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# Re–Os isotope systematics in Samoan shield lavas and the use of Os-isotopes in olivine phenocrysts to determine primary magmatic compositions

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## ABSTRACT

Samoa shield-stage lavas (from the islands of Ta'u, Savai'i, and Ofu and the seamounts of Vailulu'u and Malumalu) with Os concentrations  $>30$  ppt have  $^{187}\text{Os}/^{188}\text{Os}$  ratios that exhibit a narrow range of values between 0.128 and 0.132. Lavas with  $\leq 30$  ppt Os show more radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratios, in some cases as high as 0.191, suggesting that the  $^{187}\text{Os}/^{188}\text{Os}$  ratios of the extreme Samoan EM2 (enriched mantle 2) lavas likely have been compromised by assimilation of altered oceanic crust. The  $^{187}\text{Os}/^{188}\text{Os}$  ratios for rejuvenated-stage lavas from Savai'i are lower than shield lavas, and they exhibit some of the lowest  $^{187}\text{Os}/^{188}\text{Os}$  ratios in the global ocean island basalt database (Hauri and Hart, 1993). The difference may owe to contamination of the rejuvenated lavas with unradiogenic Os from disaggregated xenoliths from the mantle lithosphere, and their low Os isotopic composition does not reflect the EM2 mantle source of magmas. The limited range in  $^{187}\text{Os}/^{188}\text{Os}$  ratios of the higher Os-abundance shield lavas (0.128–0.132), coupled with a tremendous range of  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7045–0.7114), are characteristics of the EM2 source that can be explained by mixing a continental crustal sediment characterized by a high Sr/Os ( $\sim 10^7$ ) with a mantle peridotite that has low Sr/Os ( $\sim 10^4$ ).

Os abundances for nine whole rocks and their olivine phenocrysts show opposite trends with respect to whole rock MgO content: olivines have less than 0.1 ppb Os at 15 wt.% MgO and increase to 1–2 ppb Os in lavas with 8 wt.% MgO. Even though the Os isotopic composition of an evolved lava is susceptible to crustal assimilation, olivine phenocrysts with high Os concentrations preserve the pre-assimilation magmatic  $^{187}\text{Os}/^{188}\text{Os}$  ratio. For example, the range of  $^{187}\text{Os}/^{188}\text{Os}$  ratios measured on magmatic olivines from Samoan shield lavas (0.127 to 0.130) is lower (and narrower than) the range estimated using Os-rich ( $>30$  ppt) whole rock lavas (0.128–0.132).

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## 1. Introduction

Oceanic crust and terrigenous marine sediment enter the mantle at subduction zones (Hofmann and White, 1982; White and Hofmann, 1982), but their fate in the mantle afterwards is not well known. As a result of incorporation of subducted crust over geologic time, the Earth's mantle is chemically and isotopically heterogeneous (Hofmann, 1997; Zindler and Hart, 1986). However, the Earth's mantle mixes and stirs chaotically on geologic timescales, and any surviving portions of subducted crust are likely attenuated and their associated geochemical signatures diluted. Therefore, if oceanic and continental crust is returned to the surface in mantle upwellings, or plumes, and melted beneath hotspots, their geochemical signatures prove difficult to detect.

Samoa is a hotspot that has long been considered to host a component of recycled continental material (Farley et al., 1992; Jackson et al., 2007a; White and Hofmann, 1982; Workman et al., 2008; Wright and White, 1987). It has not been as well-studied as Hawaii and Iceland, and yet it is known to have unique compositional variability (e.g., Farley et al., 1992; Jackson et al., 2007a,b; Workman et al., 2004; Wright and White, 1987). Samoa is located on  $\sim 100$  myr old altered Pacific lithosphere and displays a petrologically-diverse suite of geochemically well-characterized lavas (e.g., Hawkins and Natland, 1975; Natland, 1980; Workman et al., 2004). Therefore, Samoan lavas are ideal for probing questions of the petrogenesis of OIB during eruption and emplacement, such as how assimilation of oceanic lithospheric materials occurs in intraplate settings, and how phenocrysts can be used in OIB suites to establish primary magma compositions. They are also ideal for questions that have global significance such as identifying the recycled signatures that can better establish the end-member EM2 (enriched mantle II) composition.

The Re–Os isotopic system is a powerful geochemical tool that helps to detect crustal assimilation and to resolve the compositional

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imprint of ambient mantle peridotite from recycled crust. The Re–Os radiogenic isotope system – where  $^{187}\text{Re}$  undergoes  $\beta^-$  decay to  $^{187}\text{Os}$ ,  $t_{1/2} = 41.6$  Ga (Shen et al., 1996; Smoliar et al., 1996) – is well suited for detecting recycled crustal signatures in hotspot lavas (e.g., Shirey and Walker, 1998). During mantle melting, Re is a moderately incompatible element and Os behaves compatibly. The disparate behavior on melting results in extreme fractionations of parent and daughter isotopes, which generates high time-integrated Re/Os (and high  $^{187}\text{Os}/^{188}\text{Os}$ ) ratios in crustal reservoirs and correspondingly low Re/Os (and low  $^{187}\text{Os}/^{188}\text{Os}$ ) ratios in the depleted mantle. This is in contrast to much smaller parent–daughter fractionation associated with melting in the more commonly measured radiogenic systems such as Sr, Nd or Pb isotopes, and highlights the potential of the Re–Os isotope system to resolve recycled crustal material in the mantle.

Os isotopes were previously reported in Samoan rejuvenated lavas from Savai'i (Hauri and Hart, 1993) and Samoan shield lavas (Jackson et al., 2008a; Workman et al., 2004). However, the data obtained on the Samoan shield lavas were acquired using an ICP-MS (inductively coupled plasma mass spectrometer) method (Jackson et al., 2008a; Workman et al., 2004), and the corresponding analytical errors were large (typically 1–2% for basalts). Such large analytical uncertainties make it problematic to resolve the small variations in  $^{187}\text{Os}/^{188}\text{Os}$  ratios that we identify in Samoan shield lavas and to see how truly uniform they are. Additionally, Re concentrations were never determined for Samoan shield lavas and the Re concentration for only a single Samoan rejuvenated lava was reported (Hauri and Hart, 1993). The sample suite examined in this study for Re and Os abundances and Os isotopic compositions includes some unusual Samoan lavas, including lavas with the highest  $^3\text{He}/^4\text{He}$  from Ofu Island (up to 34 Ra, or ratio to atmospheric; Jackson et al. 2007b) and the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  from Savai'i Island (up to 0.7208 in magmatic clinopyroxene [cpx] separates; Jackson et al. 2007b).

Complementing the new whole rock Os-isotopic data, Os isotopes and Os concentrations on olivines hosted in the same lavas were measured. The new paired whole rock-olivine data provide important clues about the behavior of Os in magmas as they evolve. Owing to their lower Os abundances, evolved lavas can be more susceptible to having their Os-isotopic compositions modified by assimilation of oceanic crustal materials and seawater. However, the elevated Os concentrations that we report in olivines from evolved lavas may better shield olivines from the effects of crustal assimilation. As a result, Os-isotopic measurements in olivines may allow us to “see through” the effects of assimilation, particularly in evolved (and therefore low-Os) lavas that are susceptible to having their primary magmatic  $^{187}\text{Os}/^{188}\text{Os}$  ratios overprinted by assimilation.

## 2. Samples and methods

All samples for which we report new Re and Os abundances and  $^{187}\text{Os}/^{188}\text{Os}$  ratios are Samoan shield lavas. These occur on Savai'i, Ta'u and Ofu Islands, as well as Malumalu and Vailulu'u seamounts

(Jackson et al., 2007a,b; Workman et al. 2004). Re and Os abundances and  $^{187}\text{Os}/^{188}\text{Os}$  ratios for Samoan rejuvenated lavas from Savai'i Island were reported in Hauri and Hart (1993). With relatively few exceptions (see Table 1) most of the samples analyzed here are new aliquots of the powders characterized geochemically in earlier studies (Jackson et al., 2007a,b; Workman et al., 2004). Powder preparation was as follows. Whole rocks were cut on a rock saw and crushed by hammer in plastic bags. The freshest chips were selected under binocular microscope with care to avoid surfaces that came into contact with the saw blade. The chips were subsequently cleaned by sonication in Milli-Q water. After drying, sample chips were powdered in an agate mortar. Additional chips were crushed in a jaw crusher, sieved and separated magnetically to concentrate the olivine fraction. The freshest olivines were selected, regardless of inclusion content, and sonicated in 6 N HCl for 30 min at room temperature, followed by rinsing and 10 min of sonication in Milli-Q water. The olivines were then re-examined to ensure that no visible groundmass or alteration phases remained. Olivines were then powdered by hand in an agate mortar that was pre-cleaned by grinding with silica followed by thorough rinsing in Milli-Q water.

The Re–Os method employed in this study was most recently described in Class et al. (2009) and Heinonen et al. (2010). Os extraction followed the Carius tube method (Shirey and Walker, 1995), which was followed by solvent extraction (Cohen and Waters, 1996) with carbon tetrachloride. The Os was then purified using micro distillation (Roy-Barman and Allègre, 1995). Re was separated by anion exchange chromatography (Morgan and Walker, 1989; Walker, 1988). Isotopic measurements of Os were made by negative thermal ionization mass spectrometry (N-TIMS) on the Thermofinnigan Triton at the Department of Terrestrial Magnetism (DTM) on Pt ribbon filaments as an  $\text{OsO}_3^-$  species; all measurements were made at low intensity on a single-collector secondary electron multiplier. All runs were corrected for their oxide compositions to their metal composition and mass bias corrected to a  $^{192}\text{Os}/^{188}\text{Os}$  ratio of 3.082614 (Creaser et al., 1991). From December 2008 to May 2010, twenty-nine separate 100 pg loads of the DTM solution standard “J-M Os” were analyzed as part of this study, and they yielded an average  $^{187}\text{Os}/^{188}\text{Os}$  ratio of 0.17366 ( $\pm 0.00045$ ,  $2\sigma$  std. dev.,  $n = 29$ ). However, variation in the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of the J-M Os standard runs was generally lower during individual analytical sessions. Runs of basalts and olivine samples were corrected for the offset between the measured and accepted (0.17399) standard values for each analytical session. In-run precision for basalts and olivine samples was 0.03 to 0.32% ( $2\sigma$ ) for  $^{187}\text{Os}/^{188}\text{Os}$  ratios (except for AVON3-76-9ol, which was 0.78%). Re concentrations were determined by isotope dilution, and measurements were made on either the P54 or the NU plasma machines hosted at DTM. The average proportion of blank Os to sample Os was 1.2% (ranging from 0.03 to 5.2%) for all whole rock samples and 1.8% (ranging from 0.04 to 4.5%) for olivine samples for which  $^{187}\text{Os}/^{188}\text{Os}$  ratios are reported. AVON3-78-3ol has a higher blank proportion – 18.1% – so Os isotopic ratios are not reported. The average proportion

### Note to Table 1

Abbreviations: whole rock is wr, olivine is ol, clinopyroxene is cpx, standard error (absolute) is s.e. (abs), replicate is rep., submarine is mar, subaerial is aer. With three exceptions, all whole rocks have had Re and Os measured on the same aliquot of powder. Os and Re were measured on different aliquots of the same batch of powder for samples ALIA-115-18 (wr), ALIA-115-03 (wr), and Ofu-04-15 (wr). In order to estimate the  $^{187}\text{Re}/^{188}\text{Os}$  ratios of the samples with “missing” Re, the Re and Os data obtained on different aliquots of powder were combined: Re concentrations for sample ALIA-115-18 were taken to be the averages of rep1 and rep2; Re concentrations for ALIA-115-03 were taken from the replicate run; Re concentrations for Ofu-04-15 were taken from the rep. Ofu-04-14 is the only whole rock sample for which Re concentrations are not reported. All lavas with the prefix “ALIA” have been age corrected using ages from Koppers et al. (2008): ALIA-115-18 is 5.29 Ma; ALIA-115-28 is 5.04 Ma; ALIA-115-03 is 5.06 Ma; ALIA-128-21 is 4.80 Ma. Lavas from all other locations are thought to have much younger ages ( $< 1$  Ma) and have not been age-corrected. The  $^{87}\text{Sr}/^{86}\text{Sr}$  of ALIA-115-18 cpx is the average of two measurements, where one measurement was made on green cpx (0.720830) and the other on black cpx (0.720232) (Jackson et al., 2007a). The Sr-isotopic composition of Ofu-04-06 cpx is reported in Jackson et al. (2009b). Whole rock Sr and Pb isotopic data are from Jackson et al. (2007a,b) and Workman et al. (2004). Owing to small sample sizes combined with relatively high blank Re to sample Re ratios, it is difficult to determine Re concentrations in most of the olivine samples examined here. Therefore, Re data are not reported for most olivine separates. All osmium standard and unknown runs with  $^{185}\text{ReO}_3/^{188}\text{OsO}_3 > 0.00035$  were discarded. AVON3-78-3 (ol) was overspiked, and the Os-isotopic composition is not reported; Os concentrations were measured precisely for this sample and are reported. Each replicate involves a new aliquot of powder that was processed independently through all steps of the wet chemistry procedure. Whole rock Sr-isotope and MgO compositions are published for all whole rock lavas (Jackson et al. 2007a,b; Workman et al., 2004), except for T54, 63-11, 63-2 and MgO for all Ofu lavas. Sr-isotopic ratios were measured on the WHOI Neptune following the procedures outlined in Workman et al. (2004). Whole rock MgO was measured in the same way as reported in Workman et al. (2004).

of blank Re to sample Re was 3.4% (ranging from 0.8 to 28%) for whole rocks; owing to the very low Re concentrations in olivines examined in this study, we report Re concentrations for just the two olivine samples

for which the average proportion of blank Re to sample Re is <50%. Throughout the study, the whole chemistry procedural blanks were <2 pg for Os and <10 pg Re. The respective blanks were 0.2 pg and

**Table 1**  
Os-isotopic compositions and Re–Os concentrations in Samoan basalts and phenocrysts.

Sample ID	Sample mass (g)	$^{187}\text{Os}/^{188}\text{Os}$ (not blank corr'd)	$^{187}\text{Os}/^{188}\text{Os}$ (blank corr'd)	In-run precision 2 $\sigma$ , s.e. (abs.)	$^{187}\text{Os}/^{188}\text{Os}$ (age corr'd)	Os conc. (ppb)	Os blank (% of total)	Re conc. (ppb)	Re blank (% of total)	$^{187}\text{Re}/^{188}\text{Os}$	Mar/aer?	$^{87}\text{Sr}/^{86}\text{Sr}$	Whole rock MgO (wt.%)
<i>Ta'u Island</i>													
AVON3-74-1 (wr)	1.09	0.12940	0.12939 ± 0.00004			5.630	0.03	0.364	2.5	0.303	mar	0.7047	25.5
T16 (wr)	0.63	0.13025	0.12958 ± 0.00020			0.208	1.55	0.423	3.7	9.45	aer	0.7046	12.4
T16 (ol)	0.51	0.12874	0.12832 ± 0.00005			0.359	0.93				aer		
T44 (wr)	1.71	0.13076	0.13066 ± 0.00016			0.155	0.25	0.044	6.1	1.37	aer	0.7051	14.2
T44 (wr) rep1	1.79	0.13128	0.13095 ± 0.00009			0.180	0.77	0.049	1.8	1.32	aer		
T44 (wr) rep2	0.87	0.13080	0.13022 ± 0.00021			0.173	1.35				aer		
T44 (wr) rep3	1.96	0.13098	0.13080 ± 0.00004			0.149	0.41				aer		
T44 (ol)	0.33	0.13028	0.12959 ± 0.00005			0.325	1.61				aer		
T54 (wr)	1.53	0.12963	0.12918 ± 0.00010			0.128	1.03	0.144	4.6	5.18	aer	0.7047	9.1
T54 (ol)	0.33	0.12845	0.12843 ± 0.00018			1.636	0.04	0.096	10.2	0.28	aer		
T25 (wr)	1.07							0.092	3.2		aer	0.7047	19.9
T25 (ol)	0.28	0.12998	0.12808 ± 0.00035			0.141	4.50				aer		
T33 (wr)	1.08	0.12977	0.12906 ± 0.00006			0.115	1.64	0.137	6.7	5.39	aer	0.7047	12.4
T33 (wr) rep	1.34							0.146	0.8		aer		
T33 (ol)	0.62	0.12890	0.12850 ± 0.00041			0.363	0.89				aer		
<i>Vailulu'u Seamount</i>													
AVON3-63-11 (wr)	0.86	0.12837	0.12829 ± 0.00004			1.228	0.19	0.490	2.4	1.88	mar	0.7054	26.4
AVON3-63-11 (ol)	0.36	0.12866	0.12765 ± 0.00007			0.214	2.28				mar		
AVON3-71-2 (wr)	0.96	0.12892	0.12883 ± 0.00003			1.105	0.19	0.666	1.6	2.9	mar	0.7059	27.4
AVON3-63-2 (wr)	1.12	0.12909	0.12895 ± 0.00003			0.589	0.30	0.656	1.4	5.3	mar	0.7054	23.9
AVON3-63-2 (ol)	0.54	0.12913	0.12844 ± 0.00006			0.239	1.56	0.298	6.2	6.0	mar		
AVON3-68-3 (wr)	1.32	0.12898	0.12863 ± 0.00006			0.192	0.79	1.013	1.5	25.2	mar	0.7054	10.7
AVON3-73-2 (wr)	1.00	0.12986	0.12883 ± 0.00014			0.086	2.40	1.233	0.8	68.7	mar	0.7054	11.4
AVON3-73-2 (wr) rep	0.98	0.12932	0.12872 ± 0.00010			0.091	1.37	1.252	0.8	65.7	mar		
<i>Malumalu Seamount</i>													
AVON3-76-9 (wr)	0.69	0.13159	0.13115 ± 0.00012			0.283	1.04	0.327	4.4	5.3	mar	0.7067	15.8
AVON3-76-9 (wr) rep1	1.26							0.279	1.3		mar		
AVON3-76-9 (wr) rep2	2.18							0.317	1.4		mar		
AVON3-76-9 (ol)	0.33	0.13019	0.12974 ± 0.00102			0.064	1.04				mar		
AVON3-77-1 (wr)	1.88	0.13206	0.13131 ± 0.00007			0.036	1.80	0.696	0.8	93.4	mar	0.7069	7.6
AVON3-77-1 (wr) rep	0.61							0.757	2.2		mar		
AVON3-77-1 (ol)	0.17	0.12742	0.12675 ± 0.00008			0.713	1.46				mar		
AVON3-77-9 (wr)	0.90							0.756	1.4		mar	0.7073	8.5
AVON3-77-9 (wr) rep	1.61							0.720	0.9		mar		
AVON3-78-1 (wr)	1.00	0.12914	0.12846 ± 0.00004			0.132	1.54	0.305	3.3	10.7	mar	0.7089	19.7
AVON3-78-1 (wr) rep	1.94	0.12882	0.12862 ± 0.00010			0.137	0.45	0.282	1.8	9.7	mar		
AVON3-78-3 (wr)	1.09	0.13156	0.13070 ± 0.00005			0.091	2.06	0.277	3.3	14.3	mar	0.7089	18.8
AVON3-78-3 (wr) rep	1.79	0.13101	0.13076 ± 0.00011			0.118	0.58	0.274	2.0	11.0	mar		
AVON3-78-3 (ol)	0.41					0.032	18.1						
<i>Savai'i Island</i>													
ALIA-115-18 (wr)	1.01	0.19088	0.19110 ± 0.00044		0.1907	0.017	1.30			4.8	mar	0.7186	5.3
ALIA-115-18 (wr) rep1	1.08							0.015	27.9		mar		
ALIA-115-18 (wr) rep2	1.68							0.018	5.2		mar		
ALIA-115-18 (cpx)	0.62	0.14170	0.14009 ± 0.00016		0.1394	0.007	5.27	0.011	46.7	7.5	mar	0.7205	
ALIA-115-28 (wr)	1.92	0.13328	0.13260 ± 0.00007		0.1316	0.063	1.68	0.165	3.1	12.3	mar	0.7100	6.6
ALIA-115-28 (wr) rep	1.37	0.13125	0.13108 ± 0.00011			0.119	0.40				mar		
ALIA-128-21 (wr)	0.82	0.18504	0.18556 ± 0.00007		0.1836	0.030	5.19	0.150	8.1	24.6	mar	0.7125	11.9
ALIA-115-03 (wr)	0.85	0.13320	0.13198 ± 0.00008		0.1318	0.080	3.05			2.8	mar	0.7114	8.2
ALIA-115-03 (wr) rep	1.16							0.046	3.0		mar		
<i>Ofu Island</i>													
Ofu-04-03 (wr)	2.30	0.12942	0.12926 ± 0.00005			0.145	0.36	0.166	2.6	5.4	aer	0.7048	14.7
Ofu-04-03 (wr) rep1	1.71	0.12929	0.12921 ± 0.00008			0.240	0.16	0.190	1.4	3.8	aer		
Ofu-04-03 (wr) rep2	2.07							0.175	2.8		aer		
Ofu-04-17 (wr)	2.54	0.12882	0.12862 ± 0.00017			0.106	0.45	0.087	4.5	3.8	aer	0.7045	18.9
Ofu-04-17 (wr) rep	0.96	0.12922	0.12856 ± 0.00022			0.142	1.48				aer		
Ofu-04-06 (wr)	1.07	0.13062	0.12941 ± 0.00018			0.067	2.87	0.172	5.4	11.7	aer	0.7046	9.8
Ofu-04-06 (wr) rep1	1.32	0.12923	0.12894 ± 0.00015			0.075	0.66	0.146	2.4	9.3	aer		
Ofu-04-06 (wr) rep2	0.79							0.187	1.1		aer		
Ofu-04-06 (ol)	0.20	0.12926	0.12787 ± 0.00009			0.276	3.19				aer	0.7046	9.8
Ofu-04-06 (cpx)	0.78	0.12907	0.12883 ± 0.00015			0.052	0.54	0.012	33.2	1.1	aer	0.7046	
Ofu-04-15 (wr)	1.84	0.12957	0.12919 ± 0.00015			0.128	0.86			1.4	aer	0.7046	10.9
Ofu-04-15 (wr) rep	1.85							0.038	2.3		aer		
Ofu-04-14 (wr)	0.38	0.12993	0.12873 ± 0.00012			0.195	2.80				aer	0.7045	16.0

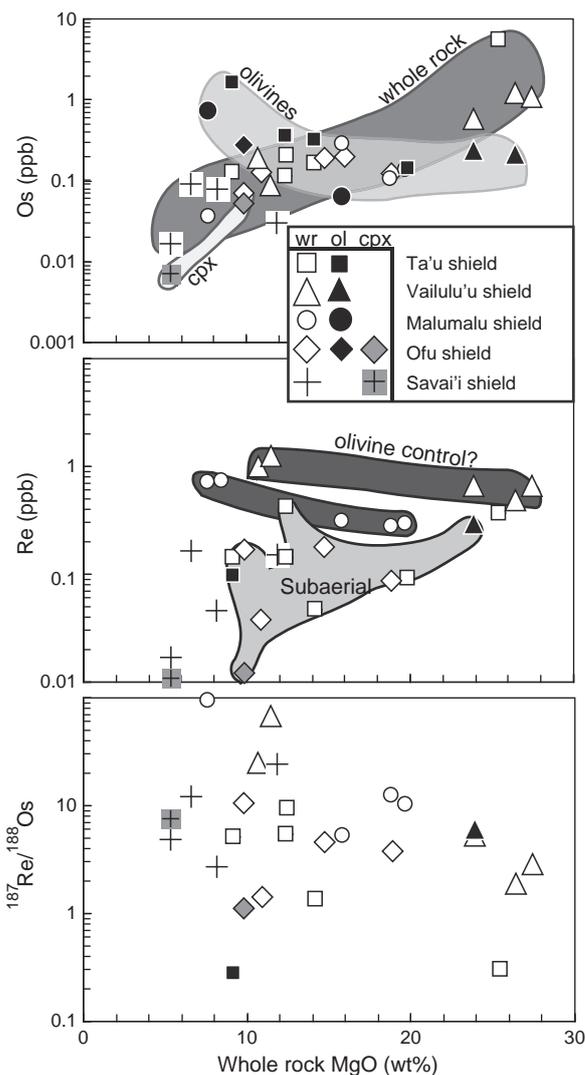
3 pg during the analytical session in which the lowest Os abundance samples – ALIA-115-18 and its host cpx – were measured.

Duplicate Os isotopic measurements were made on 7 whole rock samples, and quadruplicate measurements were made on an eighth whole rock sample (T44). The reproducibility of the  $^{187}\text{Os}/^{188}\text{Os}$  ratios is better than 0.6% for duplicate and quadruplicate measurements, except for sample ALIA-115-28 (1.2%). ALIA-115-28 is the only sample for which the measured  $^{187}\text{Os}/^{188}\text{Os}$  values are significantly outside the in-run precision of the individual measurements, and this may be due to the presence of a trace phase, or “nugget”, with an anomalous  $^{187}\text{Os}/^{188}\text{Os}$  ratio in one of the two runs. Consistent with this hypothesis, the sample with the lower  $^{187}\text{Os}/^{188}\text{Os}$  ratio has nearly twice the Os concentration. Of the 8 samples with duplicate or quadruplicate Os concentration measurements, six are reproducible to within 35%, but ALIA-115-28 (89%) and Ofu-04-03 (66%) appear to suffer from “nugget” effects; unlike ALIA-115-28, the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of the Ofu-04-03 duplicate measurements are in agreement. Therefore, unlike the ALIA-115-28 nugget, any “nugget” in Ofu-04-03 would have to be in isotopic equilibrium with the rest of the sample. Additionally, we measured Re concentrations in duplicate on 8 whole rock samples and triplicated Re concentrations on 3 whole rock samples. All Re measurements are reproducible to within 20%, except for Ofu-04-06 (28%).

The major element compositions of olivines examined in this study were measured by electron microprobe at the Geophysical Laboratory, Carnegie Institution of Washington, and the average olivine compositions are reported in Table 2. Individual olivine analyses are reported in Supplementary Table 1. During all measurements, a 30 nA beam current and a 15 kV voltage were used. A focused beam was used, and the CITZAF matrix correction was employed. Major and trace element compositions for the cpx examined in this study are reported in Jackson et al. (2008b), and the data are consistent with a magmatic origin.

### 3. Results

New Re and Os concentration data and  $^{187}\text{Os}/^{188}\text{Os}$  ratios are presented in Table 1 for whole rocks and olivine and cpx phenocrysts. Os and Re concentrations are plotted against whole rock MgO concentrations in Fig. 1. Notably, Os abundances for whole rocks and olivines show opposite trends with respect to whole rock MgO; olivines tend to show increasing Os concentrations as lavas become more evolved while whole rock Os abundances diminish. Cpx separates from ALIA-115-18 exhibit the lowest Os abundance (0.007 ppb) in this study. Rhenium abundances and  $^{187}\text{Re}/^{188}\text{Os}$  ratios in whole rocks show no overall trend with whole rock MgO. However, on an island-by-island basis, subaqueously erupted whole rocks from Vailulu'u and Malumalu seamounts show increasing Re concentrations with decreasing whole rock MgO, which may reflect olivine control. By contrast, Ofu (all samples subaerial), Ta'u (all but one sample is subaerial) and Savai'i (all samples submarine) lavas show no clear trends with MgO. Replicate Re, Os and  $^{187}\text{Re}/^{188}\text{Os}$  measurements are averaged in the figure. Rejuvenated lavas are not plotted.



**Fig. 1.** Os, Re and  $^{187}\text{Re}/^{188}\text{Os}$  as a function of whole rock MgO. Top panel: Whole rock Os concentrations decrease as whole rock MgO decreases, but Os concentrations in olivine increase. Re abundances (middle panel) and  $^{187}\text{Re}/^{188}\text{Os}$  ratios (bottom panel) show no overall trend with MgO. However, on an island-by-island basis, subaqueously erupted whole rocks from Vailulu'u and Malumalu seamounts show increasing Re concentrations with decreasing whole rock MgO, which may reflect olivine control. By contrast, Ofu (all samples subaerial), Ta'u (all but one sample is subaerial) and Savai'i (all samples submarine) lavas show no clear trends with MgO. Replicate Re, Os and  $^{187}\text{Re}/^{188}\text{Os}$  measurements are averaged in the figure. Rejuvenated lavas are not plotted.

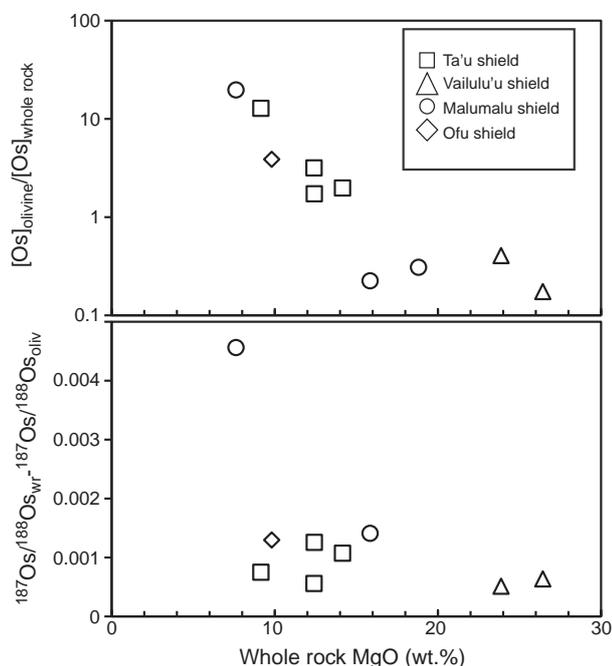
**Table 2**  
Olivine modes (% of whole rock) and average compositions (in wt.%) for Samoan olivines that were analyzed for  $^{187}\text{Os}/^{188}\text{Os}$ .

Sample ID	n	MgO (wt.%)	FeO (wt.%)	SiO <sub>2</sub> (wt.%)	NiO (wt.%)	CaO (wt.%)	Al <sub>2</sub> O <sub>3</sub> (wt.%)	MnO (wt.%)	Cr <sub>2</sub> O <sub>3</sub> (wt.%)	TiO <sub>2</sub> (wt.%)	Total (wt.%)	Fo content (wt.%)	Modal olivine (%)
T16	12	47.31	12.26	40.09	0.30	0.30	0.05	0.17	0.04	0.01	100.55	87.3	8
T44	12	42.65	18.01	38.91	0.28	0.29	0.04	0.23	0.03	0.02	100.46	80.8	15
T54	12	44.06	16.36	39.26	0.27	0.28	0.04	0.21	0.05	0.02	100.55	82.7	4
T25	13	45.46	14.61	39.51	0.30	0.29	0.04	0.20	0.05	0.02	100.47	84.7	25
T33	14	46.32	13.57	39.76	0.25	0.30	0.05	0.18	0.05	0.01	100.50	85.9	10
AVON3-63-11	13	47.64	11.65	40.08	0.30	0.36	0.05	0.17	0.06	0.01	100.33	87.9	40
AVON-3-63-2	13	48.70	10.37	40.41	0.34	0.32	0.07	0.15	0.09	0.02	100.46	89.3	34
AVON-3-76-9	15	45.28	14.77	39.48	0.25	0.31	0.04	0.18	0.04	0.02	100.36	84.5	10
AVON3-77-1	10	43.66	16.66	39.15	0.22	0.34	0.04	0.22	0.04	0.02	100.33	82.4	3
AVON3-78-1	10	44.80	15.28	39.34	0.23	0.32	0.04	0.20	0.03	0.01	100.25	83.9	30
Ofu-04-06	13	40.73	20.58	38.35	0.19	0.35	0.04	0.26	0.01	0.03	100.54	77.9	6

Individual olivine measurements are presented in Supplementary Table 1. The number of different grains analyzed is represented by “n”.

MgO, which may reflect olivine control, owing to the generally incompatible behavior of Re in silicates during magma evolution (e.g., Hauri and Hart, 1997). By contrast, Re in Ta'u, Ofu and Savai'i lavas show no clear trends with MgO. All Ofu and Ta'u lavas (with the exception of Ta'u lava AVON3-74-1) were erupted subaerially, so volatile-related Re loss (e.g., Bennett et al., 2000; Day et al., 2010; Ireland et al., 2009; Lassiter, 2003; Norman et al., 2004) may contribute to the poor relationships between whole rock Re and MgO in these lavas. Ta'u Island is the only location for which both submarine and subaerial samples are available; the single submarine sample analyzed here (AVON3-74-1) is lower than all but one of the subaerial samples from the island. This observation is consistent with the hypothesis that volatility-related Re-loss occurs in subaerially erupted samples, while submarine samples do not suffer from this process (e.g., Bennett et al., 2000; Day et al., 2010; Ireland et al., 2009; Lassiter, 2003; Norman et al., 2004). While Re abundances in submarine lavas from Vailulu'u and Malumalu may exhibit olivine control (which may be due to the fact that there is no volatile loss of Re to complicate the Re budgets of these lavas), submarine Savai'i lavas do not exhibit olivine control. This may owe to extensive whole rock isotopic heterogeneity ( $^{87}\text{Sr}/^{86}\text{Sr}$  from 0.709985 to 0.718592) in the Savai'i lavas examined in this study, which could translate to heterogeneous Re concentrations in the primary magmas.

In Fig. 2, the ratio of the concentration of Os in olivine separates to the concentration in the whole rock is plotted against whole rock MgO. With diminishing MgO, the concentration of Os in the olivine increases relative to the concentration in the whole rock, as inferred from Fig. 1. Additionally, the whole rock has increasing  $^{187}\text{Os}/^{188}\text{Os}$  ratios with diminishing MgO, but olivine Os-isotopic compositions do not exhibit a marked increase over the same range of MgO. Therefore, the difference between the  $^{187}\text{Os}/^{188}\text{Os}$  signature of the whole

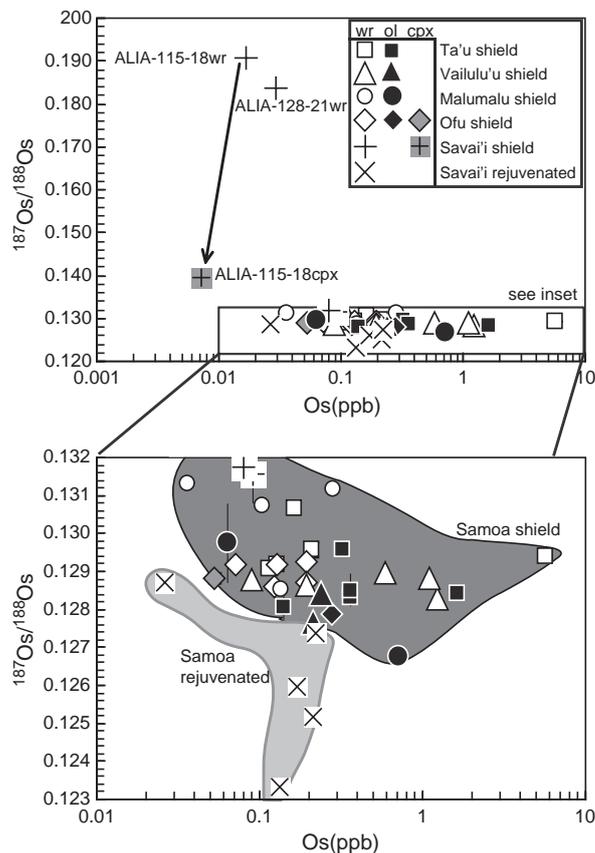


**Fig. 2.** Olivines in evolved (low MgO) lavas have higher Os concentrations and lower  $^{187}\text{Os}/^{188}\text{Os}$  that the host whole rock. Top panel: The Os concentrations of olivines are normalized to the Os concentrations of the respective host whole rocks, and the normalized value increases with diminishing whole rock MgO. The whole rock Os concentration is a raw measured value and has not been corrected for the Os contribution from the host olivines. Bottom panel: the raw difference in the  $^{187}\text{Os}/^{188}\text{Os}$  ratios between the whole rock and the olivine increases with diminishing whole rock MgO. Replicate whole rock measurements are presented as averages. Sample 78–1 is not shown in the lower panel because the Os-isotopic composition is not reported for the olivines. Whole rock is abbreviated as wr, olivine is abbreviated as oliv.

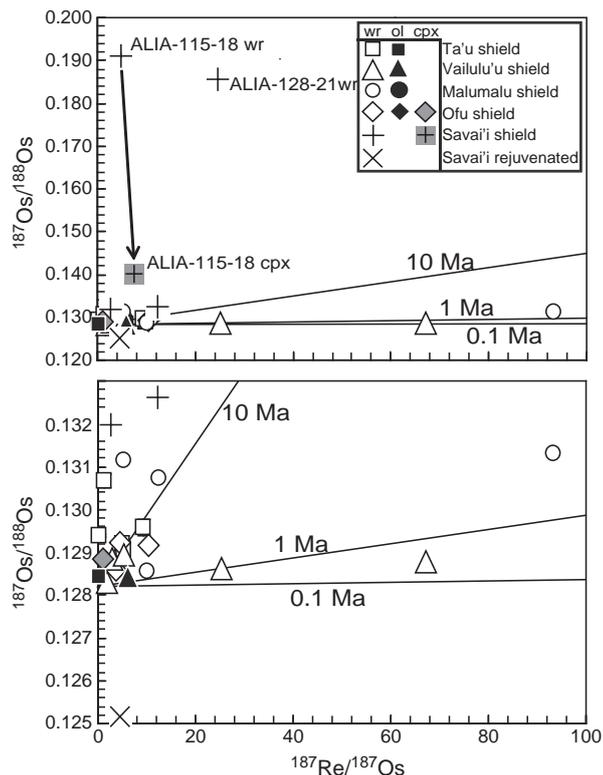
rock and olivine increases with diminishing whole rock MgO (see Fig. 2).

Fig. 3 shows that Samoan shield whole rock lavas with Os concentrations >30 ppt exhibit a narrow range of relatively unradiogenic (for OIB) Os isotopic values that range from 0.128 to 0.132. By contrast, the two whole rock lavas with Os abundances  $\leq 30$  ppt – both shield-stage lavas from Savai'i (samples ALIA-115-18 and ALIA-128-21) – have by far the highest  $^{187}\text{Os}/^{188}\text{Os}$  ratios (0.184–0.191) of this study. Olivines and cpx separates in general tend to have  $^{187}\text{Os}/^{188}\text{Os}$  ratios that are similar to or somewhat lower than the host whole rock. Magmatic olivine phenocrysts separated from the lavas preserve  $^{187}\text{Os}/^{188}\text{Os} < 0.130$  in all cases.

Samoa whole rock lavas and phenocrysts are shown in a plot of  $^{187}\text{Re}/^{188}\text{Os}$  vs.  $^{187}\text{Os}/^{188}\text{Os}$  (Fig. 4). The isotopic disequilibrium between ALIA-115-18 whole rock and host cpx is not due to radiogenic ingrowth since the lavas were erupted at 5 Ma (Koppers et al., 2008). Similarly, olivine–whole rock pairs generate two-point isochrons with ages that exceed 10 Ma, and are not considered to have age significance because all shield lavas from the region of study are <5 Ma (Koppers et al., 2008). Additionally, the radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratios (0.1836–0.1907) observed in the two Os-poor (Os  $\leq 30$  ppt) Savai'i shield lavas cannot be generated by radiogenic ingrowth in



**Fig. 3.** Os vs.  $^{187}\text{Os}/^{188}\text{Os}$  for Samoan whole rock lavas and host olivine and cpx phenocrysts. Top panel: The two whole rock lavas with Os abundances  $\leq 30$  ppt (ALIA-115-18 and ALIA-128-21) have the highest  $^{187}\text{Os}/^{188}\text{Os}$  ratios (0.184–0.191), suggesting a role for assimilation of material with an elevated  $^{187}\text{Os}/^{188}\text{Os}$  ratio. Cpx separated from one of the low-Os lavas (ALIA-115-18) preserves a significantly lower Os isotopic signature (0.1394) than the whole rock. Bottom panel (inset): All whole rock shield lavas with Os abundances >30 ppt exhibit a narrow range of Os isotopic values from 0.128 to 0.132. Magmatic olivine phenocrysts preserve  $^{187}\text{Os}/^{188}\text{Os} < 0.130$  in all cases. Rejuvenated lavas (Hauri and Hart, 1993) are shifted to lower  $^{187}\text{Os}/^{188}\text{Os}$  ratios relative to the shield lavas. Replicate whole rock measurements are presented as averages. Error bars are  $2\sigma$  standard error of the mean. The data plotted are from this study and Hauri and Hart (1993) and are by N-TIMS only.

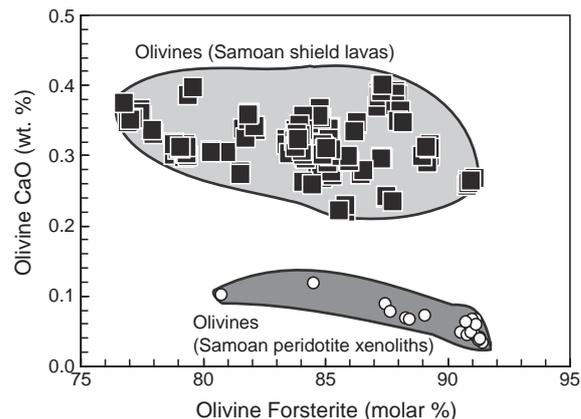


**Fig. 4.** Measured  $^{187}\text{Re}/^{188}\text{Os}$  vs.  $^{187}\text{Os}/^{188}\text{Os}$  for Samoan whole rock lavas and phenocrysts. Top panel: all Samoan lavas in this study are <5 Ma. Age reference lines are plotted for 0.1, 1 and 10 Ma. Lavas from a given seamount or island do not plot on any particular age line. The whole rock sample ALIA-115-18 and its host cpx do not define an age. Similarly, data from olivine–whole rock pairs do not form age lines with geological significance. Symbols are the same as Fig. 1. Bottom panel: A close-up of view of the dataset shows that the lavas do not clearly follow any particular age reference lines. Replicate whole rock measurements yield similar results, and average values are presented in the figure. Error bars are  $2\sigma$  standard error of the mean.

5 Ma (the approximate age of both lavas; Koppers et al., 2008) from an initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio similar to the Os-rich Samoan shield lavas.

Rejuvenated lavas from Savai'i post-date shield-stage volcanism by ~2–3 Ma (Koppers et al., 2008), and rejuvenated volcanism on Savai'i is so extensive that the subaerial portion of the volcano has been completely resurfaced. Compared to the data on Samoan shield lavas that we report here, rejuvenated Samoan lavas from Savai'i (Hauri and Hart, 1993) tend to exhibit lower  $^{187}\text{Os}/^{188}\text{Os}$  ratios (Fig. 3). In fact, the rejuvenated lavas from Savai'i have some of the least radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratios reported in the global OIB database. Savai'i rejuvenated lavas regularly host peridotite mantle xenoliths (Hauri and Hart, 1994; Hauri et al., 1993) which can host unradiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratios (Jackson et al., 2010). Therefore, to be sure that the olivine separates characterized for Os (see Table 1) are not peridotite mantle xenocrysts, we measured the olivine compositions by electron probe and compared the compositions with the olivines of Samoan peridotite xenoliths from Savai'i (Hauri and Hart, 1994). The new olivine major element data are reported in Table 2 and shown in Fig. 5. The phenocryst olivines have higher CaO abundances at a given forsterite content than olivines from Samoan peridotite mantle xenoliths, indicating that the olivines in the shield lavas we examined are not xenocrysts from the oceanic mantle.

Samoan shield lavas with elevated Os concentrations (>30 ppt) exhibit little Os isotopic variability (0.128–0.132) even though  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios measured on the same lavas show a large range (0.7045–



**Fig. 5.** Electron microprobe compositions for basalt-hosted and peridotite-hosted olivines. New shield-lava-hosted olivine compositions show no overlap in CaO with the compositions reported for olivines hosted in peridotite mantle xenoliths from Savai'i (Hauri and Hart, 1994). The lava-hosted olivines have high CaO abundances at a given olivine forsterite content that are typical of magmatic olivines, indicating that the olivines are not xenocrysts from the oceanic mantle. Olivine compositions are shown only for the samples for which we report Os isotopic compositions on olivine separates. New lava-hosted olivine data are presented as averaged values in Table 2, and individual measurements are shown in Supplementary Table 1.

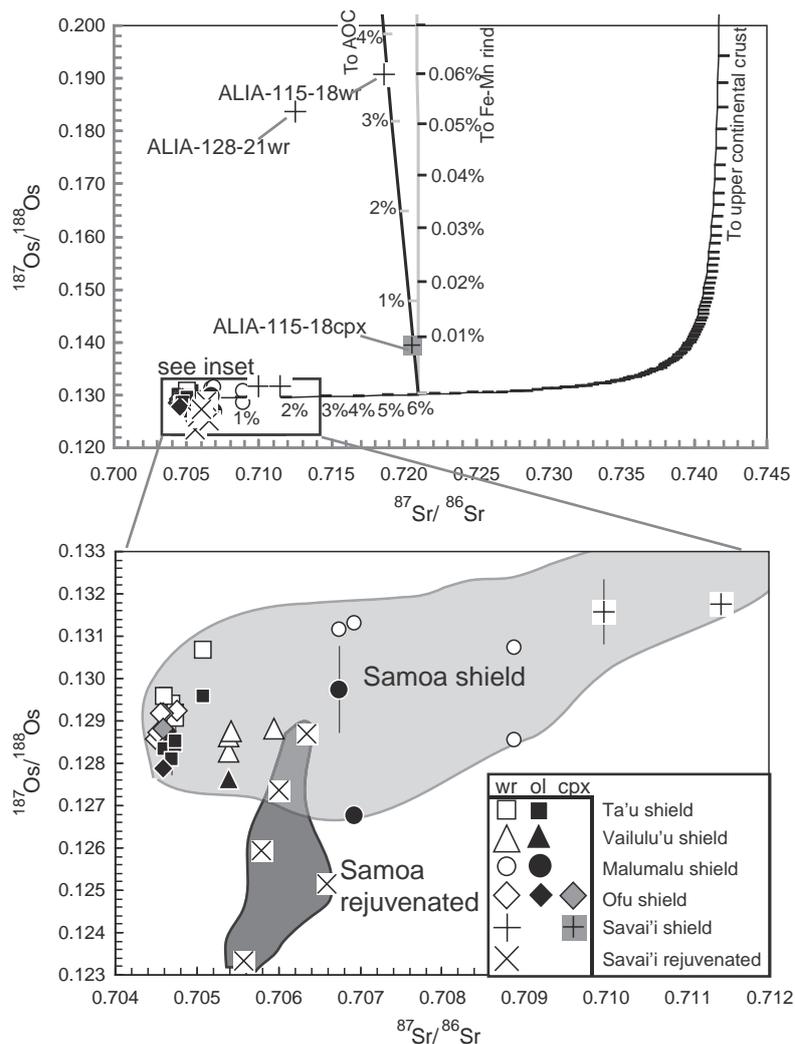
0.7114) (Fig. 6). As such, there is no correlation between  $^{87}\text{Sr}/^{86}\text{Sr}$  vs  $^{187}\text{Os}/^{188}\text{Os}$  ratios for Samoan lavas with elevated Os concentrations. By contrast, the two lavas with the lowest Os concentrations ( $\leq 30$  ppt), including cpx separates from one of these two lavas, have elevated  $^{187}\text{Os}/^{188}\text{Os}$  values that are far greater than those measured in the samples with higher Os abundances, making them suspect for assimilation of some type of crustal material with radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratios during magma ascent and emplacement.

#### 4. Discussion

##### 4.1. Os in phenocrystic olivines: potential for the preservation of primary magmatic Os-isotopic signatures in evolved Samoan lavas

Magmatic olivine phenocrysts hold great promise for establishing primary magmatic Os isotopic compositions in OIB settings. The results of our study show that olivines can have high Os contents, especially in Samoan lavas with low MgO (Figs. 1 and 2). This is important, because whole rock Os diminishes with decreasing MgO (Fig. 1), which makes evolved magmas more susceptible to assimilation. Therefore, olivines may be better suited to preserving primary magmatic  $^{187}\text{Os}/^{188}\text{Os}$  ratios than the whole rocks, particularly evolved whole rocks. Also, olivines are relatively early crystallizing phases, so they may escape some of the assimilation that can modify the isotopic composition of phases that crystallize later from more evolved (and therefore lower Os abundance) magmas. Additionally, olivines host low Re/Os ratios (Debaille et al., 2009; Hanyu et al., 2011), so they are less susceptible to post-eruptive radiogenic ingrowth than the whole rock.

We can use the paired olivine and whole rock Os abundances to explore the empirical behavior of Os in a crystallizing magmatic system at a hotspot. Olivines in Samoan lavas can have spinel or (rare) sulfide inclusions, but the majority of the inclusions are largely silicate melt in composition (Jackson and Hart, 2006). Owing to the presence of inclusions in the olivines, it is not possible to determine accurate olivine–melt partition coefficients for Os. Nevertheless, we find that, with increasing magmatic evolution and decreasing whole rock MgO, the Os concentration of the whole rock diminishes, and the concentration of Os in the bulk olivine phenocrysts (olivine + inclusions) increases with diminishing whole rock MgO.



**Fig. 6.**  $^{87}\text{Sr}/^{86}\text{Sr}$  vs  $^{187}\text{Os}/^{188}\text{Os}$  for Samoan lavas and phenocrysts. Top panel: Samoan whole rock lavas exhibit little Os isotopic variability (0.128–0.132) over a large range of  $^{87}\text{Sr}/^{86}\text{Sr}$  values (0.7045–0.7114). The model for the generation of the EM2 mantle is based on Jackson et al. (2007a), where upper continental crust is mixed (mixing line with black hachures, 1% mixing intervals) with a depleted mantle peridotite like that thought to source Samoan Ta'u lavas. However, the two lavas (ALIA-128-21 and ALIA-115-18 and cpx from ALIA-115-18) with the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios have  $^{187}\text{Os}/^{188}\text{Os}$  ratios that plot above the mixing model. These two lavas and the cpx separate have the lowest Os concentrations in this study ( $\leq 30$  ppt), and they have likely experienced crustal assimilation. We assume that these two low-Os lavas started with a magmatic  $^{187}\text{Os}/^{188}\text{Os}$  ratio predicted by the continental crust–peridotite mixing model ( $\sim 0.130$ , assuming 5–6% sediment) and an Os abundance measured in one lava (17 ppt). This magmatic composition is mixed with AOC (black line, gray hachures every 1%) or Pacific ferromanganese crust (gray line, black hachures every 0.01%). The isotopic compositions of the extreme EM2 Samoan lavas can be generated with  $\leq 0.06\%$  ferromanganese crust or  $\leq 4\%$  AOC. The compositions of the mixing endmembers are provided in Section 4.3 of the text. Bottom panel: an enlarged scale version of the top panel. Replicate whole rock measurements are averaged. Error bars are  $2\sigma$  standard error of the mean. The data plotted are by N-TIMS only (this study and Hauri and Hart, 1993).

We are not certain of the mechanism that causes Os concentrations to increase in Samoan olivines with increasing magmatic evolution. One possible explanation may relate to sulfide saturation during magmatic evolution, which in turn can be driven by phenocryst (including olivine) saturation and precipitation from the magma (Burton et al., 2002). Sulfides can be rich in Os relative to coexisting silicate phases (e.g., Burton et al., 1999a; Hart and Ravizza, 1996; Lorand et al., 2008; Roy-Barman et al., 1998). Therefore, Os concentrations in evolving magmas will diminish if sulfides, which are denser than silicate melts, simply sink in the magma chamber immediately following sulfide saturation. However, before sinking, some of the sulfides are likely to be trapped as inclusions in growing olivines (such sulfide inclusions have been observed; Jackson and Hart, 2006), thereby increasing the Os contents in phenocrystic olivines. This simple model may explain the trend of increasing olivine Os abundances with decreasing whole rock Os abundances in progressively more evolved Samoan lavas (Fig. 2).

It is important to note that sulfide is not the only trace phase that might generate the same trend. Other trace phases that, like sulfide, exhibit high  $D^{\text{Os}}$  values, like some spinels (e.g., Capobianco et al., 1994; Standish et al., 2002) and PGE-rich phases (e.g., Ballhaus et al., 2006; Bockrath et al., 2004; Luguet et al., 2007; Maier et al., 2003), might work in the place of sulfide in the simple fractionation model proposed above. Less clear is whether olivine might preferentially sequester Os as magmas become increasingly evolved. Indeed, olivine partitioning has been seen to range from compatible (e.g. Hart and Ravizza, 1996; Lassiter and Luhr, 2001; Luguet et al., 2007; Puchtel et al., 2004) to incompatible (e.g. Burton et al., 2002; Gannoun et al., 2004; Puchtel et al., 2009) in a variety of systems such as peridotites, komatiites and basalts. In particular, using optically pure, natural basaltic olivines, Burton et al. (2002) showed that Os is highly incompatible in olivine, even in olivines with forsterite contents as low as observed in our study. Irrespective of the phase that hosts the Os, be it the olivines themselves or a phase hosted in

the olivines, the key observation is that the more evolved Samoan lavas host olivines that have higher Os concentrations. This can be extremely useful for determining the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of an evolving magma at a more primitive stage that might predate assimilation.

For example, as magmas evolve, the whole rock becomes more Os-depleted and increasingly susceptible to having its primary magmatic  $^{187}\text{Os}/^{188}\text{Os}$  ratios modified by assimilation of crustal materials and/or seawater, and it becomes more difficult to infer the primary magmatic  $^{187}\text{Os}/^{188}\text{Os}$  ratio. However, Os concentrations increase in the Samoan olivines with progressive magmatic evolution. Therefore, unlike the whole rock, the olivines would become less prone to having their primary magmatic  $^{187}\text{Os}/^{188}\text{Os}$  ratios modified by assimilation. This simple model may explain why the most evolved whole rock with paired olivine measurements examined in this study (sample 77–1 with 7.6 wt.% MgO) exhibits the largest difference between measured whole rock (0.1313) and olivine (0.1268)  $^{187}\text{Os}/^{188}\text{Os}$  ratios (Fig. 2). The key observation is that the olivine and phases included in the olivine (sulfide?) from sample 77–1 preserve a less radiogenic Os isotopic signature than the whole rock, where the latter is evolved, relatively Os-poor, and sensitive to assimilation of material with high  $^{187}\text{Os}/^{188}\text{Os}$  ratios. In contrast, the olivine and phases included in the olivine preserve higher abundances of Os and are less susceptible to assimilation and may therefore better preserve the primary magmatic  $^{187}\text{Os}/^{188}\text{Os}$  ratio than the whole rock. This result is similar to the finding of Debaille et al. (2009), who observed that, in the most evolved Icelandic lavas, olivines better preserve the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of the primary magma.

The results of our study and the study of Debaille et al. (2009) suggest that olivines may better preserve the fidelity of the mantle source  $^{187}\text{Os}/^{188}\text{Os}$  ratio than whole rocks, particularly if the whole rocks are evolved. In fact, if only the  $^{187}\text{Os}/^{188}\text{Os}$  ratio measured on Samoan olivines are considered, the range of  $^{187}\text{Os}/^{188}\text{Os}$  ratios for the Samoan hotspot span from 0.127 to 0.130, a range of values that is shifted to slightly lower values than the range of values inferred from the most Os-rich (>30 ppt) Samoan lavas (0.128–0.132). In summary, olivines may allow us to “see through” the effects of assimilation, particularly in evolved (and therefore low-Os) lavas that are susceptible to having their primary magmatic  $^{187}\text{Os}/^{188}\text{Os}$  ratios overprinted by assimilation.

#### 4.2. Rejuvenated vs. shield volcanism in Samoa: implications for the EM2 mantle

Rejuvenated volcanism on the Samoan island of Savai'i is extensive, and the entire island has been resurfaced with a veneer of rejuvenated lava (e.g., Workman et al., 2004). Rejuvenated Samoan lavas from Savai'i exhibit generally lower  $^{187}\text{Os}/^{188}\text{Os}$  ratios (Hauri and Hart, 1993) than Samoan shield lavas reported in this study (Fig. 2), and the rejuvenated Savai'i lavas exhibit some of the least radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratios (0.123 to 0.129; Hauri and Hart, 1994) in the global OIB database (Figs. 6 and 7). In order to place constraints on the Os-isotopic composition and origin of the Samoan EM2 mantle, it is important to understand the source of the Os-isotopic difference between Samoan shield and rejuvenated lavas.

All the Samoan lavas reported by Hauri and Hart (1993) are rejuvenated lavas from Savai'i island, and rejuvenated lavas from Savai'i frequently host peridotite mantle xenoliths that originated in the oceanic mantle lithosphere (Hauri and Hart, 1994; Hauri et al., 1993). Peridotite xenoliths from Savai'i exhibit unradiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratios that vary down to 0.119 (Jackson et al., 2010), and xenocrystic olivines disaggregated from such xenoliths could be responsible for the low  $^{187}\text{Os}/^{188}\text{Os}$  ratios observed in the rejuvenated Savai'i lavas. It is well-known that peridotite mantle xenoliths can contaminate the Os-isotopic signature of the host lava. A mantle-xenolith bearing lava from Pico Island in the Azores was found to exhibit the least radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratio in the suite of lavas examined by Widom and Shirey (1996). Similarly, xenolith-bearing basalts from the Comoros and Canary Islands host low  $^{187}\text{Os}/^{188}\text{Os}$

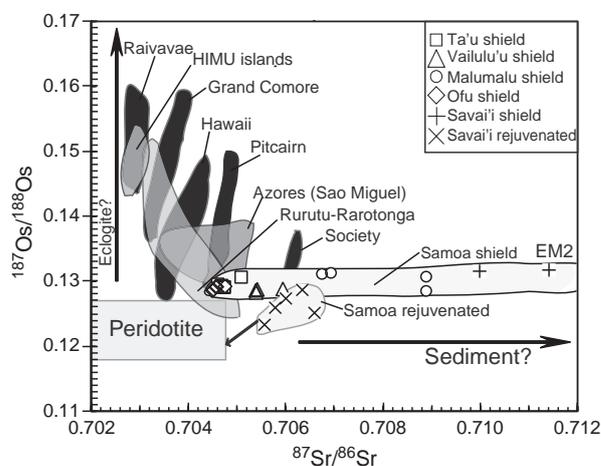
values that may reflect incorporation of unradiogenic Os in the xenoliths (Class et al., 2009; Day et al., 2010; Widom et al., 1999).

However, unradiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratios are observed in some lavas from the Azores (Schaefer et al., 2002), and these lavas do not host xenoliths, indicating that not all unradiogenic Os-isotopic signatures in OIBs result from contamination from peridotite xenoliths. Nonetheless, given the prevalence of peridotite xenoliths in Samoan rejuvenated lavas from Savai'i, we consider it likely that the Os-isotopic signatures of these lavas reflect the composition of the disaggregated xenoliths, and these isotopic signatures do not reflect the mantle source of Samoan lavas. However, we suggest that the higher range of  $^{187}\text{Os}/^{188}\text{Os}$  ratios (0.128–0.132) observed in Os-rich (>30 ppt Os) Samoan shield lavas better reflect the composition of the Samoan mantle. In support of this hypothesis, the olivine phenocrysts in Samoan shield lavas have higher CaO abundances at a given forsterite content than olivines from Samoan peridotite xenoliths (Fig. 5), and this shows that these olivines are not xenocrysts from disaggregated peridotite xenoliths but represent magmatic phenocrysts.

#### 4.3. The Os isotopic composition of EM2: evidence for a recycled continental crust component in the Samoan mantle

The enriched EM2 mantle reservoir sampled by Samoan shield lavas is thought to be generated by mixing subducted, marine sediment of terrigenous origin with a depleted peridotite (Jackson et al., 2007a; Workman et al., 2008). The addition of 5–6% of this sediment to a peridotite not only explains the elevated  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in Samoan lavas, but may also explain the unradiogenic and rather narrow range of Os isotopic compositions (0.128–0.132) observed in Samoan shield lavas with elevated Os contents (>30 ppt).

Fig. 6 shows that a peridotite–terrigenous sediment mixture produces an extremely hyperbolic mixing line that exhibits very



**Fig. 7.** Global relationship between Sr and Os isotopic compositions in OIBs. The Samoan data shown are limited to measurements made by N-TIMS with Os concentrations >30 ppt (data sources are from this study and from Hauri and Hart, 1993). The global data compilation is from Class et al. (2009), and only samples with >40 ppt Os (and >50 ppt Os for Pitcairn) are shown. The data sources for the non-Samoan data fields are the same as from Class et al. (2009), and include: Bennett et al., 1996; Brandon et al., 1999; Bryce et al., 2005; Eisele et al., 2002; Gaffney et al., 2005; Hauri and Hart, 1993; Hauri et al., 1996; Lassiter and Hauri, 1998; Roy-Barman and Allègre, 1995; Widom and Shirey, 1996. We have also included data from Parai et al. (2009). For the sake of clarity, not all hotspot lavas included in the Class et al. (2009) compilation are included here. For example, notable datasets providing paired measurements of Sr and Os isotopic compositions that are not shown include the Canary Islands (Day et al., 2010; Marcantonio et al., 1995), Cape Verde (Doucelance et al., 2003; Escrig et al., 2005), and Iceland (Brandon et al., 2007; Debaille et al., 2009; Skovgaard et al., 2001). The  $^{187}\text{Os}/^{188}\text{Os}$  range in the “peridotite” field is defined broadly using the most Os-rich chromites measured in abyssal peridotites from Standish et al. (2002); the peridotite field in the figure is meant to illustrate a poorly defined field, and is partially borrowed from the peridotite field in Fig. 4 of Class et al. (2009).

little variation in  $^{187}\text{Os}/^{188}\text{Os}$  ratios (0.1285 to 0.1301) over a wide range of  $^{87}\text{Sr}/^{86}\text{Sr}$  values (0.7045 to 0.7210). Upper continental crust ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7421$ , Sr concentration = 320 ppm,  $^{187}\text{Os}/^{188}\text{Os} = 1.05$ , Os concentration = 0.031 ppb; Jackson et al., 2007a; Peucker-Ehrenbrink and Jahn, 2001; Rudnick and Gao, 2003) is mixed with a depleted mantle peridotite like that thought to source Samoan Ta'u lavas ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7045$ , Sr concentration = 28.3 ppm,  $^{187}\text{Os}/^{188}\text{Os} = 0.1294$ , Os concentration = 3 ppb; Jackson et al., 2007a; Meisel et al., 2001). The large difference in Sr/Os ratios between the two mixing endmembers – sediment and peridotite – is responsible for the extreme hyperbolic nature of the mixing line. The mixing line shows that a small contribution of sediment (up to 5–6%), like that thought to exist in the Samoan EM2 mantle, does little to increase the  $^{187}\text{Os}/^{188}\text{Os}$  ratio, but the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is greatly increased (up to ~0.72). A key observation to be made from the mixing model is that >20% sediment is required to generate  $^{187}\text{Os}/^{188}\text{Os}$  ratios >0.132. However, such a high contribution from terrigenous sediment is not consistent with trace element patterns and Sr–Nd–O isotope systematic in extreme Samoan EM2 lavas, which indicate a maximum of 5–6% sediment in the Samoan EM2 mantle (Jackson et al., 2007a; Workman et al., 2008). In summary, the low  $^{187}\text{Os}/^{188}\text{Os}$  ratios observed in Samoan EM2 lavas with elevated Os (>30 ppt) is consistent with a maximum of 5–6% sediment in the EM2 mantle source.

A clear implication of this mixing model is that even the extreme EM2 Savai'i lavas should exhibit relatively unradiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratios (i.e., ~0.130), as the most enriched Savai'i lavas, including ALIA-115-18, sample a mantle source that is estimated to host no more than 5–6% terrigenous sediment (Fig. 6). Nonetheless, the  $^{187}\text{Os}/^{188}\text{Os}$  ratios measured in the two extreme EM2 lavas (ALIA-128-21 and ALIA-115-18) in this study are significantly higher (0.1836–0.1907) than predicted by the mixing model (~0.130). The magmatic (Jackson et al., 2008b) cpx separates from the most extreme Samoan EM2 lava also yield a high  $^{187}\text{Os}/^{188}\text{Os}$  ratio (~0.1394) that is somewhat lower than the whole rock value. The high  $^{187}\text{Os}/^{188}\text{Os}$  ratios in the extreme EM2 lavas likely relates to the fact that they have the lowest Os concentrations measured in this study ( $\leq 30$  ppt), making them susceptible to contamination by assimilation of material with radiogenic Os isotopic signatures – including altered oceanic crust (AOC) and/or ferromanganese crust – during magma ascent and emplacement (e.g., Class et al., 2009; Day et al., 2009, 2010, Ireland et al., 2009; Marcantonio et al., 1995; Reisberg et al., 1993; Widom et al., 1999).

Therefore, our preferred explanation for the discrepancy between the measured  $^{187}\text{Os}/^{188}\text{Os}$  ratios in the two extreme EM2 lavas (0.1836–0.1907) and the predicted  $^{187}\text{Os}/^{188}\text{Os}$  ratio from the terrigenous sediment–peridotite mixing model (~0.130) is as follows. First, we assume that these two EM2 lavas (ALIA-128-21 and ALIA-115-18) started with a magmatic  $^{187}\text{Os}/^{188}\text{Os}$  ratio predicted by the continental crust–peridotite mixing model (~0.130) and an Os abundance measured in sample ALIA-115-18 lava (17 ppt). Second, we assume that the high  $^{187}\text{Os}/^{188}\text{Os}$  ratios of the two extreme EM2 lavas reflect assimilation of crustal materials. In order to model the effects of assimilation, the model primary magmatic composition of the EM2 lavas is mixed with altered oceanic crust ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7092$ ,  $^{187}\text{Os}/^{188}\text{Os} = 1.042$ , Os concentration = 33 ppt; from DSDP Sites 417/418 in Peucker-Ehrenbrink et al., 2003) or Pacific ferromanganese crust ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7092$ ,  $^{187}\text{Os}/^{188}\text{Os} = 0.979$ , Os concentration = 2.176 ppb; Burton et al., 1999b). The observed isotopic compositions of the extreme Samoan EM2 lavas can be generated by a contribution of  $\leq 0.06\%$  ferromanganese crust or  $\leq 4\%$  AOC to the model EM2 primary melt composition. Similarly, the incorporation of small quantities of ferromanganese crust (0.01%) or altered oceanic crust (0.5%) during magma ascent and emplacement caused the  $^{187}\text{Os}/^{188}\text{Os}$  ratio of the ALIA-115-18 cpx to become elevated (0.1394) above the  $^{187}\text{Os}/^{188}\text{Os}$  ratio predicted by the mixing model (~0.130). Given the very low Os concentrations in whole rock sample ALIA-128-21 and ALIA-115-18 and the cpx, we consider these assimilation scenarios to be likely.

If we exclude the two extreme Samoan EM2 lavas (and cpx separates) from Savai'i with low Os abundances ( $\leq 30$  ppt), the remaining Samoan lavas exhibit a narrow range of  $^{187}\text{Os}/^{188}\text{Os}$  ratios (0.128–0.132) that we consider to reflect the EM2 mantle source. Therefore, the  $^{187}\text{Os}/^{188}\text{Os}$  isotopic composition of the EM2 mantle is much lower than the HIMU (high  $^{238}\text{U}/^{204}\text{Pb}$ , or hi “ $\mu$ ”: up to ~0.150 in Mangaia lavas; Hauri and Hart, 1993) and EM1 (enriched mantle 1: 0.140–0.150 in Os-rich Pitcairn lavas; Eisele et al., 2002) mantle reservoirs, and significantly lower than the  $^{187}\text{Os}/^{188}\text{Os}$  ratios discovered in the Canary Islands (0.175; Day et al., 2010) and the Comoros (0.16; Class et al., 2009).

The observation of a significant terrigenous sediment component in the Samoan mantle raises the question as to how the terrigenous sediment came to be mixed with peridotite to generate the EM2 mantle. One possible mechanism is that during subduction, the veneer of terrigenous sediment on top of the downgoing slab is melted, incorporated into the mantle wedge peridotite, and this sediment–metasomatized mantle from the wedge is incorporated into the convecting mantle to be later entrained by an upwelling mantle plume. This model is similar to the models put forward by Elliott et al. (2006) and Lassiter et al. (2003). These simple conceptual models may also help to explain the apparent conundrum of a diminished recycled oceanic crust component in OIB lavas with enhanced recycled terrigenous sediment signatures, an observation that is based on the inverse trend between  $^{187}\text{Os}/^{188}\text{Os}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the global OIB dataset (Class et al., 2009; Hauri and Hart, 1993) (Fig. 7): Lavas with a recycled oceanic crust component have low  $^{87}\text{Sr}/^{86}\text{Sr}$  and high  $^{187}\text{Os}/^{188}\text{Os}$  ratios (e.g., HIMU lavas from Mangaia and Tubuai and HIMU-type lavas from the Canary Islands; Day et al., 2009, 2010; Hauri and Hart, 1993; Marcantonio et al. 1995; Widom et al., 1999), while lavas with recycled continental crust have high  $^{87}\text{Sr}/^{86}\text{Sr}$  and low  $^{187}\text{Os}/^{188}\text{Os}$  ratios (e.g., EM2 lavas from Samoa) (Fig. 7). Both recycled oceanic crust and terrigenous sediment are subducted together as a single package. However, the lower solidus temperature of sediment may cause it to melt at shallower levels in the subduction zone than oceanic crust, where it is incorporated into the mantle wedge, possibly decoupling the sediment and oceanic components before they enter the convecting mantle. This model may explain the perplexing lack of recycled oceanic crust in the Samoan mantle source, in spite of the strong evidence for recycled continentally-derived marine sediment.

## 5. Conclusions

The two lavas with most extreme EM2 signature examined in this study, and cpx separated from one of these lavas (whole rock  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.7186, and up to 0.7208 in cpx separates), exhibit radiogenic  $^{187}\text{Os}/^{188}\text{Os}$  ratios (0.139 in the cpx, and 0.184 and 0.191 in two whole rocks). However, the cpx separates (7 ppt Os) and the host whole rocks (17–30 ppt Os) are Os-poor and susceptible to assimilation during magma ascent and emplacement. When samples with low Os abundances ( $\leq 30$  ppt) are discounted, the new dataset reveals that the Os isotopic compositions of Samoan lavas exhibit unradiogenic values with little variability (0.128–0.132) over a wide range of  $^{87}\text{Sr}/^{86}\text{Sr}$  values (0.7045 to 0.7114), and we suggest that this narrow range of  $^{187}\text{Os}/^{188}\text{Os}$  ratios is more reasonable for the EM2 mantle. In fact, EM2 lavas from other hotspots have been noted to have lower  $^{187}\text{Os}/^{188}\text{Os}$  ratios than the HIMU and EM1 mantle endmembers (e.g., Class et al., 2009), and unradiogenic Os isotopic compositions appear to be a salient feature of the EM2 mantle.

Rejuvenated lavas from the Samoan island of Savai'i have the lowest  $^{187}\text{Os}/^{188}\text{Os}$  ratios in the Samoan hotspot (Hauri and Hart, 1993). These rejuvenated lavas exhibit a lower range of  $^{187}\text{Os}/^{188}\text{Os}$  ratios (0.123 to 0.129) than the Os-rich (>30 ppt) shield stage lavas (0.128–0.132). The difference in the Os-isotopic composition between Samoan shield and rejuvenated lavas may owe to contamination of the rejuvenated lavas with unradiogenic Os from disaggregated xenoliths from the mantle

lithosphere, and the low  $^{187}\text{Os}/^{188}\text{Os}$  ratios of the rejuvenated lavas are not representative of the Os-isotopic composition of the EM2 mantle.

Data from nine Samoan whole rock–olivine pairs indicate that olivines exhibit increasing Os concentrations as lavas become more evolved, while whole rock Os concentrations diminish. Therefore, while evolved Samoan lavas have low Os concentrations, and are susceptible to assimilation, they host olivines with high Os concentrations that are less susceptible to assimilation. Therefore, the high Os concentrations of the olivines in evolved lavas make them ideally suited to preserving the primary magmatic  $^{187}\text{Os}/^{188}\text{Os}$  ratio that may no longer be recorded in evolved whole rocks. Using the  $^{187}\text{Os}/^{188}\text{Os}$  ratios collected on magmatic olivines from Samoan shield lavas, the Os-isotopic composition of the Samoan mantle is 0.127 to 0.130, a range that is lower (and narrower than) the range estimated using Os-rich (>30 ppt) whole rock lavas (0.128–0.132).

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