow basalts were hand-picked and mounted with epoxy for ion microprobe analyses. Volatile abundances (H_2O, CO_2, F, S and Cl) were determined by triplicate analyses (on multiple glass chips) on the Cameca IMS 6f ion microprobe at the Department of Terrestrial Magmatism with a 5-10 nA Cs^+ primary beam. See Hauri et al. (2002) for a full description of the mircobeam method. Trace elements were determined on the same area of glass using the same instrument, but with an O^- primary beam. Reproducibility of the volatile concentrations is typically 2-6% (2σ); accuracy is estimated at 10% (2σ) for H_2O and 5% for the other volatiles, based on an error analysis of uncertainties and scatter of standard data about the calibration lines for mafic glasses.

For Sr isotope analyses, glass chips were hand-picked and leached for 1 hour in 6N HCl. Sr was separated by a standard cation exchange procedure described in Taras and Hart (1987). Isotopic analyses were carried out on the NEPTUNE multi-collector ICP/MS at W.H.O.I.; ^{87}Sr/^{86}Sr values are corrected to 0.71024 for NBS 987 and carry a 2σ precision equal to ±25 ppm (Hart et al., 2004b).

4. RESULTS

Volatile and other trace element concentrations for Samoan glasses are listed in Table 1. Major element abundances of the glasses were analyzed by electron microprobe at MIT and have been previously published (Workman et al., 2004). Sr, Nd and Pb isotope measurements have been made on a few whole rock samples (for which we now report glass data) and are also published in Workman et al. (2004). New $^{87}Sr/^{86}Sr$ measurements on glass samples are reported in Table 1, and range from 0.70452 to 0.70841, within the previously established range for whole rock analyses of Samoan lavas (Workman et al., 2004). The $^{87}Sr/^{86}Sr$ compositions of glass and whole rock pairs for individual samples have been found to be within analytical error (Jackson et al., unpubl.).

4.1. Water and carbon dioxide in glasses

The Samoan lavas show a large range in raw H_2O (0.63 – 1.50 wt%) and CO_2 (6 – 233 ppm) contents (fig. 2a; Table 1). Such water contents are highly elevated over MORBs (fig. 2b), but are very similar to Hawaii's submarine lavas from Loihi Seamount (Dixon and Clague, 2001) and the North Arch lava field (Dixon et al., 1997), and to melt inclusion data from the Austral Islands (Lassiter et al., 2002). Water content in OIB lavas is generally lower than in arc lavas (where water can be up to ~6 wt%) but in the same range as back-arc basin lavas (e.g. Newman et al., 2000, for the Marianas system).

The presence of vesicles (1-30 vol%; Table 1) in every sample indicates that these lavas were all vapor saturated during eruption onto the seafloor. Some vapor loss can be accounted for by correcting for vesicle gases (i.e. the manifestation of closed system degassing). As a test for the severity of water loss, vesicle abundances were determined in 3 of the most vesicle-rich samples, 73-01, 73-03, and 78-03, by point-counting standard-sized thin sections. By volume, these contain 31%, 20% and 24% vesicles, respectively. Adding equilibrium vapor compositions back into the glasses, following the procedure described in Dixon et al. (2002), results in increases in bulk water content on the order of 0.03 to 0.05 wt%. Because this level of correction is within error of the analyses, we chose not to make vesicle corrections for all samples in the Samoan suite. After vesicle correction, the three point-counted samples would still have some of the lowest water abundances in the suite; it is likely that these lavas have experienced open-system degassing with bubble loss, prior to their final eruption and emplacement on the seafloor.

H_2O-CO_2 solubility models (Stolper and Holloway, 1988; Dixon et al., 1995; Dixon, 1997) show that CO_2 is much more insoluble than H_2O in basaltic magmas. As a result, with Samoan water contents, vapor compositions during open-system degassing are almost entirely CO_2 until pressures drop below ~100 bars (ocean depth of 1000 meters) (Newman and Lowenstern, 2002). In Figure 2a, the arrow at the end of the degassing trend marks the sharp change from CO_2-dominated to H_2O-dominated vapor compositions; above this point, open-system degassing results in nearly negligible water loss.

In Figure 2c, calculated equilibrium saturation pressures (using the Dixon [1997] model for H_2O-CO_2 saturation in alkali basalts) are plotted with collection depth. Lavas that lie very close to the 1:1 line erupted close to their dredge depth. Lavas below the 1:1 line are are interpreted to have erupted more shallowly and flowed down slope; lavas above the line experienced incomplete degassing (i.e. rapid quenching). Note that some scatter is because dredges are along flanks of the volcanoes and hence may traverse 100's of meter of depth contours (see fig.1); the quoted dredge depth is the average for each dredge and may not represent every sample accurately.

As indicated by carbon dioxide concentrations and pressures of equilibration, both the most and the least degassed samples are from Vailulu'u: the deep dredges (71 and 72 from 4200 m and 3800 m deep, respectively) show water contents up to 1.50 wt%, and the shallowest dredges (63, 68, 70, and 73 at or near 1000 m) have water contents down to 0.63 wt%. The low water in the shallow dredges is the result of degassing a water-rich vapor (fig. 2a). Ta'u and Malumalu lavas all have high enough pressures of equilibration (fig. 2c) to preclude loss of significant water by open system degassing.

In summary, degassing has affected CO_2 in all samples, and H_2O only in the most shallowly erupted samples from Vailulu'u. Additional support for minimal water loss is the fact that most melt inclusions have water contents identical (within error) to their host matrix glasses, but with equal or higher CO_2 (Tables 1 and 2; the one exception is a melt inclusion from sample 71-03, which has lower CO_2 and H_2O than its matrix glass). One melt inclusion from sample 72-12 shows the highest pressure of vapor saturation at 818 bars, indicating a minimum crystal fractionation depth of 1.6 km within the oceanic crust (3840 meters dredge depth plus 1600 meters igneous crust at a rock density of 2800 kg/m^3).

4.2. Trace elements and fractionation correction

All the glasses presented here are evolved beyond clinopyroxene saturation, as identified by: 1) low Mg#'s (molar percent of Mg/[Mg+Fe^{+2}]), ranging from 39 to 61; 2) positive correlations between Mg# and CaO; 3) presence of clinopyroxene phenocrysts in whole rock samples; and 4) liquid lines of descent predicted by the pMELTS model (see fig. 3a). They are all alkali basalts, with SiO_2 from 45.5 to 48.9 wt% and total alkalis (K_2O+Na_2O) from 3.2 to 6.1 wt% (fig. 3b). The glasses are generally further along on fractionation trends than their whole rocks (fig. 3a) due to the exclusion of phenocrysts in the glasses. Mg#'s of aphyric whole rocks are equal to or slightly higher than their glasses, but some glasses come from picritic samples with Mg#'s up to 81-84.

Trace element patterns of the glasses closely parallel whole rock trace element patterns (from Workman et al., 2004) of each volcano. La/Sm and Sm/Yb ratios for glass and whole rock pairs are usually within analytical error, showing that the fractionation of olivine and clinopyroxene has had little effect on incompatible element ratios. Hence, using the data in this way (as elemental ratios) would be the most reliable in assessing primary melt characteristics.

La/Sm values of the glasses range from 3.3 to 7.5 and correlate positively with $^{87}Sr/^{86}Sr$, a proxy for source enrichment (i.e. Ta'u has the lowest and Malumalu has the highest La/Sm; not shown). Sm/Yb, on the other hand, does not correlate with enrichment, and the three volcanoes overlap in values from 2.9 – 5.6. For comparison, N-MORB La/Sm and Sm/Yb ratios are each ~1.0 (Hofmann, 1988). The steepness of the rare-earth element slopes indicates melting within the stability field of garnet lherzolite or melting to small degrees within the stability field of spinel lherzolite (Hauri et al., 1994; Salters et al., 2002), as to be expected to occur beneath an old tectonic plate where the bottom of the lithosphere (e.g. Li et al., 2004) is near the garnet to spinel transition (Kogiso et al., 1998; Robinson and Wood, 1998; Klemme and O'Neill, 2000).

In order to estimate the compositions of primitive Samoan magmas, we have corrected the raw trace element data for crystal fractionation by using the pMELTS trends (Ghiorso et al., 2002) to calculate the remaining liquid mass as a function of Mg# (see fig. 3a for details). The degree of fractionation ranges from 17% to 66%, with the majority of lavas falling within the range of 30 – 46% fractionated. Figure 3a shows that Malumalu and Ta'u lavas lie along very similar fractionation lines. Vailulu'u lavas are on a separate trend at higher CaO, with shallow dredges (63, 68, 70 and 73) being more fractionated on average than deep dredges (70 and 71). We assume that the fractionating minerals have trace element concentrations of zero.

The same fractionation corrections have been applied to the volatile contents, assuming that crystal fractionation happened at vapor under-saturated conditions. Figure 4 shows the fractionation-corrected abundances of volatile elements and a select group of trace elements, listed in the order of increasing compatibility during mantle melting. Concentrations are normalized to primitive upper mantle (PUM); most values for PUM are taken from McDonough and Sun (1995) except for CO_2 and H_2O, which are calculated assuming that PUM has a CO_2/Nb ratio of 239 (Saal et al., 2002) and an H_2O/Ce ratio of 200 (the value for FOZO observed by Dixon et al., 2002). This plot allows for a brief overview of the relative enrichments of volatile elements compared to the trace elements. For all volcanoes, the negative anomalies for CO_2, H_2O, and S indicate that these volatiles are less enriched in the lavas than lithophile elements of similar compatibility (this partially reflects volatile degassing, especially for CO_2); the opposite is true for the positive anomaly at Cl for most of the Vailulu'u lavas. F is the only volatile element that is consistently "conformable" with the lithophile elements in all samples. In the following sections, we attempt to discern which of these signals are primary and how they can be used to understand the composition and evolution of the mantle.

4.3. Water and carbon dioxide in primary magmas

After correcting for crystal fractionation (see section 4.2), we estimate primary magmas to have H_2O in the range of 0.4 – 1.1 wt%. Shallowly erupted Vailulu'u lavas are once again at the lower limit of this range, representing the greatest losses of water by both open- and closed-system degassing.

Original CO_2 concentrations in the primary magmas can be estimated using the observation that CO_2/Nb ratios are roughly constant in volatile under-saturated MORB melt inclusions from the Siquieros Transform (Saal et al., 2002) – it is still highly uncertain whether or not this ratio applies to OIBs. Using fractionation-corrected Nb concentrations and CO_2/Nb equal to 239 (Saal et al., 2002), 95% of the data suggest primary CO_2 contents in the narrow range of 0.8 to 1.2 wt%.

We have used the H2O-CO_2 degassing program by Newman and Lowenstern (2002; based on the model by Dixon, 1997, for degassing of alkali basalts) to estimate the maximum water loss from deep, open-system degassing, and find that a primary magma with 47 wt% SiO_2 and initial volatile content of 1.2 wt% H_2O and 1.0 wt% CO_2 will still have 1.15 wt% H_2O after CO_2 has degassed to ~10 ppm. This difference is within the analytical error for water and provides evidence that the observed water contents for all lavas except those from the shallow Vailulu'u dredges (63, 68, 70 and 73) are robust estimates of original abundances of water.

At the pMELTS-modeled fractionation pressures of 3-4 kbar, the data indicate that CO_2 is the only strongly oversaturated volatile component, as it is very insoluble in basaltic magmas (Stolper and Holloway, 1988; Dixon et al., 1995; Dixon, 1997). Carbonatitic metasomatism has been documented in Samoan xenoliths (Hauri et al., 1993), and may be further evidence for deep CO_2 degassing.

4.4. Fluorine

Raw F contents range from 800 to 1890 ppm and are well correlated with incompatible trace elements including P, Na, K and Ti (fig. 5; Table 1). Fractionation-corrected values for F are 480 to 880 ppm and closely overlap primitive Hawaiian melt inclusions that have 300 to 1000 ppm F (Hauri, 2002). These values are similar to other plume related lavas, but are significantly higher than in MORBs (e.g. Schilling et al., 1980; fig. 5).

There are no resolvable differences in the relative enrichment of F between the different volcanoes or the different dredges; instead there is a constant F/Nd ratio of 21.7 ± 2.6 (2σ) across the whole sample suite, indicating F compatibility equal to that of Nd. Figure 5 shows that Samoa glasses, together with normal MORBs (PETBD database: http://beta.www.petdb.org/), very depleted MORBs (from the Siquieros Transform; Saal et al., 2002; Saal et al., unpubl.) and Primitive Upper Mantle (McDonough and Sun, 1995), all fall along a F/Nd line of 21. Siquieros samples alone (Saal et al., 2002) show a mean F/Nd of 19.4 ± 2.6 (1σ), whereas all MORBs show F/Nd = 20.1 ± 5.8 (1σ). Continental crust is also estimated to have a F/Nd ratio within this range (at 20.7; Wanke et al., 1984). To our knowledge, the only basalts that fall dramatically off this line are melt inclusions from the Austral Islands showing F/Nd ratios that are generally 60-70 (Lassiter et al., 2002). Elevated F may be a characteristic of the HIMU mantle end-member that is represented by lavas from the Austral island chain (Hauri and Hart, 1993). However, Vailulu'u glasses, which are thought to contain a small HIMU component (Workman et al., 2004), show no systematic elevation of F.

4.5. Sulfur

Sulfur in the Samoan glasses ranges from 781 – 2651 ppm, consistent with other oceanic basalts (Wallace and Carmichael, 1992). As discussed above, most glasses are saturated with a sulfide phase, so have likely lost some S by fractionation. Figure 6 shows the rough positive correlation between S/Dy and Mg# of the whole suite of Samoan glasses (note that S and Dy have been suggested to have similar compatibilities during mantle melting [Saal et al., 2002], so S/Dy should not change as a function of melting or olivine/clinopyroxene crystallization, but will decrease if sulfides are fractionated from a melt). However, for a given Mg#, there is a very wide range of S/Dy, suggesting that fractionation of sulfides may not be the only factor in controlling relative S depletions.

At the FeO contents of Samoan glasses (10.5 – 14.2 wt%), S concentrations are higher than they are in sulfide-saturated MORBs, possibly because Samoan lavas have higher oxygen fugacities (see Dixon, 1997; Dixon and Clague, 2001). Sulfide saturation is a complicated function of fO_2, temperature, pressure and melt composition (e.g. Wallace and Carmichael, 1992; Mavrogenes and O'Neill, 1999), making further analysis of S beyond the scope of this paper.

4.6. Chlorine

Raw Cl contents of the Samoan glasses fall within the range of 451-1815 ppm (Table 1); fractionation-corrected values are 269-1412 ppm, similar to other plume related magmas (e.g. Dixon and Clague, 2001; Simons et al., 2002), but much greater than estimated parental MORBs (at <100 ppm; Michael and Cornell, 1998). Glasses from Vailulu'u and dredge 76 from Malumalu have the highest Cl, while Ta'u glasses fill the lower half of the whole range. Cl saturation in basaltic melts is greater than 2 wt% at these water contents (Webster et al., 1999), so we expect that there was no Cl degassing at any point in the evolution of the magmas.

Curiously, of all the volatile and trace elements, Cl is best correlated with S across the whole Samoan suite (fig. 7). There is no reason to expect these two elements to have either similar compatibilities or similar behavior in magmatic systems. Figure 8 shows the relationship between Cl and K (the element most often used in assessing relative Cl enrichments; see below).

The lowest Cl/K ratios (~0.04) are found primarily in glasses from Ta'u (dredges 74 and 75) and Malumalu (dredge 78), and the highest ratios are from a collection of Vailulu'u dredges that range in Cl/K from 0.10 – 0.15.

There is much precedent for interpreting high Cl concentrations in oceanic basalts as being a product of seawater assimilation (Michael and Cornell, 1998; Kent et al., 1999; Lassiter et al., 2002; Simons et al., 2002; Stroncik and Haase, 2004) due to very high concentrations of Cl in seawater and especially in brines (Kent et al., 1999). For example, 15% brine derived from seawater contains about 10 wt% Cl (Kent et al., 1999), and it would take only 1% of this brine to elevate a magma's Cl content from 500 to 1500 ppm (almost the full range in Samoa). With the same amount of brine, there would be a negligible effect on most other trace elements (including K), so the easiest way to identify assimilated chlorine is when there is variable Cl concentration at invariable concentrations of other trace lithophile elements. The Samoan suite presents a challenge because there is variable (and high) K content in conjunction with variable (and high) Cl content; the same relationship is observed for Cl with other trace elements, including fluid-immobile elements such as Nb.

A study by Michael and Cornell (1998) found that Cl/K ratios in MORBs that are unaffected by seawater contamination range from 0.01 – 0.07, with depleted MORBs at the low end and enriched MORBs at the high end of this range. By omitting samples that fall along brine assimilation trends, Stroncik and Haase (2004) also found Cl/K ratios in OIBs to be a function of source signatures, as recognized by their correlation with Sr and Pb isotopic values. They report enriched mantle (EM1 and EM2) lavas to have low Cl/K ratios (down to 0.02) and HIMU lavas to have Cl/K ratios up to 0.08 (Stroncik and Haase, 2004). Also, plume-influenced glasses from the Easter Seamount Chain, having Cl concentrations interpreted as primary based on good correlations between Cl and La, show Cl/K ratios from 0.05 up to 0.12 (Simons et al., 2002), similar to our Samoan glasses.

The relationship between Cl/K and $^{87}Sr/^{86}Sr$ for Samoa is displayed in Figure 8. The most extreme EM2 lavas (Malumalu, dredge 78) at high $^{87}Sr/^{86}Sr$ have some of the lowest Cl/K. With decreasing $^{87}Sr/^{86}Sr$, Cl/K ratios increase up to a maximum value of 0.15 in the Vailulu'u lavas (that have a small HIMU component; see background section above) and then drop to MORB-type values in Ta'u. This result is in general agreement with Stroncik and Haase (2004), despite our absolute Cl/K and $^{87}Sr/^{86}Sr$ ranging to significantly higher values. On the other hand, the minimum Cl/K ratio from each volcano is ~0.04 and could be taken as the primary composition for all of Samoan magmas before Cl contamination.

There are a few observations that do not support high levels of Cl assimilation. If 1% of a brine (or any seawater-derived fluid) was assimilated, water contents of the lavas would approximately double, but anomalous water contents are not observed in any of the lavas. Also, the few melt inclusions we have analyzed (Table 2) have Cl contents usually within error of their host matrix glasses. Lastly, Figure 7 indicates that high Cl magmas also have high S, and no known assimilant, (including hydrothermally altered oceanic crust) contains both Cl and S in such similar proportions.

A study on chlorine isotopes (e.g. Magenheim et al., 1995) might provide compelling evidence against an assimilation origin for the high Cl, and ultimately may be the only way to define the proportion of igneous- to assimilation-derived Cl.

5. SOURCE VARIATIONS IN WATER ENRICHMENT

Since water plays such an important role in mantle melting and rheology, it is crucial to understand the possible variations in water content of mantle source materials. Furthermore, it has been suggested (e.g. Dixon et al., 2002) that variations in water enrichment/depletion can be used to identify the origins of some mantle heterogeneity. These issues are explored below in light of the new Samoan dataset.

During mantle melting, the compatibility of water is similar to Ce and La, as determined both observationally (e.g. Michael, 1995; Danyushevsky et al., 2000) and experimentally (Hauri et al., in revision). As such, ratios of H_2O/Ce and/or H_2O/La have been used as direct indicators of mantle source compositions. For example, low H_2O/Ce ratios in Loihi magmas (Dixon and Clague, 2001) and plume-influenced MORBs (Dixon et al., 2002) have been used to argue for the presence of recycled oceanic crust and sediment that had been efficiently dehydrated during subduction.

The relationship between H_2O/La and ^{87}Sr/^{86}Sr in Samoan basalts (fig. 9) extends the observation by Dixon et al. (2002) that enriched mantle sources have relative depletion of water (note that H_2O/La is used rather than H_2O/Ce since H_2O and La are most similar in compatibility during melting of garnet lherzolite [Hauri et al., in revision]). The Samoan glasses have a wide range in ^{87}Sr/^{86}Sr (0.7045 – 0.7089) that is inversely correlated with H_2O/La (ranging from 120 to

316). The highest H_2O/La ratios in Samoa overlap with the low H_2O/La end of the plume-influenced Discovery lavas from the S. Atlantic (Dixon et al., 2002). Otherwise, all Samoa glasses have much lower H_2O/La ratios than do average MORBs or average Loihi lavas (Dixon and Clague, 2001; Dixon et al., 2002). Ultimately, it seems that the greater the "enrichment" of the mantle (in terms of heavy isotopes and trace elements), the greater the apparent dehydration.

We do not believe that this relationship is an artifact of secondary processes in Samoan glasses. There is no coincidental correlation between $^{87}Sr/^{86}Sr$ and dredge depth (i.e. possible degassing). In the above section on water and carbon dioxide, we have shown that degassing has not resulted in significant water loss for any of the samples plotted in Figure 9. As supporting evidence, water contents in melt inclusions are equal to or less than the water contents in the glasses at equal or higher CO_2 (Tables 1 and 2). The slightly higher water in some glasses may reflect a greater degree of fractionation of these melts – this is not confirmed since we lack major element compositions for the melt inclusions. For the sake of argument, if the water content in samples from dredge 78 was the same as the highest water in Samoa, then the H_2O/La ratio of dredge 78 samples would be ~200 (instead of 120) – still well below values for MORB, Loihi and Discovery. Finally, if water has been assimilated from seawater or brine, then the H_2O/La ratios plotted in Figure 9 would be maximum values, and the signal we observe would be a dampened one; however, H_2O/La does not correlate with any potential "assimilation" proxies such as Cl/K.

6. ORIGIN OF EM2's "DEHYDRATION"

The origin of the EM2 mantle end-member is classically explained as the recycling of oceanic crust plus terrigeneous sediment through subduction zones (e.g. Weaver, 1991). However, our recent work on extreme EM2 lavas from Samoa (found at Malumalu, in particular) argues against simple mixing of a sedimentary component into depleted mantle based on trace element and isotopic trends in the Samoan lavas (see Workman et al. [2004] for detail). Instead, the origin of EM2 is explained as ancient (2.5 Ga), recycled, metasomatized lower oceanic lithosphere; a small degree, upper mantle melt (like those imagined to be formed at depth beneath mid-ocean ridges or island arcs) impregnated a depleted lithosphere, then the material was subducted and stored in the mantle (Workman et al., 2004). This is simply one scenario that works to explain the observations in Samoa that the EM2 source has a trace element pattern more reflective of upper mantle magmatic fractionation processes than sedimentary compositions, but does not completely rule out a subduction-related origin for EM2 (in other words, we do not necessarily know *where* the metasomatism has taken place).

The above model for the *formation* of EM2 cannot account for the low H_2O/La ratios observed in the Samoan glasses since (non-arc) mantle melting cannot produce large fractionations of water from La owing to their similar compatibilities. In addition, since the model EM2 reservoir is created in the lower oceanic lithosphere, it will be isolated from the subduction zone dehydration processes affecting the crust/sediment package in the upper part of the subducted slab. However, the *aging* of EM2 *can* account for our observations. This is how: very fast diffusion of hydrogen in mantle minerals (Mackwell and Kohlstedt, 1990; Wang et al., 1996; Woods et al., 2000; Stalder and Skogby, 2003) will cause recycled material with high initial water content to lose water to the drier ambient mantle during storage within the deep Earth.

Let us assume an initial chemical condition of EM2 at its formation: using the Workman et al. (2004) estimate for La and Ce concentrations in the EM2 end-member (0.90 ppm and 1.9 ppm, respectively) and assuming the initial H_2O/Ce ratio was similar to the common mantle, FOZO (i.e. 200; Dixon et al., 2002), then the starting H_2O content of EM2 would be 385 ppm (fig. 10). This contrasts with the Depleted MORB Mantle (DMM) which is estimated to contain 0.19 ppm La, 0.55 ppm Ce and 82.5 ppm H_2O (Workman and Hart, 2005). It has been known for decades that the diffusion rates of most lithophile trace elements (the rare-earth-elements, for example) are so slow that mantle heterogeneities will not equilibrate for these elements over more than 10 meters during the whole age of the Earth (Hofmann and Hart, 1978; Van Orman et al., 2001). On the other hand, experimental data for the diffusion of hydrogen in upper mantle minerals (Mackwell and Kohlstedt, 1990; Wang et al., 1996; Woods et al., 2000; Stalder and Skogby, 2003) indicate that diffusive mobility of water is extremely rapid; as a result, the enhanced solid-state mobility of hydrogen can potentially shift H_2O/La ratios in the absence of any melting or mantle-fluid interactions (fig. 10). The following paragraph is an example calculation addressing the timescales and length-scales of such water diffusion in the upper mantle.

We have chosen to model diffusion of water out of a semi-infinite slab following Eq. 21 in Jaeger (1968); the slab is of EM2 composition (initial water content of 385 ppm) and is conceptually placed in an infinite sink of ambient MORB mantle (with 82.5 ppm water). The interface between the two materials is immobile (i.e. non-convective). Mackwell and Kohlstedt (1990) provide an Arrhenius equation for the temperature dependence of hydrogen diffusion in olivine which leads to a diffusion coefficient of 1.4×10^{-8} m^2/s at 1600°C, for the fast [100] direction. Olivine is the most abundant upper mantle mineral and likely will control the slab-scale equilibration time. Using the above information, an entire 7 km thick slab (a heterogeneity on the order of the thickness of oceanic crust) will dehydrate to ~130 ppm water in 220 million years and to ~90 ppm in 1 billion years, well within the estimated age of EM2 (~2.5 Ga). Diffusion rates of water in diopside are about 5 times faster than olivine at 1600°C (Woods et al., 2000), so will help to speed the slab's equilibration times. Since much of the mantle is at temperatures higher than 1600°C, these are conservative estimates. Also, the effects of enhanced diffusion through grain boundaries will serve to quicken equilibration.

Figure 10 is a conceptual diagram for the diffusive equilibration of water during the recycling and storage of EM2 and other sources with initially elevated water. Assuming all reservoirs here are peridotite lithologies, when "wet" EM2 is introduced to "dry" depleted mantle, water will diffuse out of EM2 and into the "infinite sink" of ambient depleted mantle until their water activites are equal (at DMM = 82.5 ppm). When EM2 equilibrates with the depleted mantle and the two components have the same water content, the resulting H_2O/Ce is 43 and H_2O/La is 92 in the EM2 component; these values are nearly identical to the values seen in the high $^{87}Sr/^{86}Sr$ glasses from Malumalu (see fig. 9 for H_2O/La). Less-enriched sources, lying initially between EM2 and DMM along a $H_2O/La = 500$ line, will lose water when recycled to the mantle until they reach the 82.5 ppm water line. Thus, in aged sources, H_2O/La increases as the degree of enrichment decreases. This analysis shows that the observed differences in H_2O/La ratios in these mantle sources are not the result of different water contents, but instead are due to differences in REE enrichment at similar water contents.

The above discussion is focused on *dehydration* of enriched reservoirs, but the same thinking will apply to *re-hydration* of dry mantle reservoirs. If subducted material becomes extensively dehydrated (e.g. as called upon by Dixon et al. [2002]), storage within the mantle will result in a *re-hydration* of the slab until the slab and mantle are in chemical equilibrium in terms of water content. This is a nearly unavoidable consequence of recycling, unless slab temperatures stay very cold (much less than 1500°C) or recycling times are very rapid (< 50 million years).

7. CONCLUDING REMARKS

Volatile and trace element abundances for nearly 100 submarine basaltic glasses from the three youngest Samoan volcanoes have been presented here. We have found that water abundance relative to trace element abundance correlates inversely with source enrichment. This has been interpreted as diffusive dehydration of the EM2 source during its aging/storage in a drier ambient mantle. As a result, differences in the H_2O/La ratios of Samoan mantle components are due to differences in REE enrichment at fairly constant H_2O.

However, this is a somewhat incomplete picture since 1) diffusion rates of water in high-pressure mantle assemblages are unknown and 2) other lithologies (especially pyroxenites) may be present in the mantle as subducted oceanic crust (e.g. Hirschmann and Stolper, 1996) and may naturally contain higher water contents at equilibration with ambient mantle.

If the diffusion rates of hydrogen in high-pressure mantle minerals are similar to those at low-pressure, water may be one of the only elements whose abundance is nearly constant over significant distances in the mantle, assuming similar source lithologies. This “diffusive dehydration” model has important implications for the interpretation of mantle H_2O/La and H_2O/Ce ratios. Whether or not subducted materials have higher or lower H_2O/La than the upper mantle, slabs and mantle wedge material stored in the Earth for significant periods of time will experience rapid diffusive equilibration of hydrogen by either losing or gaining hydrogen to or from the ambient mantle.

The direction of diffusive hydrogen transport will depend not on the H_2O/La ratio but on the bulk H_2O contents of juxtaposed mantle sources. Indeed, subducted oceanic crust and sediment could enter the deep mantle with a low H_2O/La ratio (e.g. Dixon et al., 2002) but a bulk H_2O content that is still higher than the surrounding mantle, and thereby lose even more water via “diffusive dehydration”. Alternatively, if dehydration and melting are extremely efficient in subduction zones, then recycled material may enter the deep mantle extremely dry, and become re-hydrated via diffusive exchange with the surrounding mantle. Either way, an evaluation of the absolute abundance of water in mantle sources requires more than simply knowing the ratio of H_2O to REE in derivative lavas. Robust estimates of lithophile element concentrations, from accurate inversion of complete major element, trace element and isotopic data, must be the starting point for investigating the variability of water in the mantle in any tectonic setting.

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FIGURE CAPTIONS

Figure 1. Location map for Samoan glasses. Thick lines with adjacent numbers mark individual dredges; note that some dredges traverse more contours than others. Depth contours are plotted using AVON 2/3 shipboard bathymetry data. Note that what appears to be a small seamount east of Ta'u Island is an artifact of having an imprecise database of island coastlines. Inset shows greater Samoan region, including the northernmost extent of the Tonga Trench.

Figure 2. Panel a) shows water and carbon dioxide contents of Samoan glasses plotted with equilibrium vapor saturation curves and degassing trends of Dixon (1997) for alkali basalt; because open-system degassing trends are nearly vertical on this diagram, we expect that water loss has been negligible for all glasses except those at pressures less than 100 bars. Panel b) compares H_2O and CO_2 contents of Samoan glasses from this study to magmas in other settings. Panel c) plots average dredge depths for individual dredges with calculated saturation pressures (Dixon, 1997) for each sample; most lavas lie near the 1:1 line, so 1) are saturated with an H_2O-CO_2 vapor and 2) did not flow far downhill from shallower extrusion depths. Each dredge traverses multiple depth contours (up to 800 meters; see fig. 1), so there is some ambiguity about the exact collection depth.

Figure 3. Panel a) shows CaO plotted with Mg# for Samoan whole rocks (Workman et al., 2004) and glasses (this study). Crystal fractionation trends plotted here have been calculated using pMELTS predicted liquid lines of decent (Ghiorso et al., 2002), starting with some of the most primitive whole rock compositions. Best fits to the observed glass compositional trends are from pMELTS anhydrous runs at pressures of 3-4 kbar. Runs with 1wt% water are nearly identical to those plotted here, but with 1 kbar higher pressure. Panel b) is a total alkali-silica diagram of MacDonald and Katsura (1964), indicating that all the Samoan glasses are alkali basalt.

Figure 4. Fractionation-corrected trace and volatile element concentrations, listed in the order of increasing compatibility during mantle melting. Values are normalized to Primitive Upper Mantle (PUM) of McDonough and Sun (1995), except for water (at 335 ppm assuming $H_2O/Ce = 200$) and carbon dioxide (at 157 ppm assuming $CO_2/Nb = 239$ [Saal et al., 2002]).

Figure 5. Plot of Nd and F concentrations in Samoan glasses from this study, normal MORBs (from the PETBD online database: http://beta.www.petdb.org/), very depleted MORBs (Saal et al., 2002; Saal et al., unpubl.) and Primitive Upper Mantle (McDonough and Sun, 1995). Collectively these oceanic lavas define a constant F/Nd ratio of 21, showing that F has a compatibility equal to Nd during upper mantle melting.

Figure 6. Plot of S/Dy with Mg# of the Samoan glasses. Mg# = molar percent Mg/(Mg+0.85Fe). S has been suggested to have similar compatibility to Dy, so S/Dy ratios of melts should be similar to that of their source as long there has been no sulfide fractionation or SO_2 degassing. Since sulfides were observed in all dredges except those marked with **, and there is a rough positive correlation between S/Dy (as well any S/REE ratio) and Mg#, we interpret these lavas to have lost some of their initial sulfur content by sulfide fractionation.

Figure 7. Fractionation-corrected S and Cl concentrations in Samoan basaltic glasses. Note from Figure 2 that the glasses with highest S and Cl are from the least evolved glasses of the Samoan suite. Although most glasses are saturated with sulfides, the correlation between Cl and S suggests that S loss by fractionation of a Fe-S liquid may be minimal.

Figure 8. Two-panel diagram to show the systematics of Cl in Samoan glasses. Top panel shows fractionation-corrected concentrations of K and Cl with two lines of constant Cl/K shown for reference. The lower panel shows that Cl/K ratios many vary with the $^{87}Sr/^{86}Sr$ source proxy.

Figure 9. Plot of H_2O/La against $^{87}Sr/^{86}Sr$ in Samoan submarine glasses from this study along with plume-influenced glasses from the Discovery anomaly in the S. Atlantic (Dixon et al., 2002), average Loihi glasses (Dixon and Clague, 2001), and average normal MORB based on an H_2O/Ce ratio of 150 (Dixon et al., 2002). Note that the shallowly dredged, degassed Vailulu'u samples (from dredges 63, 68, 70 and 73) are not included on this plot (see fig. 4). The negative slope here indicates that increasingly enriched mantle has decreasing relative enrichment of water in its source. This water depletion in EM2 is interpreted to be the result of diffusive loss of water during storage of EM2 in a dry ambient mantle. The amount of water lost from EM2 is estimated to be ~75% its original (i.e. "pre-recycled") abundance.

Figure 10. This plot is a conceptual diagram for the diffusive equilibration of water during the recycling and storage of EM2. At its formation, EM2 had "normal" enrichment of water, with H_2O/Ce of 200 and H_2O/La of 430 at 385 ppm H_2O. During storage of this material with high H_2O in an ambient mantle with lower H_2O, water is diffusively lost from EM2 – but La is not due to their contrasting rates of diffusion. When EM2 has equilibrated with the upper mantle (82.5 ppm, heavy dashed line), this otherwise enriched reservoir has an H_2O/La ratio of 92. Less enriched sources (that lay in-between EM2 and DMM), will likewise lose water while stored in a drier mantle, but, as a result of lower REE abundance, will equilibrate to higher H_2O/La. This leads to the negative relationship between H_2O/La and $^{87}Sr/^{86}Sr$ seen in Figure 9.